PESTICIDE DISCHARGES FROM IRRIGATED AGRICULTURE IN THE MURRAY IRRIGATION AREA, NEW SOUTH WALES, AUSTRALIA

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ABSTRACT

Pesticide discharges were monitored in a drainage system from the Murray Irrigation Area in south-western New South Wales using surface water sampling and gas chromatography/mass spectrometry (GC/MS) and other chromatography-based analyses. The drainage system monitored (~90 km long) included an artificial drain, natural creek and river during the irrigation season, and the drain and creek during the non-irrigation season. During the irrigation season, enzyme-linked immuno-sorbent assay (ELISA) for molinate and passive samplers containing 2,2,4-trimethylpentane (TRIMPS) were also used to assess their relative merits in measuring and monitoring pesticide discharges.

A wide range of pesticides were analysed, but during the irrigation season, only molinate and thiobencarb were frequently detected in the drain, associated with irrigated rice crops. These pesticides were also detected at the most upstream site of the receiving creek but not further downstream. During the non-irrigation season, atrazine and simazine were often detected in the drain, while dimethoate and glyphosate were occasionally detected.

During the irrigation season, the passive samplers detected thiobencarb that was not detected from surface water samples. ELISA was regarded as a useful screening method for molinate, although the method showed higher concentrations of molinate than GC/MS analysis.

Key words: surface water samples, enzyme-linked immuno-sorbent assay, passive samplers, molinate, thiobencarb.

INTRODUCTION

Water is one of the primary mechanisms by which pesticides are transported from application areas to other parts of the environment (Larson *et al.* 1997). The discharge of pesticides associated with irrigated agriculture into receiving waters is therefore of concern to natural resource managers and to the community due to the potential adverse effects of pesticides on the environment and human health. To ensure that pesticide discharges are properly managed, it is essential that reliable data on pesticide contamination of surface waters are gathered at appropriate temporal and spatial scales.

A variety of techniques have been used to measure the concentrations of pesticides in surface waters of the Australian aquatic environment (Peterson *et al.* 1995; Thomas *et al.* 1998; Leonard *et al.* 1999; MIL 1999; Muschal 1999). For example, 'snap-shot' surveys of surface water concentrations are the most common method for determining pesticide concentrations. Samples are then analysed using, for example, gas chromatography/mass spectrometry (GC/MS) or enzyme-linked immuno-sorbent assay (ELISA). Passive samplers containing lipids or solvents can also be deployed. Deployed passive samplers allow for the accumulation of pesticides within the sequestering medium over the period of deployment. The devices are then retrieved and the pesticides are extracted and measured. Alternatively, endemic or experimentally transplanted biota may be useful in assessing bioaccumulation of pesticides. Each of these techniques has merits (and disadvantages) in terms of logistics, costs, detection levels of analyses and interpretations of results (eg. see Table 1 in Lu *et al.* 2002). It may be necessary to use more than one technique to monitor the distribution and fate of pesticides in the aquatic environment in order to ensure that pesticide discharges are properly managed at various temporal and spatial scales (Sabaliūnas and Södergren 1997; Larson *et al.* 1997; Lu *et al.* 2002).

In this study, the concentrations of a range of pesticides were monitored in a drainage system in the Murray Irrigation Area of south-western New South Wales, Australia. The Murray Irrigation Area comprises approximately 797,000 ha with 2,425 farms and has an annual bulk water entitlement of 1.5 million megalitres (ML). Water is sourced from the Murray and Edward Rivers and is distributed via 3,600 km of irrigation supply channels. Land use comprises dryland pasture (34% of total area), winter irrigated pasture (18%), winter crops (26%), and rice (6%). Irrigation water delivered from 1998 to 1999 totalled 1,167,775 ML of which rice used 54%, annual pasture 22%, perennial pasture 14% and winter cereals 4% (MIL 1999).

Pesticides are used for weed and insect control in crops, pastures, irrigation supply and drainage systems throughout the area (MIL 1997, 1999). The major chemicals used in the area include atrazine, chlorsulfuron, chlorpyrifos, diclofop-methyl, endosulfan, glyphosate, MCPA, molinate, omethoate and trifluralin (MIL 1997).

In this study, the concentrations of pesticides in surface waters were monitored during irrigation and non-irrigation seasons, with the aid of gas chromatography/mass spectrometry (GC/MS) and other chromatography-based analyses. In addition, during the irrigation season, the concentrations of pesticide in surface water were monitored using passive samplers containing trimethylpentane (TRIMPS) and ELISA. The ELISA was specifically for analysis of molinate. The aims of the study were to determine 1) if TRIMPS deployed over varying time periods detected and accumulated pesticides used in the MIL region, 2) if the two different methods

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of analysis for molinate (GC/MS and ELISA) yielded similar concentration results, 3) the differences in pesticide concentrations between irrigation and non-irrigation seasons, and 4) if runoff from rainfall increased pesticide concentrations.

METHODS

Study site

The study focused on a drainage system consisting of Lalalty Drain, Tuppal Creek and Edward River (Figure 1). Lalalty Drain provides water for rice growing during the irrigation season and broad-acre winter cropping activity during the non-irrigation season and receives agricultural tail waters all year round. Lalalty Drain discharges directly into Tuppal Creek, which flows west and discharges into the Edward River which continues to flow north-west towards Deniliquin. Sampling was undertaken during the irrigation season of mid October 1998 to early February 1999 and again during the non-irrigation season of late May to mid August 2001.

Sampling during the irrigation season

During the irrigation season, sites were located in Lalalty Drain (LALI), Tuppal Creek (TUPX, TUPY and TUPZ) and in the Edward River upstream (EDW1 and EDW2) and downstream (EDW3 and EDW4) of the confluence with Tuppal Creek (Figure 1). The most downstream site in the Edward River (EDW4) was located immediately upstream from the off-take for the Deniliquin town water supply.

The passive sampler (TRIMPS) consists of a low-density polyethylene membrane bag, approximately 3 cm x 10 cm (Scubs Brand, Schur Consumer Products A/S, Vejle, Denmark), with a mean membrane thickness of 40 µm (Leonard *et al.* 2002). Each passive sampler was pre-rinsed overnight in 2,2,4-trimethylpentane to leach out compounds adsorbed on the membrane.

Trimethylpentane (10 mL) was then added to each passive sampler, which was sealed by a plastic dialysis clip (Sigma-Aldrich, Sydney, Australia) at the top to prevent leakage (Peterson *et al.* 1995). Each bag was wrapped in plastic mesh to prevent damage and placed randomly in a stainless steel cage (55 cm x 43 cm x 25 cm) with a mesh size of 10 mm. The cages were anchored to logs, trees or fence posts located on the bank with a rope and placed on the bottom of the water body. Depths varied from 0.5 m in Lalalty Drain to 2 m in the Edward River. Cages were placed as close to the middle of the channel as possible.

A total of 36 TRIMPS were deployed at each of the sites LALI, TUPX, TUPY and TUPZ in mid October 1998 to examine cumulative uptake. At each of the 12 sampling occasions, respectively 8, 13, 14, 15, 16, 17, 22, 29, 36, 54, 85 and 114 days after deployment, three bags were retrieved randomly from each site (cumulative TRIMPS). In addition, to examine the usefulness of TRIMPS over short time periods, TRIMPS was deployed in triplicate at sites LALI and TUPX on 26, 27, 28 and 29 October 1999 and retrieved approximately 24 hours after each deployment (daily TRIMPS). In Edward River, only cumulative TRIMPS were deployed in triplicate in mid October 1998 and were retrieved with replacement at approximately three weekly intervals until early January 1999 (four sampling occasions).

Between 21 October - 18 November 1998, three and four independent surface water samples (~0.2 m below the water surface) were collected on nine sampling occasions for ELISA and laboratory (chromatography-based) analyses respectively, coinciding with each retrieval of TRIMPS from each site.

Sampling during the non-irrigation season

During the non-irrigation season (late May to mid August), three routine monitoring sites were sampled in the Lalalty Drain (LALL, LALW and TUPJGT). At LALL and LALW, duplicate surface water samples were collected every 2 to 4 days between 29 May - 16 August 2001 (28 sampling occasions) while at TUPJGT single or duplicate samples were collected every 2 to 4 days between 29 June - 16 August 2001 (14 sampling occasions).

When the control gates at LALL and TUPJGT opened, single surface water samples were collected daily at the discharge point for Lalalty drain (TUPJ) and in Tuppal Creek (TUPCK and TUPCKD) (Figure 1) between16 - 19 July 2001. The sampling during this period (16 to 19 July) was referred to as event monitoring in this study.

Pesticide analyses for surface water samples and TRIMPS during irrigation and non-irrigation seasons

At each site, surface water samples except those for ELISA were poured into 1-L hexane-rinsed amber glass bottles fitted with lids lined with aluminium foil. TRIMPS retrieved from each site were placed in glass jars. All samples were chilled on collection and delivered to the NSW EPA laboratory within 24 hours.

All surface water samples except those for ELISA were liquid-liquid extracted with dichloromethane (USEPA 1996). The dichloromethane was evaporated using a Turbovap (Zymark) and solvent exchanged to hexane. The contents of TRIMPS were transferred directly to an analysis vial. The samples were analysed using gas chromatography/mass spectrometry (GC/MS), gas chromatography/electron capture detection (GC/ECD), and liquid chromatography/mass spectrometry (LC/MS) (USEPA 1994, 1996, 1998). The pesticides targeted during this study and their detection limits are presented in Appendix 1.

In addition to the GC/MS analysis, molinate was analysed with ELISA. The ELISA kits (EnviroLogix Inc. USA) use polyclonal antibodies which bind the pesticide and pesticide enzyme conjugate. The volume of each surface water sample was 100 mL, from which duplicate 100 µL subsamples were used for the assay. A standard curve was made from five known concentrations of molinate (0.5, 4, 10, 15 and 30 µg L^{-1}). Deionised water was used as blanks. The results were measured using a Bio-Rad Microplate reader and associated software. ELISA was conducted on surface water samples only (not TRIMPS) and within five hours after collection of samples. The concentration of pesticides was expressed as micrograms per litre of water (µg L^{-1}) for all surface water samples (chromatography-based analyses and ELISA) and micrograms per litre of solvent (µg L^{-1} solvent) for all TRIMPS samples.

Data on daily rainfall (mm day^{-1}) in the study area during irrigation and non-irrigation seasons were provided by the Bureau of Meteorology (Finley weather station No. 074253: 35°71'S, 145°62'E). Data on daily discharge (ML day^{-1}) at LALI during irrigation and non-irrigation seasons were provided by Murray

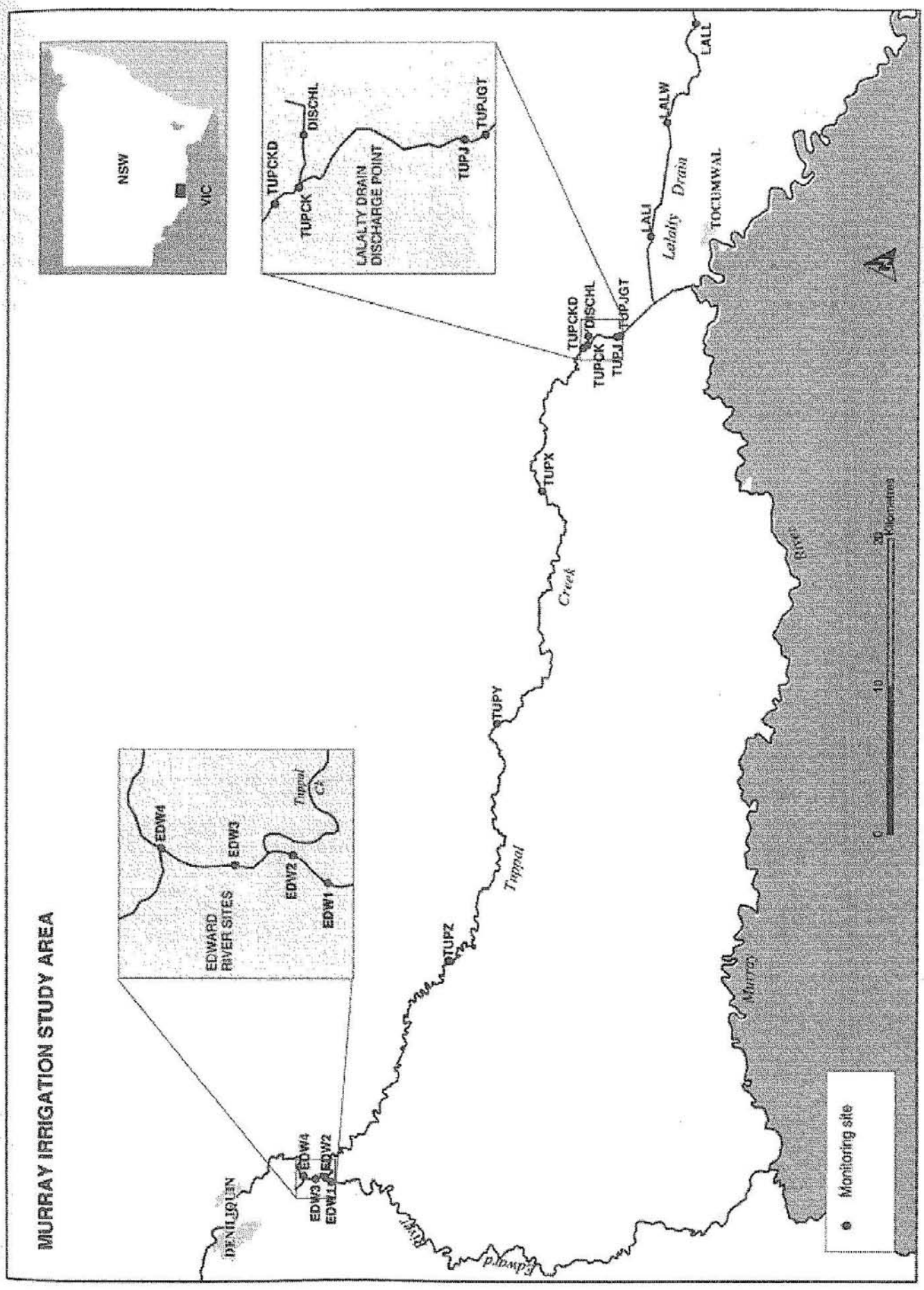

Figure 1. *Murray irrigation sampling sites.*

Appendix 1. Pesticides analysed and their detection limits during the summer irrigation (mid October 1998 to early February 1999) and winter non-irrigation (late May to mid August 2001) seasons

Pesticide monitored	Detection limit for surface water samples (µg L^{-1})	Detection limit for TRIMPS[a] (µg bag^{-1})
Summer irrigation season only		
Aldrin	0.02	0.2
Alpha-chlordane	0.02	0.2
Beta-BHC	0.02	0.2
Bromoxynil	0.5	50.0
Carbophenothion	0.1	2.0
Crotoxphos	0.1	2.0
Delta-BHC	0.02	0.2
Diazinon	0.1	2.0
Dichlorvos	0.1	2.0
Dieldrin	0.02	0.2
Endrin	0.02	0.2
Ethion	0.1	2.0
Ethyl-chlorpyrifos	0.1	2.0
Ethyl-parathion	0.1	2.0
Fenthion	0.1	2.0
Fenitrothion	0.1	2.0
Heptachlor	0.02	0.2
Heptachlor epoxide	0.02	0.2
Hexachlorobenzene	0.02	0.2
Lindane	0.02	0.2
Malathion	0.1	2.0
Methidation	0.1	2.0
Methoxychlor	0.02	0.2
Methyl-azinphos	0.1	2.0
Methyl-bensulfuron	1.0	1.0
Methyl-chlorpyrifos	0.1	2.0
Methyl-parathion	0.1	2.0
Mevinphos	0.1	2.0
Molinate	0.5	1.0
Oxychlordane	0.02	0.2
Pentachlorophenol	0.5	50.0
Phorate	0.1	2.0
Picloram	0.5	50.0
p,p' DDD	0.02	0.2
p,p' DDE	0.02	0.2
p,p' DDT	0.02	0.2
Profenofos	0.1	2.0
Propetamphos	0.1	2.0
Sulprofos	0.1	2.0
Tetrachlorvinphos	0.1	2.0
Thiobencarb	10.0	1.0
Winter non-irrigation season only		
Bifenthrin	0.03	n.a.[b]
Chlorpyrifos	0.03	n.a.
Chlorsulfuron	0.01	n.a.
Cypermethrin	1.0	n.a.
Dichlofop-methyl	1.0	n.a.
Glyphosate	1.0	n.a.
MCPP	1.0	n.a.
Omethoate	0.1	n.a.
Simazine	0.03	n.a.
Triflualin	0.1	n.a.
2,4,5-TP	1.0	n.a.
Both the summer irrigation and winter non-irrigation seasons		
Atrazine	0.5 (0.03 for w.s.)	1.0
Chopyralid	0.5 (1.0 for w.s.)	50.0
Dicamba	0.5 (1.0 for w.s.)	50.0
Dichloprop	0.5 (1.0 for w.s.)	50.0
Dimethoate	0.5 (0.1 for w.s.)	1.0
Endosulfan I (alpha)	0.02 (0.1 for w.s.)	2.0
Endosulfan II (beta)	0.02 (0.1 for w.s)	2.0
Endosulfan sulphate	0.02 (0.1 for w.s)	2.0
Haloxyfop	0.5 (1.0 for w.s.)	50.0
MCPA	0.5 (1.0 for w.s.)	50.0
Molinate	0.5 (0.03 for w.s)	1.0
Triclopyr	0.5 (1.0 for w.s.)	50.0
2,4-D	0.5 (1.0 for w.s.)	50.0
2,4-DB	0.5 (1.0 for w.s.)	50.0
2,4,5-T	0.5 (1.0 for w.s.)	50.0

[a] Passive samplers containing 2,2,4-trimethylpentane which were used during the summer irrigation season only;
[b] Not analysed.

Irrigation Limited (MIL). All statistical analyses were made with the SAS computer program (SAS 1999). For statistical analyses, pesticide concentrations below detection limits were assumed to be half that of their respective detection limits.

RESULTS

Rainfall

During the summer irrigation season, the study area received a total rainfall of 93 mm between 13 October 1998 - 4 February 1999. There was a single distinctive rainfall event in mid November during this period (Figure 2A). During the winter non-irrigation season, the study area received a total rainfall of 58 mm between 28 May - 17 August 2001. There were relatively distinct rainfall events during this period (in mid June and mid July) (Figure 2B).

Daily stream discharge at LALI

During the irrigation season, elevated discharges of up to 46 ML day^{-1} were measured in mid November 1998, with a median flow rate of 7.4 ML day^{-1} between October 1998 - February 1999 at LALI (Figure 2A). The daily stream discharge throughout the non-irrigation season was relatively low, with a median flow rate of 0.033 ML day^{-1} between June - August 2001 (Figure 2B). During event monitoring (when control gates opened in Lalalty Drain between16 - 19 July 2001), flow reached around 4 ML day^{-1} on 17 and 18 July.

Pesticide discharges during the irrigation season

Only molinate, oxychlordane and thiobencarb were detected during the irrigation season (mid October 1998 to early February 1999). There were differences in pesticide detection between collection methods (surface water samples versus TRIMPS for thiobencarb) at LALI and TUPX and differences in concentration between analytical methods (GC/MS versus ELISA for molinate) at TUPX.

Molinate in surface water

Molinate was detected in surface water samples on 56% and 100% of sampling occasions at LALI and TUPX respectively. Highest mean molinate concentrations measured with GC/MS and ELISA were 11.3 µg L^{-1} and 12.9 µg L^{-1} respectively at LALI on 29 October 1998 (Figure 3A). There was no significant difference in the overall mean molinate concentrations measured between the two methods at LALI (paired 2-sample t-test, n = 9, $p = 0.069$). At TUPX, the highest mean molinate concentrations measured with GC/MS and ELISA were 3.1 µg L^{-1} and 9.3 µg L^{-1} respectively on 11 November 1998 (Figure 3B). While the patterns of molinate detections through time at TUPX by GC/MS and ELISA were similar, there was a significant difference in the overall mean molinate concentrations measured between the two methods at TUPX (paired 2-sample t-test, n = 9, $p = 0.0007$). Molinate was not detected in either GC/MS or ELISA samples at any of the six monitoring sites downstream of TUPX.

ANZECC and ARMCANZ (2000) recommend a trigger value of 3.4 µg L^{-1} for molinate to provide protection of 95% of freshwater species. At LALI, the trigger value was exceeded for 22% of sampling occasions with GC/MS but 44% of sampling occasions with ELISA. At TUPX, the trigger value was exceeded in none of the sampling occasions with GC/MS but 67% of sampling occasions with ELISA.

Oxychlordane in surface water

Oxychlordane was only detected (detection limit: 0.02 µg L^{-1}) in a single surface water sample at LALI in late October. Although ANZECC and ARMCANZ (2000) recommend a trigger value of 0.08 µg L^{-1} for the protection of 95% of freshwater species for chlordane, no trigger value is available for oxychlordane.

Retrieval of TRIMPS and solvent retained after deployment

Of the 216 TRIMPS deployed, 179 TRIMPS (83%) were retrieved from sites and were delivered to the laboratory without damage. The volume of solvent (2,2,4-trimethylpentane) retained in TRIMPS ranged from 3 to 10 mL (mean 8.4 mL; mode 9.0 mL). The minimum volume of solvent was in a single cumulative TRIMPS retrieved from TUPZ on 30 October 1998 (17 days after deployment). Overall, 77% of the TRIMPS retained a solvent volume of 8 mL or above.

Biofouling of TRIMPS

Biofouling (the growth of a periphytic layer or biofilm on the membrane) was not evident for any daily or cumulative TRIMPS deployed during the study. Some biofouling was observed on the plastic mesh that surrounded the cumulative TRIMPS deployed in Edward River.

Molinate in TRIMPS

At LALI, molinate was not detected in daily TRIMPS retrieved on 27 October 1998 but was detected at an extremely high concentration of 5851 µg L^{-1} solvent in one of the three daily TRIMPS retrieved on 28 October. Molinate was not detected in the other two daily TRIMPS retrieved on the same day, suggesting that the measured concentration (5851 µg L^{-1} solvent) on 28 October should be viewed with caution. Mean molinate concentrations of 336 and 161 µg L^{-1} solvent were detected in daily TRIMPS retrieved from LALI on 29 and 30 October 1998 respectively.

Cumulative TRIMPS retrieved from LALI on 29, 30 October and 4 November 1998 (16, 17 and 22 days after deployment respectively) detected molinate, with mean concentrations of 446, 356 and 98 µg L^{-1} solvent respectively (Figure 3C).

At TUPX, molinate was not detected in daily TRIMPS but was detected in cumulative TRIMPS (mean 191 µg L^{-1} solvent) retrieved on 11 November 1998 (29 days after deployment), even though the GC/MS or ELISA detected molinate prior to that date (Figure 3D). Molinate was not detected in TRIMPS retrieved from any of the six monitoring sites downstream of TUPX.

Thiobencarb in TRIMPS

Thiobencarb was only detected in cumulative TRIMPS on 100% and 33% of sampling occasions at LALI and TUPX respectively.

At LALI, the thiobencarb concentrations in cumulative TRIMPS increased from 330 µg L^{-1} solvent on 21 October (8 days after deployment) to 1969 µg L^{-1} solvent on 4 November 1998 (22 days after deployment) (Figure 4A). The maximum thiobencarb concentration of 4593 µg L^{-1} solvent was measured in cumulative TRIMPS retrieved on 18 November 1998 (36 days after deployment). After 18 November, the thiobencarb concentrations in cumulative TRIMPS varied from 250 to 284 µg L^{-1} solvent.

At TUPX, the thiobencarb was not detected in cumulative TRIMPS until 11 November (29 days after deployment) but then attained the maximum concentration of 557 µg L^{-1} solvent on 18 November

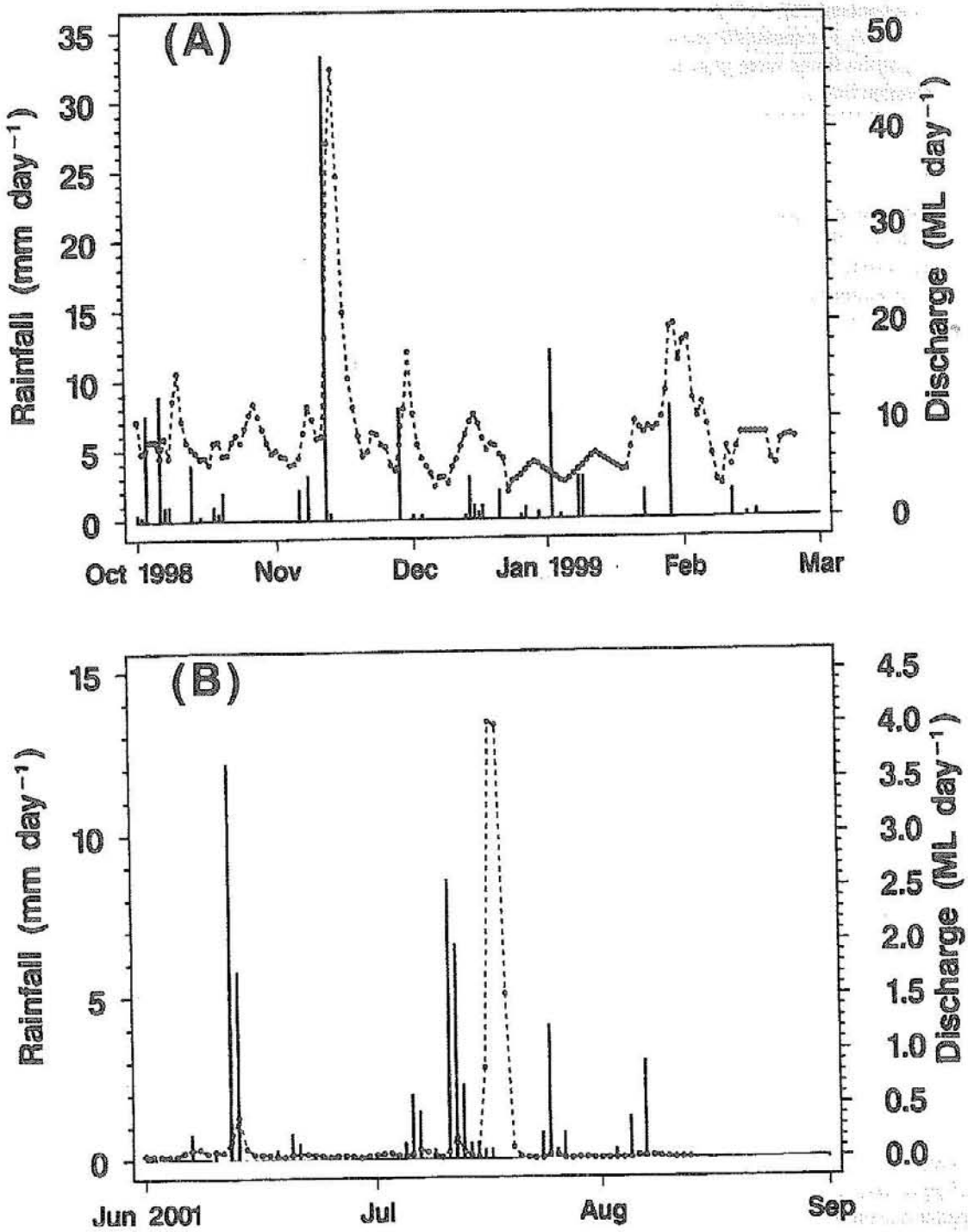

Figure 2. Daily rainfall (vertical solid line) at Finley Bureau of Meteorology Weather Station and daily discharge (dashed line with closed circles) measured at LALI: (A) irrigation season (October 1998 to February 1999); (B) non-irrigation season (June to August 2001). Since the rainfall data at Finley BMWS were not available between 25 October-18 November 1998, the rainfall data at Tocumwal Airport BMWS (Station No. 074106: 35°81'S, 145°59'E) were used during that period.

1998 (36 days after deployment) (Figure 4B). Thiobencarb was detected in cumulative TRIMPS retrieved on all three subsequent sampling occasions, with mean concentrations ranging from 184 to 144 µg L^{-1} solvent.

Relationship between daily discharge at LALI and pesticide detection

At both LALI and TUPX, there was no significant correlation between daily stream discharge and the mean concentration of molinate in surface water, irrespective of the analytical methods used (GC/MS or ELISA) (simple correlation coefficient for both $\log_{10}$-transformed and untransformed data: $n = 9$, $r < 0.24$, $p > 0.5$ for each correlation). Furthermore, at LALI, there was no significant correlation between daily stream discharge and the concentrations of molinate and thiobencarb detected in cumulative TRIMPS ($n = 11$, $r < 0.02$, $p > 0.53$ for each correlation).

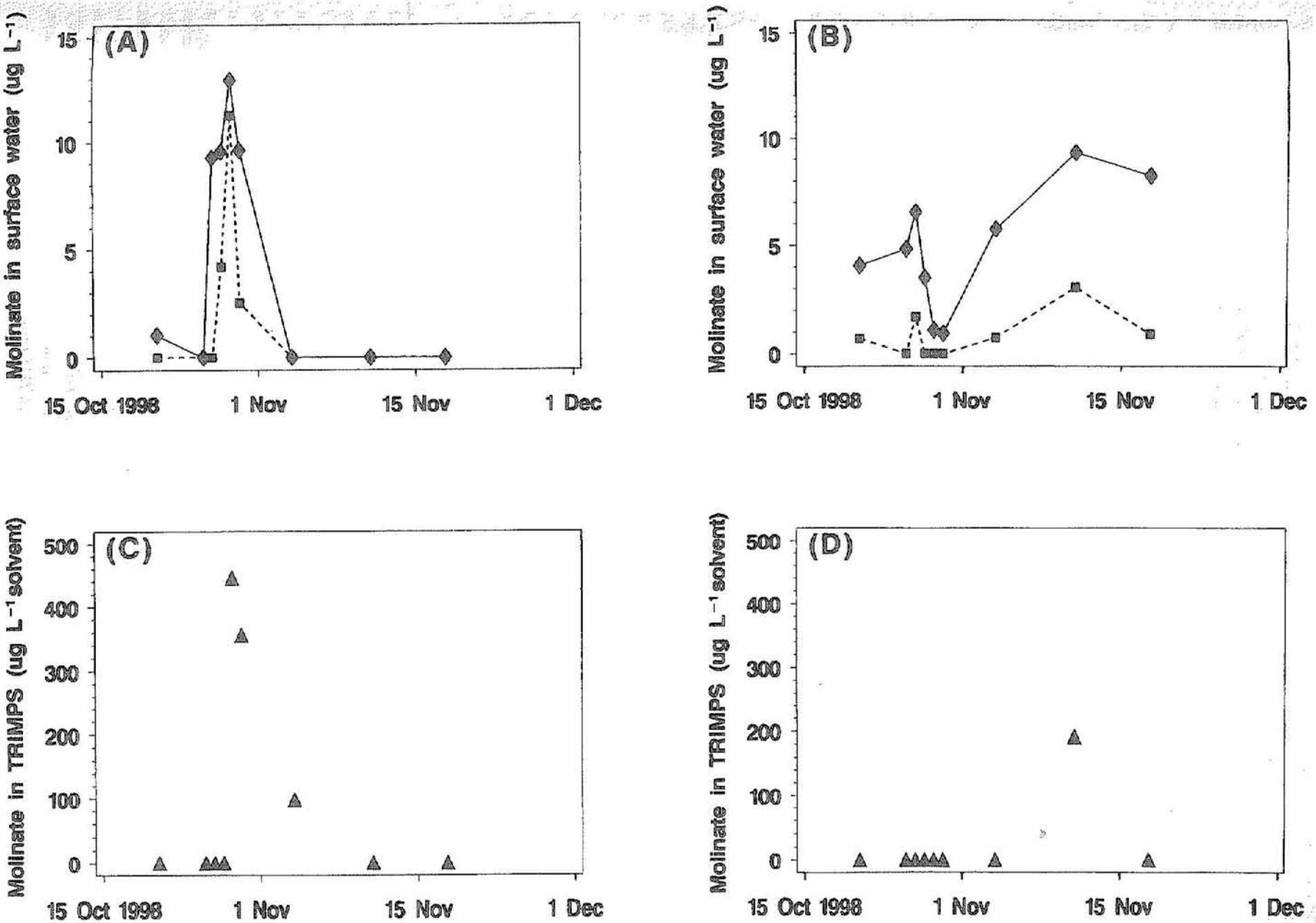

Figure 3. *Mean molinate concentrations during irrigation season (n = 1 to 3 for each observation): (A) surface water samples at LALI using GC/MS (closed squares with dotted lines) and ELISA (solid line with closed diamonds); (B) surface water samples at TUPX using GC/MS (dotted line with closed squares) and ELISA (solid line with closed diamonds); (C) cumulative TRIMPS at LALI; (D) cumulative TRIMPS at TUPX. Mean concentrations below the detection limits were plotted as zero. Molinate was not detected in any of the samples after 18 November 1998 and was not plotted after that date.*

Pesticide discharges during the non-irrigation season

Only atrazine, simazine, dimethoate and glyphosate were detected during the non-irrigation season (late May to mid August 2001).

Atrazine in surface water

Atrazine was detected at all sites monitored, with the most frequent detection at LALW (89% of sampling occasions) during routine monitoring (Figure 5). The maximum mean concentration of atrazine was 0.195 mg L^{-1}, measured on 13 June 2001 at LALL following the mid-June rainfall event (Figure 5). This concentration was, however, below the ANZECC and ARMCANZ (2000) recommended trigger value for the protection of 95% of freshwater species (13 mg L^{-1}). At LALL, relatively high concentrations of atrazine were again detected in late July. During event monitoring (16 to 19 July 2001), the maximum atrazine concentration was 0.10 mg L^{-1}, measured at TUPCK.

Simazine in surface water

Simazine was detected at all sites, with the most frequent detection (100% of sampling occasions) at LALW during routine monitoring (Figure 6). The maximum mean concentration of simazine was 0.40 mg L^{-1}, measured on 13 June 2001 at LALL following the mid-June rainfall event (Figure 6). This concentration was below the ANZECC and ARMCANZ (2000) recommended trigger value for the protection of 95% of freshwater species (3.2 mg L^{-1}). The maximum concentration of simazine during event monitoring was 0.04 mg L^{-1}, measured at TUPJ, TUPCK and TUPCKD.

Glyphosate in surface water

Glyphosate was detected on 21% and 7% of the sampling occasions at LALL and LALW respectively, during routine monitoring. The maximum mean glyphosate concentration of 6 mg L^{-1} was measured at LALL on 10 August 2001. This concentration was well below the ANZECC and ARMCANZ (2000) recommended trigger value for the protection of 95% of freshwater species (1200 mg L^{-1}). During event sampling, glyphosate was detected on a single occasion at LALL (3 µg L^{-1}).

Dimethoate in surface water

Dimethoate was detected on only 3% of the sampling occasions at LALL and LALW during routine monitoring. During event monitoring, dimethoate was detected on a single occasion at TUPCK (0.2 µg L^{-1}). Dimethoate was the only pesticide during event sampling, of which the measured concentration exceeded the ANZECC and ARMCANZ (2000) recommended trigger value for the protection of 95% of freshwater species (0.15 mg L^{-1}).

DISCUSSION

Pesticide discharges during irrigation and non-irrigation seasons

Seven out of 67 pesticides analysed were detected during the study. Of these, during the irrigation season (mid October 1998 to early February 1999), molinate and thiobencarb were frequently detected at LALI and TUPX, but were not detected at all other sites. Oxychlordane was detected at LALI on a single occasion. During the non-irrigation season (late May to mid August 2001), atrazine and simazine were frequently detected at all sites, while dimethoate and glyphosate were detected on fewer occasions.

Because there were differences in the pesticides targeted between irrigation and non-irrigation seasons (Appendix 1), the strict inter-season comparison of pesticide discharges is difficult. Nevertheless, the discharge of molinate and thiobencarb during the irrigation season is likely to be related to the discharge from rice fields of wastewater that contains these pesticides. The variation in concentrations of these pesticides appears, however, to be independent of the drain discharge, even though the relatively small number of observations was available for correlation analyses (n = 9 to 11). Detection of no pesticides downstream of TUPX is probably attributable to a combination of factors including chemical breakdown/volatilisation, adsorption to particulate matter and downstream dilution (Thomas *et al.* 1998).

The mean molinate concentrations at TUPX were significantly and negatively correlated with those at LALI (upstream site) during the irrigation season of 21 October to 18 November 1998 (n = 9, Spearman rank correlation coefficient or $r_s = -0.70$, $p = 0.037$ with GC/MS results and $r_s = -0.80$, $p = 0.0095$ with ELISA results). The observed negative correlation may reflect a time lag in the movement of peak molinate concentrations downstream. It is also possible that molinate discharges occurred from the sub-catchment located between LALI and TUPX, particularly from mid to late November 1998.

The frequent detection of atrazine and simazine during the low-flow non-irrigation season may be due to the intrusion of contaminated groundwater, spraying near or directly into the channel to reduce weed infestations or the persistence of these chemicals in channel sediments. In particular, flow at LALL (the furthest upstream site) is thought to be greatly influenced by groundwater discharge, because median electrical conductivity values at this site were similar to those of the local groundwater (> 15,000 mS cm^{-1}) (MIL 1999). Furthermore, elevated atrazine and simazine concentrations detected after the mid-June rainfall event (and subsequent runoff) suggest that both chemicals can be mobilised during relatively elevated flow events. In the US, atrazine is the most common pesticide detected in groundwater (USEPA 1990).

GC/MS versus ELISA for molinate

Comparisons of GC/MS and ELISA methods for molinate during the 1998/99 irrigation season showed that overall ELISA yielded significantly higher mean concentrations than did GC/MS analysis at TUPX but not at LALI. In this study, samples for ELISA were analysed within five hours after collection, while samples for GC/MS were analysed up to 48 hours after collection. From this point of view, relatively higher concentrations of molinate may be expected from ELISA than from GC/MS because of possible reduced loss of molinate from water samples through volatilisation and adsorption to sample vials. However, this does not account for non-significant difference in the overall mean concentrations measured between the two methods at LALI. Some site-specific factors(s) may be responsible for the observed difference in results between the two sites (LALI and TUPX). Further detailed study is necessary to elucidate such causal factors. Nevertheless, ELISA is regarded as a useful screening method for molinate since a relatively short period is required to obtain results that tend to be conservative, relative to GC/MS results.

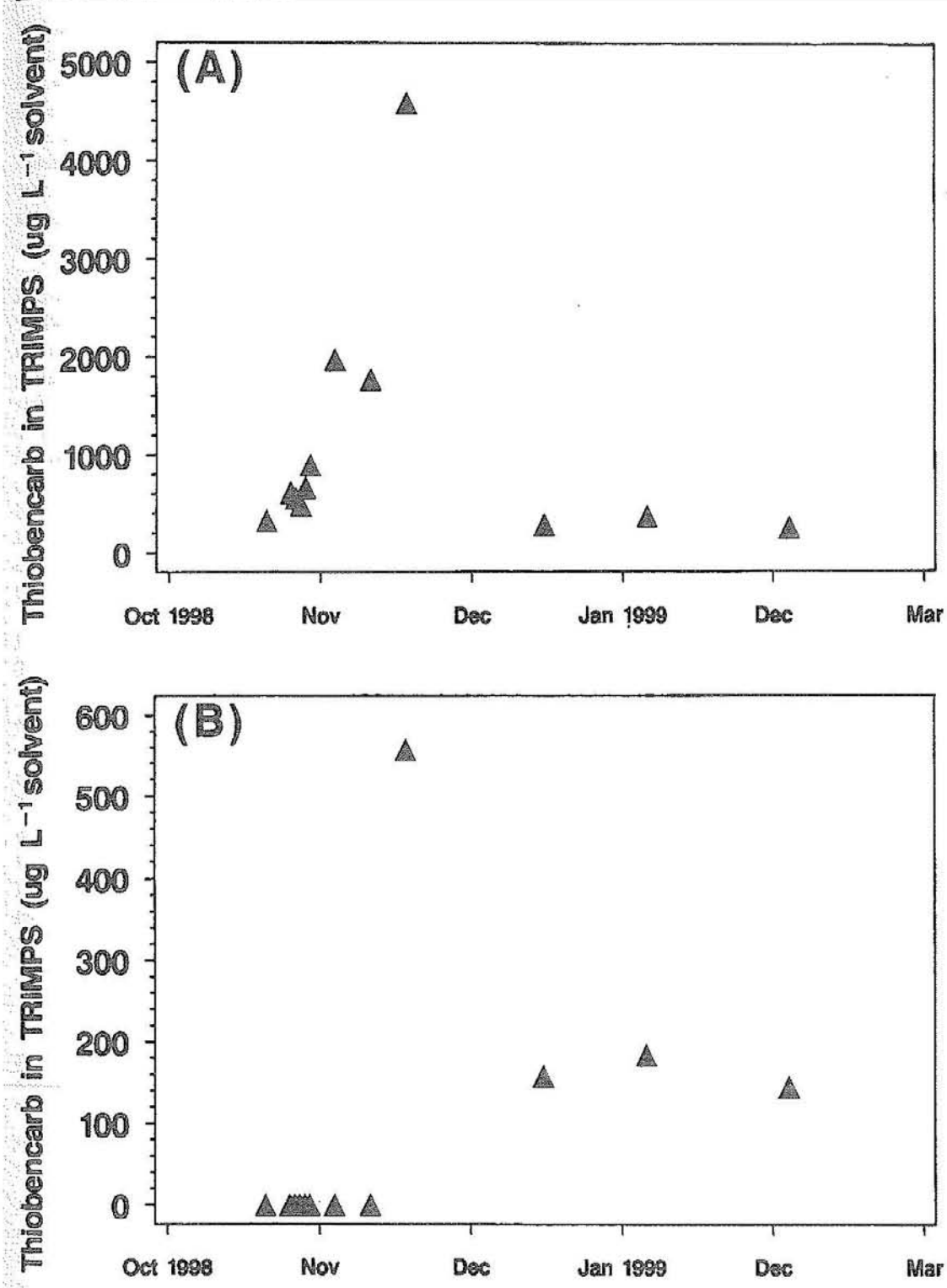

Figure 4. Mean thiobencarb concentrations during irrigation season (n = 1 to 3 for each observation): (A) cumulative TRIMPS retrieved from LALI; (B) cumulative TRIMPS retrieved from TUPX. Mean concentrations below the detection limits were plotted as zero.

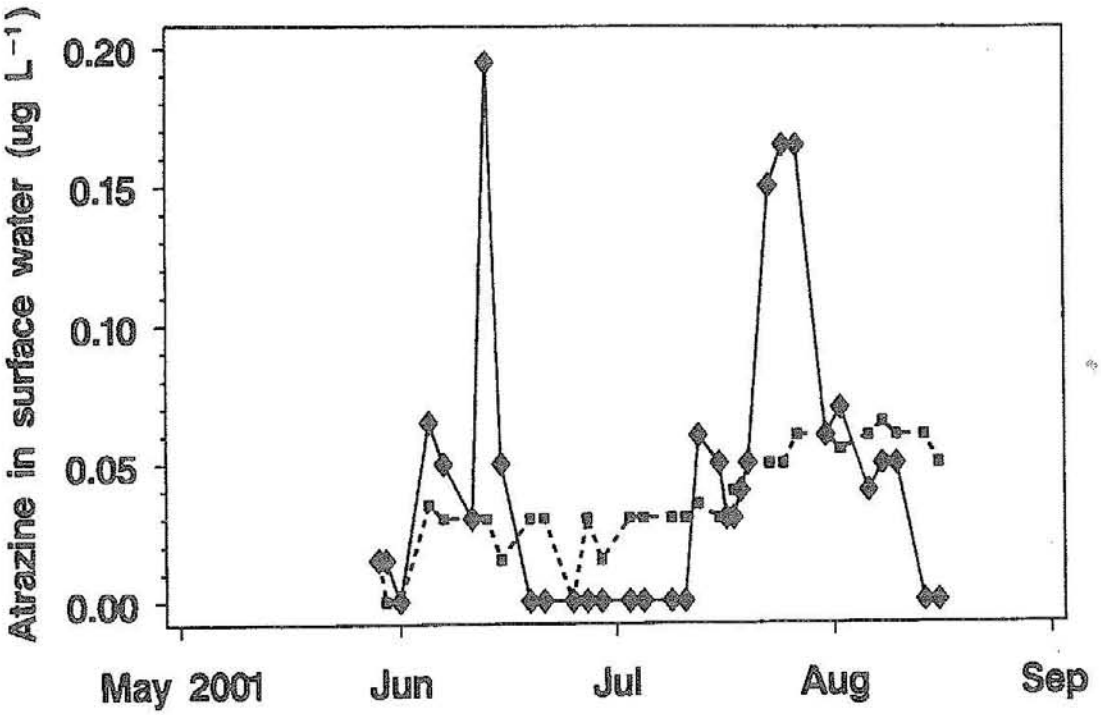

Figure 5. Mean atrazine concentrations during non-irrigation season at LALW (dotted line with closed squares) and LALL (solid line with closed diamonds), measured from surface water samples (n = 1 to 2 for each observation). Mean concentrations below the detection limit were plotted as zero.

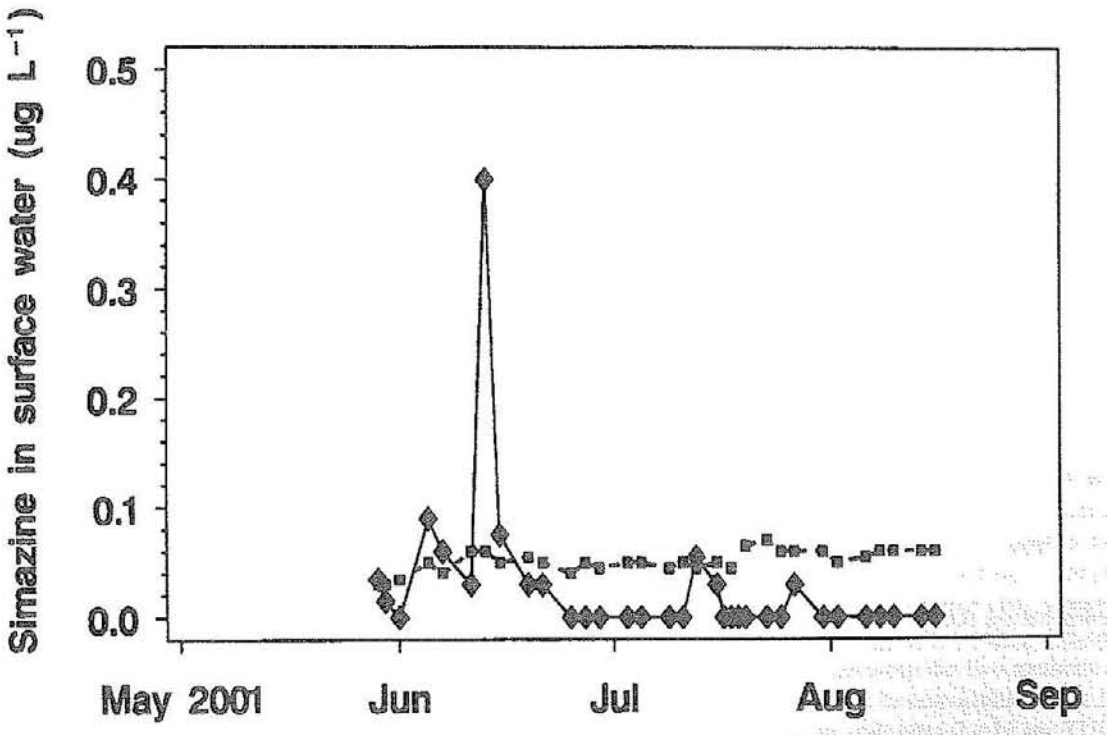

Figure 6. Mean simazine concentrations during non-irrigation season at LALW (dotted line with closed squares) and LALL (solid line with closed diamonds), measured from surface water samples (n = 1 to 2 for each observation). Mean concentrations below the detection limit were plotted as zero.

Volume of solvent retained in TRIMPS

Seventy-seven percent of the recovered TRIMPS retained a solvent (2,2,4-trimethylpentane) volume of 8 mL or above (80% of the initial volume) after deployment. This result is similar to that of other studies reporting retention rates of 80 to 90% of the initial volume of solvent for this type of passive sampler (Peterson *et al.* 1995; Leonard *et al.* 1999; Muschal 1999). Occasional losses of solvent from passive samplers are attributed to leakage due to faulty seals (Muschal 1999).

Biofouling of TRIMPS

TRIMPS-based estimates can be affected by biofouling which introduces an intermediate step (ie. partitioning between water-periphyton and then between periphyton and membrane), and also slows the uptake rate of chemicals by diminishing the available surface area of the membrane (Gale *et al.* 1997). Biofouling was not visibly evident on the membrane of TRIMPS during this study (see also Peterson *et al.* 1995). Therefore, the likely effect of biofouling on the uptake of pesticides was thought to be minimal. Muschal (1999) notes that the absence of biofouling is probably due to the solvent impregnating the membrane and acting as an anti-fouling agent as described by Johnson (1991).

Pesticide detection by TRIMPS

The cumulative TRIMPS showed that thiobencarb was being used as an additional or alternative herbicide to molinate in the catchment during the 1998/99 irrigation season. The presence of thiobencarb would have gone undetected had only surface water sampling and deployment of daily TRIMPS been used. The use of cumulative TRIMPS demonstrated an advantage over surface water sampling and daily TRIMPS in detecting thiobencarb during the 1998/99 irrigation season. In other NSW rivers, Muschal (1999) used similar passive samplers between 5 - 27 days and successfully detected pesticides that were not found using conventional methods.

Solvent-containing passive samplers are said to have advantages over conventional water sampling and use of biota, since they can be deployed in extreme-condition environments (eg. toxic industrial effluents, anaerobic conditions, etc.) and may remain operative for relatively long time periods (Johnson 1991; Sabaliūnas and Södergren 1997; Muschal 1999; Leonard *et al.* 2002; Lu *et al.* 2002). They have the potential to become a cost-effective, time-integrated monitoring tool of hydrophobic chemical pollutants in aquatic environments.

Although the TRIMPS containing trimethylpentane were able to detect molinate and thiobencarb, the relationship between pesticide concentrations in TRIMPS (expressed as micrograms per litre of solvent in this study) and pesticide concentrations in ambient waters is unclear in this study. The concentration inside the TRIMPS is a time-integrated concentration, and is not indicative of the concentration in surface water at any one time.

Mathematical models may be used for the estimation of water concentrations of chemical pollutants from their concentrations inside solvent-containing passive samplers (Johnson 1991; Huckins *et al.*1993; Gale 1998; Leonard *et al.* 2002). To apply the models, linear kinetic parameters (eg. uptake and depuration rate constants, and volume of water extracted per unit time) need to be obtained for each chemical under a constant water flow rate and chemical concentration in laboratory experiments (Sabaliūnas and Södergren 1997; Booij *et al.* 1998). Assuming isotropic exchange kinetics govern the uptake of chemicals in these devices, then one half-life may be the maximum time period when the chemical displays linear uptake kinetics, as they obey first order kinetics (Huckins *et al.* 1993; Leonard *et al.* 2002). The deployment time of the passive samplers in the field needs to be less than one half-life of the release rate of the chemical under study. Recent studies have shown that the release half-life for molinate from trimethylpentane-containing passive samplers was approximately three days (Leonard *et al.* 2002). This indicates that this type of passive sampler device may not be suitable for use to obtain an estimate of the average water concentrations of molinate in the field since the uptake and release kinetics for molinate are very rapid. Leonard *et al.* (2002) showed that only chemicals with a log $K_{ow} > 3.5$ displayed suitable uptake kinetics into trimethylpentane-containing passive samplers. These hydrophobic chemicals with a log $K_{ow} > 3.5$ may be calibrated with the trimethylpentane-containing passive samplers in order to estimate average water concentrations from the chemical uptake into field-deployed devices (see also Gale 1998). Thiobencarb, which was frequently detected in cumulative TRIMPS in this study, has a log K_{ow} of 3.42 (Tomlin 1994), suggesting that it may be difficult to estimate its average water concentrations with TRIMPS results. Further laboratory and *in situ* studies are necessary to better understand the accumulation process of various pesticides in TRIMPS, so that the potential advantages of TRIMPS can be realised.

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