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Pesticide Monitoring in Goulburn-Murray Waters Irrigation Supply Channels Covering the Six Irrigation Areas [2004 -2006 Irrigation Season Study Report]

June 2006

Published: Primary Industries Research Victoria

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Environmental Health and Chemistry
Department of Primary Industries, Werribee

General disclaimer

G-MW Docs 2056533

Authorised by the Victorian Government, 621 Sneydes Road, Werribee 3030

Printed by PIRVic Werribee, Victoria.

ISBN : 1 876356 96 0

Pesticide Monitoring in Goulburn-Murray Water's Irrigation Supply Channels Covering the Six Irrigation Areas (2004-2006 Irrigation Season Study Report)

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June 2006

Department of Primary Industries

Citation

Rose, G and Kibria, G. (2006). Pesticide Monitoring in Goulburn-Murray Water's Irrigation Supply Channels covering the Six Irrigation Areas [2004-2006 Irrigation Season Study Report]. Report Prepared under a research collaboration agreement between G-MW and PIRVic. Goulburn Murray Rural Water Authority (G-MW), Tatura and Primary Industries Research, Vic, Werribee

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Acknowledgments

The authors acknowledge the help and cooperation received from following:

G-MW : Central Goulburn Irrigation Area (Max Cail, Gary Whyte); Murray-Valley (Dave Derby, Rob Williams); Shepparton (Mark Newton); Rochester-Campaspe (David Fehring), Torrumbarry (Ian Hetherington); Pyramid–Boort (David Hellsten); Goulburn Weir (Steve Hall), and EMPA2 Reference Team Members

Primary Industries Research Victoria (PIRVic Werribee-State Chemistry laboratory): Pei Zhang, Davorka Tucman, Simon Phelan, Aaron Elkins, Dr Jun Du, Dr Craige Trenerry, Colin Cook

Centre for Ecotoxicology, Department of Environment & Conservation (DEC), NSW : Dr Ross Hyne and Melissa Aistrope

Others : Nolan-Itu (Rob Medley, Tara Bassette, Daniel A'vard) and ; **Ecowise-WSL** (Andrew Higgins, Hao Zhang)

1. Executive Summary

During 2004-05 and 2005-06 irrigation seasons, a pesticide and heavy metals monitoring study was conducted at 15 potential risk sites located within the six Goulburn-Murray Water irrigation areas in northern Victoria. The risk sites included intensive orchards (pome & stone fruit), vineyards, vegetables (intensive tomatoes), channel offtakes, channel outfall, stock & domestic and town supplies, and aquaculture. The study includes deployment and retrieval of passive samplers, spot water sampling and analysis and interpretation of results of targeted pesticides and related heavy metals. The monitoring found three agriculture chemicals on a regular basis across the six irrigation areas. These were : endosulfan (an organochlorine insecticide), atrazine (herbicide) and copper (fungicide). The two other chemicals that were found on an irregular basis were chlorpyrifos and parathion methyl (organophosphates).

In the 2004-05 seasons endosulfan was detected at 8 of the 14 sites in passive samplers on a regular basis, with elevated concentrations at 3 sites (Mooroopna, Ardmona, Kyabram). Chlorpyrifos was detected on two occasions at Shepparton. Atrazine was detected at 9 of the 14 sites in spot water samples). Copper was detected at most sites in spot water samples.

In the 2005-06 seasons endosulfan was detected at each of the 15 sites in passive samplers at least once with elevated concentrations at four sites (Shepparton, Mooroopna, Ardmona and Kyabram). Endosulfan was detected in passive samplers on 3 occasions at Nagambie in 2005-06 when it was not detected in 2004-05. Chlorpyrifos was detected in 2005-06 in passive samplers at 4 sites, with elevated concentrations at Shepparton and Ardmona. Parathion methyl was detected in passive samplers at Shepparton and Ardmona. Atrazine was detected in spot water samples at each of the 15 sites for the majority of sample dates. Copper was detected at most sites, but at elevated concentrations at Torganah, Mooroopna, Tatura, West Boort, Appin, Kerang Town, and Kangaroo Lakes. The three agriculture chemicals that were frequently detected were associated with intensive orchards (stone, pome fruit), vineyards, pastures and forage and vegetable (tomatoes) .

By comparison with national water quality guidelines (ANZECC – raw water for drinking water supply, recreational, irrigation, and aquaculture) and ecotoxicological data (mammalian, fish, algae and daphnia, Tomlin (2000)), the water quality was found to be within the national standards for most primary purposes (irrigation, stock & domestic supply, town supply) for all the six irrigation areas investigated. However, water endosulfan concentrations at Mooroopna, Ardmona, Shepparton and Kyabram, estimated from passive sampler's concentrations would have exceeded the recommended ANZECC guidelines (0.003 μg/L) for the purpose of aquaculture or fish farming. Water chlorpyrifos concentrations estimated from passive samplers at Shepparton, Katamatite, Mooroopna and Ardmona have also exceeded the ANZECC guidelines for the purpose of aquaculture or fish farming.

As there are no national guidelines for atrazine for all purposes, Canadian Environmental Quality Standards (2003) for irrigation, and livestock and drinking were used for comparison. The atrazine concentrations found were within the Canadian Guidelines for drinking, recreation, agriculture water uses and aquatic life protection. Copper concentrations detected in irrigation channel water were found to be safe for drinking, irrigation, aquaculture and livestock. As there are no sample

data to identify the origin of these concentrations, these concentrations are possibly attributable to natural or agriculture sources.

By comparison with Australian, New Zealand and USA drinking water and human health values the detected and average values for endosulfan, chlorpyrifos, parathion methyl, atrazine and copper were found to be with guideline values.

By comparison with ANZECC (2000) guideline for endosulfan , chlorpyrifos, atrazine and copper the water quality of receiving water bodies (as channel outfall) would be safe for the protection of freshwater ecosystems and aquatic environment The guidelines thresholds values for the protection of aquatic ecosystems have been included in this report for comparison only. The ‘State Environment Protection Policy for the Waters of Victoria (EPA, 2003)’ does not assign beneficial uses to "artificial irrigation channels". This includes G-MW's irrigation channels. Whilst the policy makes clear that this should not to be taken as authorisation of illegal contamination of such channels, it means that aquatic ecosystems in the channels are not afforded the same concentration of legal protection as those in natural waterways into which the channels sometimes outfall. Therefore it will be useful to know the relationship between pesticide and heavy metal concentrations in the channels and guideline reference thresholds for the protection of aquatic ecosystems, but the key consideration will be how those concentrations in channel outfalls elevate concentrations in receiving natural waterways (considering dilution with the bulk of rivers water) and the relationship of those values to the guideline thresholds (EPA 2003).

The current report combines the two years monitoring results of pesticides and related heavy metals in the six irrigation areas. Based on the two years research study on pesticides and heavy metals concentrations in channels it can be concluded that channel water in the six irrigation areas is of good quality and is safe for most beneficial usages including irrigation, stock & domestic supply, town supply and recreation. However, the study results suggest that there is potential risk of using channel water for the purpose of aquaculture or fish farming in particular where intensive orchards and vegetables (tomato) are being grown.

It is recommended that pesticides monitoring should be continued for a further one year for those sites where elevated concentrations of endosulfan and chlopyrifos were regularly detected. This monitoring would be completed in the context of verifying that risk assessments and suitable controls and risk mitigation strategies have been implemented adjacent to these sites. These sites are : Shepparton (SIA), Ardmona (CG), Mooroopna (CG), Kyabram (CG).

2. Contents

3. Background

Goulburn-Murray Water (G-MW) is the largest rural water supply authority in Australia, supplying water for irrigation, domestic and stock drinking and town supplies. G-MW's region covers 68,000 square kilometres from the Great Dividing Range north to the River Murray and from Corryong down river to Nyah near Swan Hill. The bulk of water is supplied through gravity irrigation channels (7,150 km) to dairy farms, orchards (stone, pome fruit, olive), vineyards, crops (canola, beans, wheat, rice), tomatoes and aquaculture. These agricultural enterprises use a range of pesticides to control pests and weeds. It is suspected that water contaminated with pesticides can be unfit for human consumption, stock drinking, fish farming, irrigation and food processing. It is sometimes necessary to outfall small volumes of channel waters into natural waterways. Any pesticide contained in this outfall water could impact on aquatic biota living in these natural waters. It is therefore essential to ascertain the concentrations of chemical contaminants (pesticides and related heavy metals) in G-MW's supply channels to establish risk concentrations and ensure that appropriate measures can be taken to reduce risks from such chemicals.

A preliminary pesticide use survey (conducted in 2001 by G-MW) found that more than 75 pesticides (36 herbicides, 23 insecticides, 17 fungicides) were used in different farming sectors across the six Irrigation Areas (Central Goulburn, Shepparton, Murray Valley, Rochester-Campaspe, Torrumbarry, and Pyramid-Hill); see Krake, Breewel and Kibria (2001). Consequently, G-MW engaged the Commonwealth Scientific Industrial and Research Organisation (CSIRO) to make a first tier assessment of the risks associated with these pesticides to water quality and through changed water quality to humans, stock, food industries, pastures, and aquaculture and aquatic flora, fauna and aquatic ecosystems. The State Environment Protection Policy for the Waters of Victoria (EPA, 2003) does not assign beneficial uses to "artificial irrigation channels". This includes G-MW's irrigation channels. Whilst the policy makes clear that this should not to be taken as authorisation of illegal contamination of such channels, it means that aquatic ecosystems in the channels are not afforded the same concentration of legal protection as those in natural waterways into which the channels sometimes outfall. Therefore it will be useful to know the relationship between pesticide and heavy metal concentrations in the channels and guideline reference thresholds for the protection of aquatic ecosystems, but the key consideration will be how those concentrations in channel outfalls elevate concentrations in receiving natural waterways and the relationship of those values to the guideline thresholds (EPA 2003).

The risk assessment found that, 10 pesticides (out of 75 pesticides assessed) are of highest risks to humans, stock, food industries, pastures, and aquaculture and aquatic flora, fauna and aquatic ecosystems (see Kookana, Barnes, Correll and Kibria, 2003). The 10 pesticides that were assessed to be of highest overall risk to all receptors were ; organophosphates (OP), azinphos-methyl, omethoate, parathion methyl and chlorpyrifos; fungicides (F), copper hydroxide, mancozeb and thiram; synthetic pyrethroids (SP), esfenvalerate and bifenthrin and the carbamate (C) methomyl. The CSIRO study recommended monitoring of 10 high risk pesticides in G-MW irrigation channels to establish high risk sites within G-MW irrigation areas. However, both CSIRO and DPI (State Chemistry Laboratory) suggested inclusion of some medium risk pesticides such as endosulfan, atrazine, and molinate during pesticide monitoring in channels.

Accordingly, a pilot study (Central Goulburn Irrigation Area) was conducted in 2003-2004 to trial new passive sampling techniques to monitor pesticide concentrations in G-MW channels. The trial included the preparation of passive samplers, their deployment and retrieval in channels for pesticide analysis. Spot sampling of channel waters was also undertaken for comparison with passive samplers and for analysis of selected heavy metals. The pilot study found that the passive sampling techniques are viable and effective techniques for monitoring of pesticides in channels (see Rose and Kibria 2004). The pilot study model has been extended to the channels in the six irrigation areas and ran for two irrigation seasons (2004/05 and 2005/06). This report combines the two years monitoring results of pesticides and related heavy metals in the six irrigation areas.

4. Scope of the work

Goulburn Murray Water (G-MW) signed a collaborative research agreement with the Primary Industries Research, Victoria (PIRVic), Werribee Centre (State Chemistry Laboratory), in 2004 to analyse environmental samples collected from the six irrigation areas during 2004-05 and 2005-06 and 2005-2006 irrigation seasons. The 2004-05 and 2005-06 analysis results reported here are from the 15 potential risk sites identified (see Figure 1, Table 1) in the six irrigation areas (Central Goulburn, Murray Valley, Rochester-Campaspe, Torrumbarry, Pyramid-Boort, and Shepparton). The risk sites identified includes fruit (stone & pome fruit, vineyards and olives), vegetable (tomatoes), water supply (stock & domestic, town), aquaculture, and channel outfall and channel offtakes. For the 2005-06 season an additional channel offtake Torrumbarry Weir was included in the sampling making 15 sites (14 sites in 2004-05). The sites selected were based on surveys conducted in the six irrigation areas with the help of field staff, the intensity of farming in each irrigation area, and the proximity of farms in relation to irrigation channels.

The monitoring targeted pesticides and related heavy metals that are of highest to moderate risks to different receptors based on CSIRO study (see Appendix 1). The main purpose of the research study was to investigate pesticide and related heavy metals concentrations in the six irrigation areas. G-MW provided funds only for analysis of environmental samples and as part of the collaboration, PIRVic (Werribee) developed methods for analysis of G-MW's samples appropriate for the project.

The highlights of 2004-05 and 2005-06 passive monitoring are as follows:

- covered the most potential risk sites
- covered the six irrigation areas
- an improvement of solvent analysis methods (compared to pilot study)
- inclusion of blank and triplicate samples (for quality assurance)
- production of peer reviewed technical report (Dr Ross Hyne and his team members reviewed the report)

The sites included intensive orchards (pome & stone fruit), vineyards, vegetables (tomatoes), town supply, stock & domestic supply, aquaculture. In relation to risk to ecosystems at risk , the threshold levels for Aquatic ecosystems (95% protection) for endosulfan, and chlorpyrifos, also copper have been included.

▪

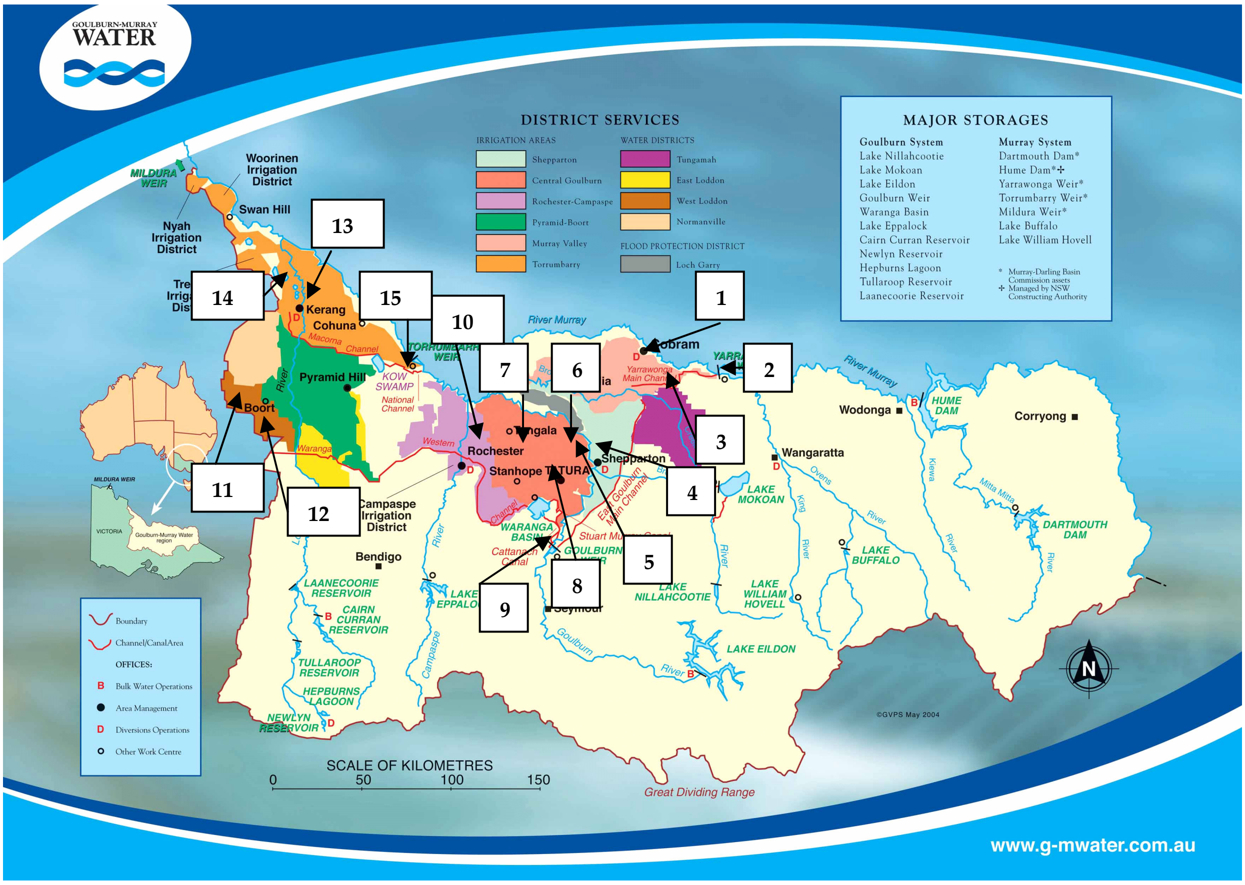

Figure 1. Goulburn Murray Water regions and the location of passive sampling/ monitoring sites in the six irrigation areas during 2005-06 and 2005-2006 irrigation seasons.

Table 1: **Description of pesticide monitoring sites in the six irrigation areas during 2004-05 and 2005-06 and 2005-2006 irrigation seasons**

Site number & Irrigation Area	Active region	Location and GPS	Prime targets	Comments
1-Murray Valley Irrigation Area (MVIA)	Torgannah	Channel-1 MV Highway, Koonoomoo Rd, Purgatory Lane GPS 55-359093E, 59-76183N	Intensive orchards (stone & pome fruit)	▪ Upstream- intensive orchards, pasture ▪ Downstream- outfall to Torgannah lagoon, hobby farm
2- MVIA	Burramine	Channel-Yarrawonga Main 8 mile regulator, Occupational bridge (Burramine Rd-MV Highway), 20km North from Cobram GPS 55-394622E, 60-15073N	Channel off-take for Murray system	▪ Channel off-take ▪ Upstream –pasture, crop
3- MVIA	Katamatite	Channel 7/3 Cobram-Benall Rd, Scada 8ft regulator (okanes regulator) GPS 55-383996E, 60-07565N	Town supply & outfall	▪ Upstream-pasture, crop ▪ Downstream-outfall to Booscy Creek &-Broken Creek town supply (water to 300 people)
4-Shepparton Irrigation Area (SIA)	Shepparton	Channel 12, below Fingerboards regulator (asset number ST45682). GPS 55-356447E, 59-77465N	Intensive Orchards (stone & pome fruit)	▪ Upstream-intensive orchards ▪ Downstream-pasture, (horticulture, crops, S&D)
5-Central Goulburn Irrigation Area (CGIA)	Mooroopna	Channel 15/6/4 Ebbots regulator, Scada 1564, GPS 55-356435E, 59-75124N	Channel outfall	▪ Upstream-channels of Murchison, Toolamba, Ardmona pass through orchards, tomatoes and pastures dairy ▪ Downstream-outfall to Goulburn River
6- CGIA	Ardmona	Channel 4 Gaffying regulator, Regulator 339, GPS 55-346409E, 5951889-N	Intensive orchards (stone & pome fruit)	▪ Upstream orchards, pasture ▪ Downstream-pasture
7-CGIA	Kyabram	Channel 8 Mercuris regulator-Regulator No TN 1131 minus 20/8-TN 1132 flow GPS 55-330243E, 59-85958N	Tomatoes	▪ Upstream-Tomatoes ▪ Downstream-Pasture
8-CGIA	Tatura	Channel 3/5 Regulator RN 385 GPS 55-340603E, 59-63685N	Town supply	▪ Upstream-pasture and crop ▪ Downstream- town supply (supplies water to Tatura Milk, Rosella, and Tatura residents)
9. Reference site	Nagambie	Stuart Murray Canal Goulburn Weir GPS 55-340603E; 59-63684N	Channel off-take for Goulburn System	▪ Channel off-take ▪ Upstream-vineyards, tomatoes,, pasture, crop, fish farms
10- Rochester-Campaspe Irrigation Area (R-CIA)	Corop	Rochester Channel 1 (WWC), Downstream of Bickley's Regulator, (Regulator 100) GPS 55-303680E; 59-72344N	Tomatoes & Vines & Town supply	▪ Upstream-vine & tomatoes ▪ Downstream- town supply, D&S, pasture
11-Pyramid Boort Irrigation Area (PBIA)	West Boort	Channel 5 (WWC), 36 mile regulator , SCADA control (PM regulator no PH 1309) GPS 54-7374790E; 59-97514N	Orchards (olive) & Town Supply	▪ Upstream-olives ▪ Downstream- Stock & domestic (160), town supply
12-P-BIA	Appin	Channel 8/2, regulator no IPM PH 1106 (2218/2231) GPS 54-755344E; 60-17025N	Tomatoes & Aquaculture & Outfall	▪ Upstream-tomatoes, crop (wheat, canola) ▪ Downstream-Aquaculture Murray Cod), outfall to Lake Meran & Loddon River
13. Torrumbarry Irrigation area (TIA)	Kerang town	Channel 14/2, regulator-last regulator of 14/2, 1km upstream of Loddon-Murray Water channel off-take Access Rd : Collins Rd-Bendigo HW GPS 54-750149E; 60-61599N	Town supply	▪ Upstream-pasture ▪ Downstream-town supply
14 TIA	Kangaroo Lake	Channel 7 (main channel to Swan Hill) Mystic Park Rd-MV Highway GPS 54-750151E; 60-61600N	Vine yard	▪ Upstream-vine, pasture ▪ Channel water supplies to Swan Hill ▪ Downstream to Ramsar Lake
15 Torrumbarry (2005-06 site)	Gunbower	National Channel	Channel off-take-Torrumbarry	▪ Channel off-take ▪ Upstream –Echuca town

5. Objectives

- To monitor time integrated accumulation of pesticides in passive samplers with solvent 2,2,4 - trimethylpentane and solvent mixture 1-dodecanol : 2,2,4 - trimethylpentane
- To monitor range and quantity of pesticides and heavy metals in spot samples with respect to different monitoring sites for quality assurance of results obtained with passive sampling technique
- Provide some information on pesticide usage in the study area and enhance DPI's ability to sustain irrigated agricultural industries

6. Study Description

6.1 Pesticide monitoring strategy

Routine sampling can monitor chemical contaminants in the aquatic environment. However if concentrations are low, or vary over time and have to be measured over a long period of time, it can be expensive and require intensive sampling. An alternative would be to use a sampling technique that takes place *in situ* (directly in the environment) and can be used for longer periods of time, and be able to accumulate substances where concentrations are low or variable. It would also be an advantage to be able to screen the presence of a large number of substances and operate virtually unattended. This alternative technique is known as 'passive sampling'. In this instance, the passive sampling technique developed (Dr Ross Hyne, Centre for Ecotoxicology, NSW) for monitoring of pesticides in aquatic environment has been adopted, Leonard, Hyne and Pablo (2002). The technique is limited to pesticides with log K_{ow} >2.5. K_{ow} is the octanol-water partitioning coefficient : a measurement of how a chemical is distributed at equilibrium between octanol (a fat analogue) and water. A higher log K_{ow} indicates the chemical is more fat soluble than water soluble.

A 'passive sampler' is a non-biological object capable of accumulating substances against a concentration gradient without supply of power or energy. The passive samplers work by the laws of diffusion and provide time-integrated concentrations of contaminants in an environment. For common pesticides, laboratory studies using spiked water solutions have provided concentration factor curves which enable average water concentrations to be determined with reasonable accuracy from passive sampler concentrations over the deployment period (see section 6.2). There is a good relationship between pesticide concentrations determined using trimethylpentane containing passive samplers with those calculated from daily river-water extraction; therefore it is a good device for assessing, for example, river–water quality. Furthermore, the membrane based passive samplers are a promising tool for the time–integrated monitoring of hydrophobic contaminants such as pesticides in aquatic ecosystems (Hyne, Pablo, Aistrope, Leonard and Ahmad (2004), Leonard, Hyne and Pablo (2002)). The determined time - integrated pesticide water concentrations determined facilitate a comparison with the national and international water quality guideline values for drinking, recreation, irrigation, livestock, aquatic ecosystems protection and aquaculture. However, despite the advantages with 'passive samplers' they are generally limited to hydrophobic substances with high K_{ow} values. In order to monitor hydrophobic pesticides (listed in Appendix 1) in G-MW supply channels, the following monitoring strategies were undertaken:

1. Deployment of passive samplers with solvent 2,2,4 trimethylpentane (TRIMPS) (target for pesticides with high partition coefficient or K_{ow} values (>3.5), mainly organochlorine (OC) and synthetic pyrethroids (SP))
2. Deployment of passive samplers with solvent mixture 1-dodecanol : 2,2,4 Trimethylpentane (3:2) (target for pesticides with low partition coefficient or K_{ow} (>2.5 but less than 3.5), and mainly herbicides (H), organophosphates (OP) and carbamates (C)
3. Spot samples (targeted for all pesticides listed in Appendix I including OP, OC, H, SP, C and heavy metals (Cu, Cd, Zn, Pb)

6.2 Determination of time integrated pesticide water concentrations

The principle of the passive sampling technique is that the pesticides are more soluble in the organic solvents and migrate through the semi-permeable film into the sampler bags. The concentration of the pesticides in the solvent inside the sampler bags is an accumulation of all water passing over the bags for the deployment period (in this case 28 days). The analytical results were then converted into time integrated water concentrations following the regression equation and concentration factor available (see Leonard, Hyne and Pablo, 2002, see also Table 2).

Table 2: Example of calculating average endosulfan, chlorpyrifos and parathion methyl water concentration at Site (Ardmona), from Period 3 TRIMPS extract.

Site number	Date	Total days deployed (X)	Compound	Replic.-1 conc. (µg/L)	Replic. -2 conc.(µg/L)	Av. Conc. (µg/L)	Concentration Factor curve	Formulae and Concentration factor (CF) Note : x=number of days deployed	Average Water concentration
Endosulfan									
6	Oct-05	28	α -Endosulfan	2.1	2.5	2.3	y = 1.01x + 1.70	=Power(10,1.1*(Log(X))+1.7)) CF: 1958.226	0.00117
6	Oct-05	28	β -Endosulfan	2.0	2.4	2.2	y = 1.01x +1.61	=Power(10,1.1*(Log(X))+1.61)) CF : 1591.746	0.00138
6	Oct-05	28	Endosulfan SO_4	4.4	5.4	4.9	y = 1.11x + 1.67	=Power(10,1.1*(Log(X))+1.67)) CF : 1354.034	0.00361
			Total endosulfan						0.00617
Chlorpyrifos									
6	Oct-05	28	Chlorpyrifos	72	100	86	Y=0.95+1.88	=Power(10,0.95*(Log(x))+1.88)) CF : 1798.043232	0.04782

6.3 Monitoring sites

Sampling Area : G-MWs Six Irrigation Areas including Central Goulburn, Rochester-Campaspe, Murray-Valley, Shepparton, Torrumbarry and Pyramid-Boort (see Figure 1)

Number of pesticide monitoring sites : 14 in 2004-05, 15 in 2005-06 (see Table 1)

6.4 Monitoring Schedule

Sampling frequency :

passive sampling - once replaced four weeks

Spot sampling - once every four weeks

Table 3: Passive sampler's deployment & retrieval dates during 2004-05 and 2005-06 irrigation season (G-MW) (every four weeks interval) (see below)

Period/date	Passive samplers collection date from Melbourne passive samplers deployment dates	Passive samples retrieval dates (samplers with 2,2,4 trimethylpentane) from the six irrigation areas	Passive samples retrieval dates (samplers with 1, Dodecanol : 2,2,4 trimethylpentane) from the six irrigation areas	Spot samples collection dates
1				
August/04 (year-1)	Missed out-delays in irrigation season, OHS procedures development	Not sampled	Not sampled	Not sampled
August 05 (year 2)	15 August 2005 16-18 August 2006	13-15 September 2005	13-15 September 2005	13-15 September 2005
2				
September/04 (year 1)	Missed out-delays in irrigation season, OHS procedures development	Not sampled	Not sampled	Not sampled
September/05 (year 2)	12 September 2005 13-15 September 2006	11-13 October 2005	11-13 October 2005	11-13 October 2005
3				
October/04 (year 1)	4 October 2004 5-7 October 2004	2-4 November 2004	2-4 November 2004	2-4 November 2004
October/05 (year 2)	10 October 2004 11-13 October 2004	8-10 November 2005	8-10 November 2005	8-10 November 2005
4				
November/04 (year 1)	1 November 2004 2-4 November 2004	30 November-2 December 2004	30 November-2 December 2004	30 November - 2 December 2004
November/05 (year 2)	7 November 2005 8-10 November 2005	6-8 December 2005	6-8 December 2005	6-8 December 2005
5				
December/04 (year 1)	29 November 2004 30 November-2 December 2004	28-30 December 2004	28-30 December 2004	28-30 December 2004
December/05 (year 2)	5 December 2005 6-8 December 2005	3-5 January 2006	3-5 January 2006	3-5 January 2006
6				
Janurary/05 (year 1)	27 December 2004 28-30 December 2004	25-27 January 2005	25-27 January 2005	25-27 January 2005
Janurary/06 (year 2)	2 January 2005 3-5 January 2005	31 January-2 February 2006	31 January-2 February 2006	31 January-2 February 2006
7				
February/05 (year 1)	24 January2005 25-27 January 2005	22-24 February 2005	22-24 February 2005	22-24 February 2005
February/06 (year 2)	30 January 2006 31 January 2006- 2 February 2006	28 February – 2 March 2006	28 February – 2 March 2006	28 February - 2 March 2006
8				
March/05 (year 1)	21 February 2005 22-24 February 2005	22-24 March 2005	22-24 March 2005	22-24 March 2005
March/06 (year 2)	27 February 2006 28 February -2 March 2006	28-30 March 2006	28-30 March 2006	28-30 March 2006
9				
April/05 (year 1)	21 March 2005 22-24 March 2005	19-21 April 2005	19-21 April 2005	19-21 April 2005
April/06 (year 2)	27 March 2006 28-30 March 2006	25-27 April 2006	25-27 April 2006	25-27 April 2006

6.5 Duration of Monitoring

For pesticide monitoring, 2004-05 and 2005-06 irrigation seasons were divided into the following :

Initial irrigation season	- August- September, October
Mid irrigation season	- November, December, January
Late irrigation season	- February, March and April

(note : no sampling was possible in August and September 2004 due to delays in irrigation season-see Table 3)

6.6 Description of Relevant Methods

Preparation of passive samplers

Passive samplers were prepared at the Ecowise-WSL, Richmond Laboratory following the occupational health and safety (OHS) procedures developed by G-MW (Kibria 2003) (see Figure 2,3,4). Two types of passive samplers were used, one with solvent 2,2,4-trimethylpentane (TRIMPS) plus reference material tri-n-butylphosphate (TBP) and the other with solvent mixture of 1-dodecanol : 2,2,4-trimethylpentane (3:2) plus monolinuron Pestanal® [(*N′*-(4-chlorophenyl)-*N*-methoxy-*N*-methylurea] as reference material (full details of preparation of passive samplers are given in Kibria 2003). Addition of tributylphosphate internal standard used in TRIMPS for sample periods 1-5 was discontinued after sample period 5. This was to allow for organophosphates residues to be determined without interference on GC from tributylphospate. Addition of monolinuron internal standard used in Dodecanol + TRIMPS for sample periods 1-5 was discontinued after sample period 5. This was to allow for pesticide residues to be determined without interference on GC from monolinuron .

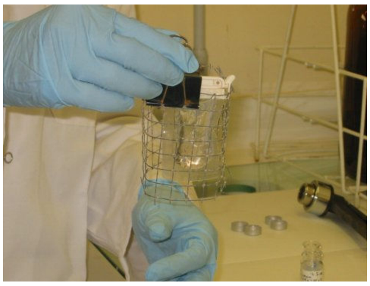

Figure 2. Passive samplers filled with solvent

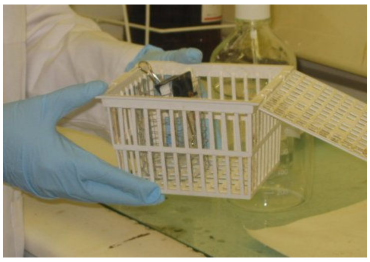

Figure 3. Passive samplers in a sampling basket

Figure 4. Passive samplers deployed in irrigation channels.

Deployment and retrieval of passive samplers

Nolan-ITU was engaged to perform deployment and retrieval of passive samplers and spot samples. The samplers were deployed in risk sites for a period of time (28 days) (see Figure 3 & 4) After 28 days, the passive samplers were retrieved, and the solvent from the deployed bags were collected into a glass vial (23x46mm). The vials with solvent were then placed into a small foam box wrapped with ice bricks and dispatched via a fast courier to DPI, Werribee Laboratory

Spot sampling

Spot sampling was done once every four weeks. A grab sampler was used to collect 2L of water (into polyethylene terphthalate (PET) bottle - gamma sterile) from each site. Spot samples bottles were placed into a large foam box wrapped with ice bricks and dispatched via a fast courier to

DPI Werribee lab for analysis via a courier.

Water temperature
During 2005-06 irrigation season surface water temperature of each site was also recorded using a fractional degree thermometer (405mm blue LO-tox TM filled). This was to record water temperature during each deployment and retrieval period (see Figure 5 and Appendix 2).

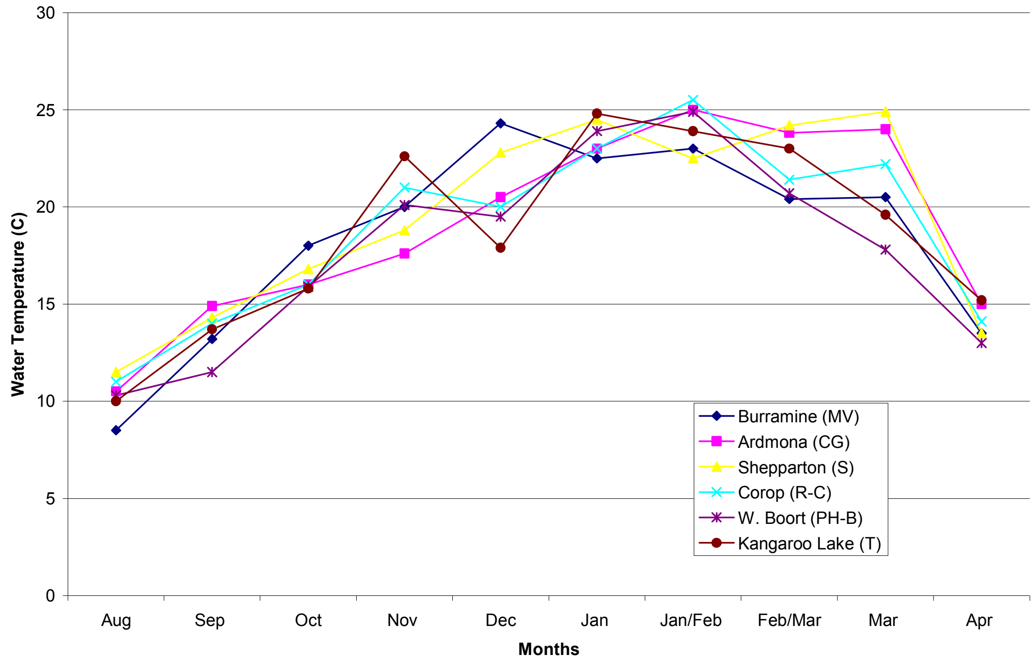

Figure 5 : Surface Water Temperature of Some Selected Sites

6.7 Analytical technique

Passive samples
The trimethyl pentane (TRIMPS) samples were diluted and then injected to a gas chromatograph with a pulsed flame photometric detector (GC-PFPD) for organohosphates. Endosulfan and synthetic pyrethroids were detected by injection onto a GC with electron capture detection (GC-ECD). Fungicides, herbicides and carbamates were determined by injection on GC with a nitrogen-phosphorus detector (GC-NPD). Tributyl phosphate was determined on each sample as the sampling rate internal standard using the GC-NPD screen test. In each case the sample injection was simultaneously screened on two capillary columns of different stationary phase polarity, usually 5% phenyl on dimethylpolysiloxane and 50% phenyl on dimethylpolysiloxane.

TRIMPS plus dodecanol samples were injected on a liquid chromatography-triple quadrupole mass spectrometer (LC-MSMS) in full scan mode. Monolinuron was determined on each sample using a photodiode array detector set at wavelength = 245 nm in series with the mass spectrometer. Pesticides were determined using positive ion mode with electrospray interface. The mass spectrometer was set up in multiple reaction monitoring mode with selected ion fragmentation for each parent ion. A 2.1 mm id by 150 mm length Waters Xterra C18 reverse phase column was used with a 10 μL injection. The mobile phase was a linear gradient starting with 20% methanol in 5mM ammonium acetate buffer (pH = 7) with a final mixture of 90% methanol in acetate buffer.

Spot samples
A 1.0 L sub sample of water was extracted with 100mL of dichloromethane (DCM), and then re-extracted twice with 50 mL of DCM. The DCM extracts were combined and dried through a sodium sulphate column. The extract was reduced and inverted into hexane which was then reduced to 1mL.

In 2004-05, the final extract was analysed with GC-PFPD (pulsed flame photometric detector) for OPs and GC-NPD (nitrogen phosphorous detector), for carbamates and molinate, trifluralin, pendimethalin, atrazine and chlorothalonil. In 2005-06, chlorpyrifos, parathion methyl and phorate were determined by injection to a gas chromatograph with a pulsed flame photometric detector (GC-PFPD). In 2005-06 trifularin, pendimethalin and chlorothalonil were determined on GC-NPD.

In 2005-06, solid phase extraction with Bond Elute PPL and C18 was separately applied to water samples with eluants combined and inverted into methanol followed by LC-MSMS determination as above for omothate, methomyl, thiodicarb, atrazine, and molinate and azinphos methyl. In 2005-06 trifularin, pendimethalin and chlorothalonil were determined on GC-NPD. following 1:5 dilutions with hexane.

Organochlorines and synthetic pyrethroids were analysed by GC-ECD (electron capture detector). Taufluvalinate was extracted with dichloromethane as above, after sample acidification and determined on GC-ECD.

Metals were determined by sub-sampling of a representative aliquot of the sample and acidification. Samples were then analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (see Appendix 3 for pesticides detected by different methods used in this study).

6.8 Quality assurance

For each batch of passive sampler solvent a blank TRIMPs and blank TRIMPS+dodecanol solution were retained for testing. In addition a blank of each sampler solvent was retained immediately before the subsequent deployment to confirm the pesticide free status of the samplers. Each sampling involved the deployment of triplicate membrane devices. Each of the three samplers for TRIMPS and TRIMPS+dodecanol were retrieved at the end of the sampling period and consigned separately in vials for testing at DPI, Werribee. Two of the three solvent samples in each case were randomly tested to determine internal standard and pesticide concentrations. The triplicate sample was retained as a confirmatory and alternative quality assurance sample. Normally two solvent samples tested and showing no residues would deem analysis of the triplicate sample as unnecessary.

6.9 Occupational health and safety issues

A site specific risk assessment (hazard/aspect identification) was conducted, and a safe work instructions (risk control measures) was developed for all of the 15 sampling sites

7. Results

7.1 Passive Sampler solvent samples-TRIMPS

Fifteen site samples for 7 sampling periods during 2004-05 and 9 sampling periods during 2005-06, as listed in Table 1, were screened for the following pesticides at the limit of reporting (LOR) stated (see Table 4).

Table 4: Pesticides sampled by passive samplers with solvent trimethylpentane and their limit of reporting (LOR) after direct injection into analytical instrument

Pesticides	2004-05 LOR, (µg/L) : period 1-5	2004-05 LOR, (µg/L) : period 6-7	2005-06 LOR, (µg/L) : period 1-9
ORGANOCHLORINE			
α Endosulfan	1	1	1
β Endosulfan	1	1	1
Endosulfan sulfate	4	4	4
PYRETHROIDS			
Esfenvalerate	10	10	10
Bifenthrin	10	10	10
Taufluvalinate	10	10	10
ORGANOPHOSPHATES			
Phorate		50	10
Parathion methyl		50	10
Azinphos methyl		50	10
Chlorpyrifos		50	20

Endosulfan in passive samples (TRIMPS)

In the 2004-05 and 2005-06 irrigation season, endosulfan was detected at 8 sites on a regular basis (range : ***0.00145- 0.0291µg/L***-see also Appendix 4). The 8 sites where endosulfan was found on a regular basis are Torganah (Murray Valley), Mooroopna (Central Goulburn), Ardmona (Central Goulburn), Kyabram (Central Goulburn), Corop (Rochester-Campaspe), West Boort (Pyramid-Boort), Appin (Pyramid-Boort) and Kangaroo Lake (Torrumbarry).

Endosulfan was detected at elevated concentrations only at 4 sites (Shepparton, Mooroopna, Ardmona, and Kyabram) (see Figures 6,7,8,9 and 10). These sites are in proximity to intensive horticultural (orchards and tomato) industries. In the 2005-06 seasons endosulfan was detected in passive sampler on 3 occasions at Nagambie in 2005-06 when it was not detected in 2004-05 (see Figure 10). Endosulfan is registered for insect control on a number of crops including pome fruit, stone fruit and vegetables.

Figures 6,7,8,9 & 10 shows the average endosulfan water concentration (±SE) at higher risk sites (range measured : *0.00145-0.0291µg*/L) for each deployment period calculated 4 -week for TRIMPS. Red line represented ANZECC guideline values for aquaculture or fish farming (<0.003µg/L).

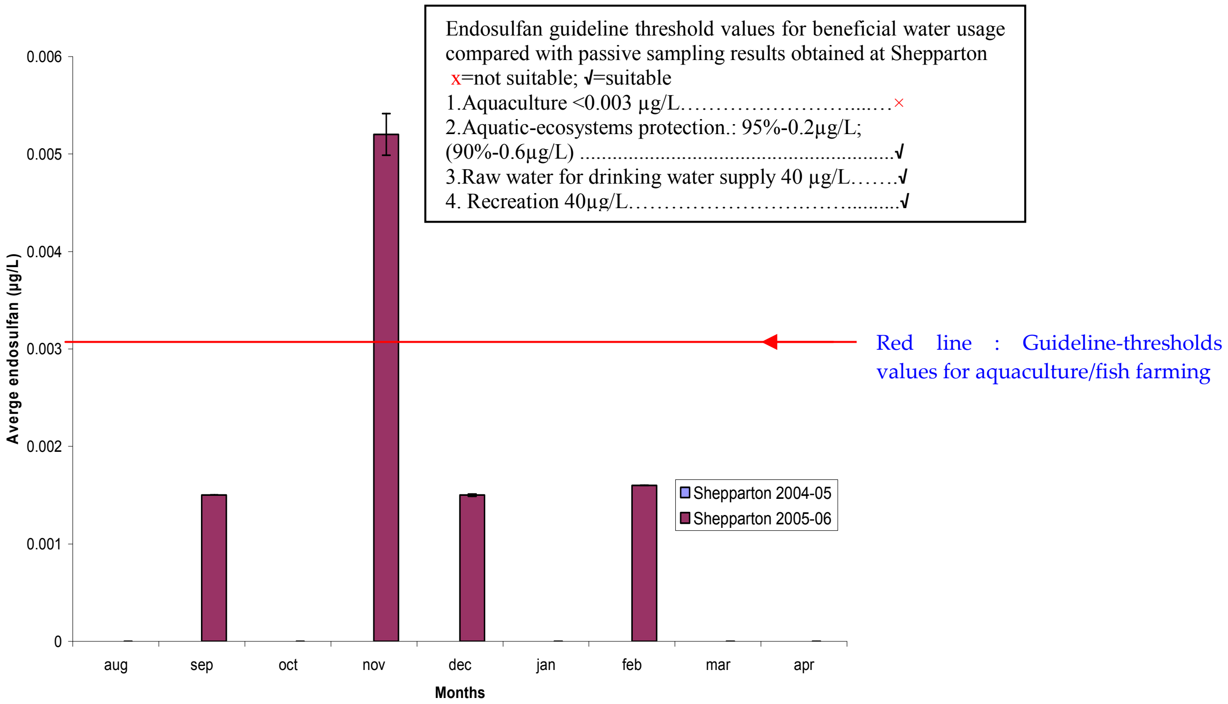

Figure 6 : Shepparton - site 4

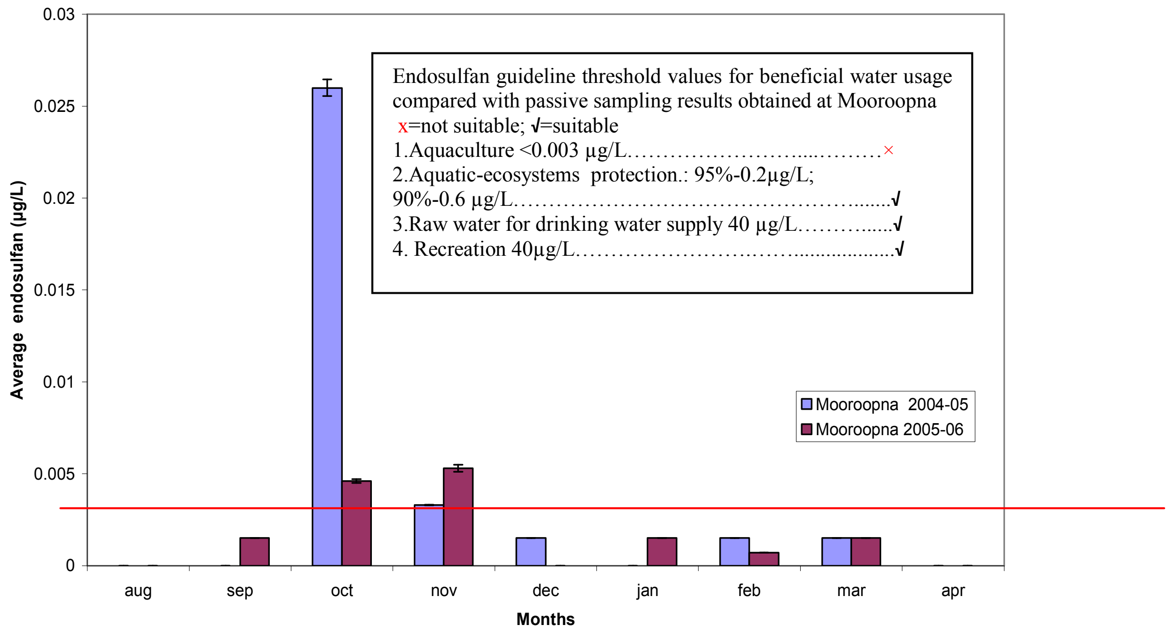

Figure 7: Mooroopna-site 5

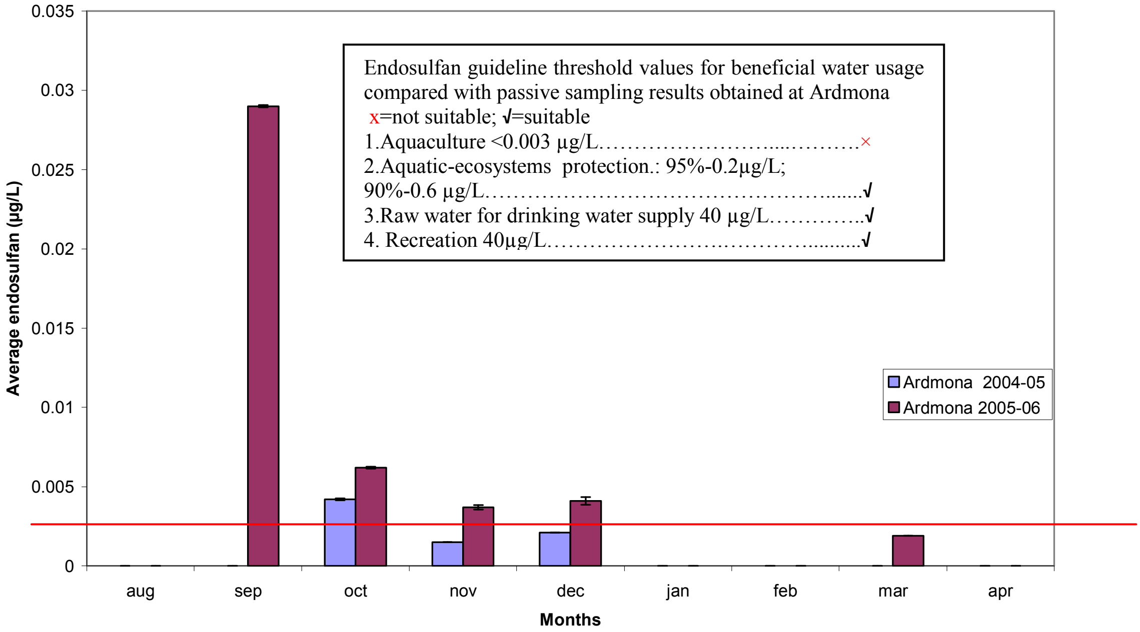

Figure 8 : Ardmona - site 6

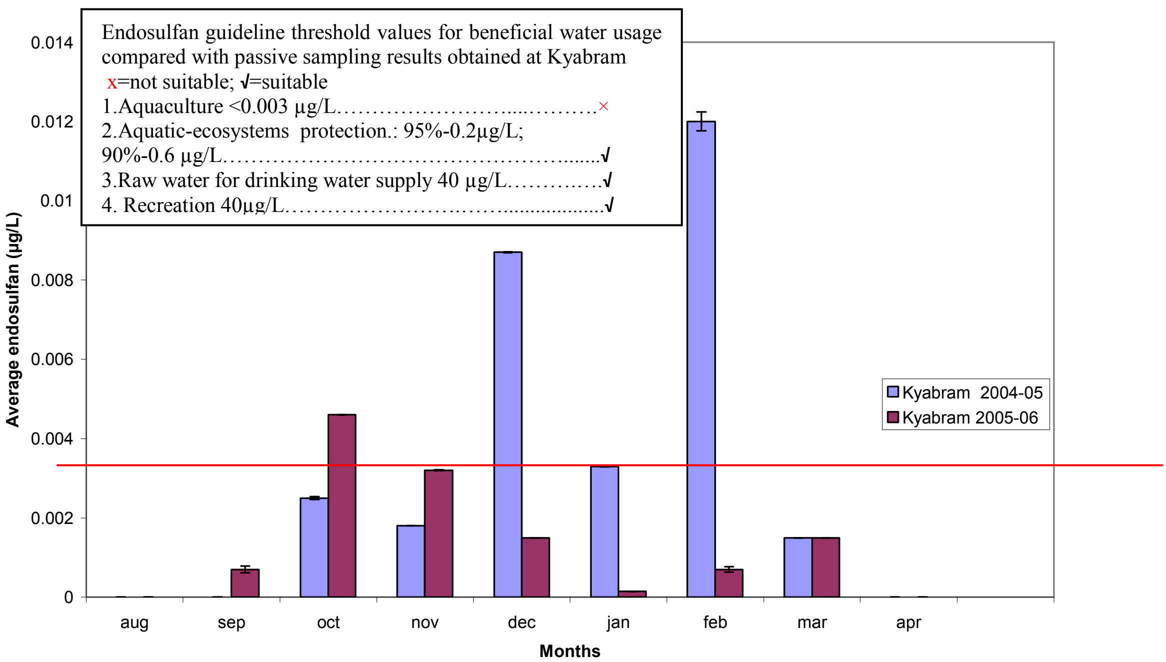

Figure 9 : Kyabram (site 7)

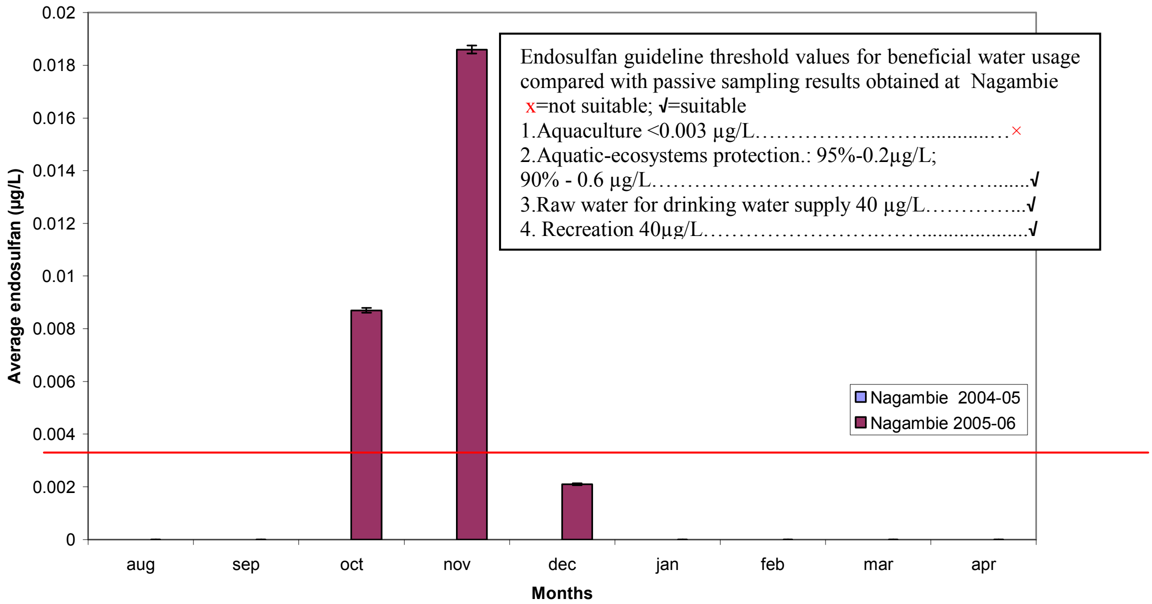

Figure 10 : Nagambie (site 9)

Chlorpyrifos in passive samples (TRIMPS)

Chlorpyrifos was detected in 2005-06 in passive samplers at 5 sites (range measured : ***0.008-0.058 µg/L****;* see also Appendix 5). Chlorpyrifos was detected once only at Katamatite and Mooroopna, but detected in 5 periods at Shepparton and in 4 periods at Ardmona (see Figures 11 & 12). In the 2004-05 season chlorpyrifos was detected on two occasions at Shepparton (see Appendix 5).

Figures 11 and 12 shows the 4 week average chlorpyrifos (±SE) water concentration at higher risk sites (range measured : 0.008-0.058 µg/L) for each deployment period for TRIMPS. Red line represented ANZECC guideline values for aquaculture or fish farming (<0.001 µg/L).

n

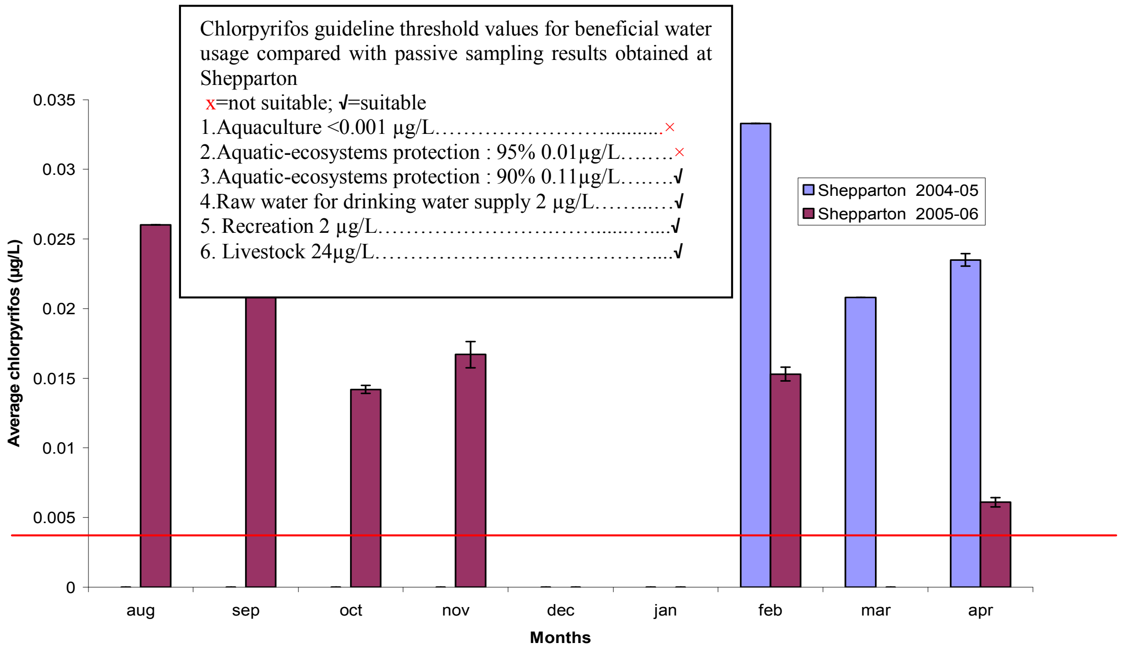

Figure 11 : Shepparton (site 4)

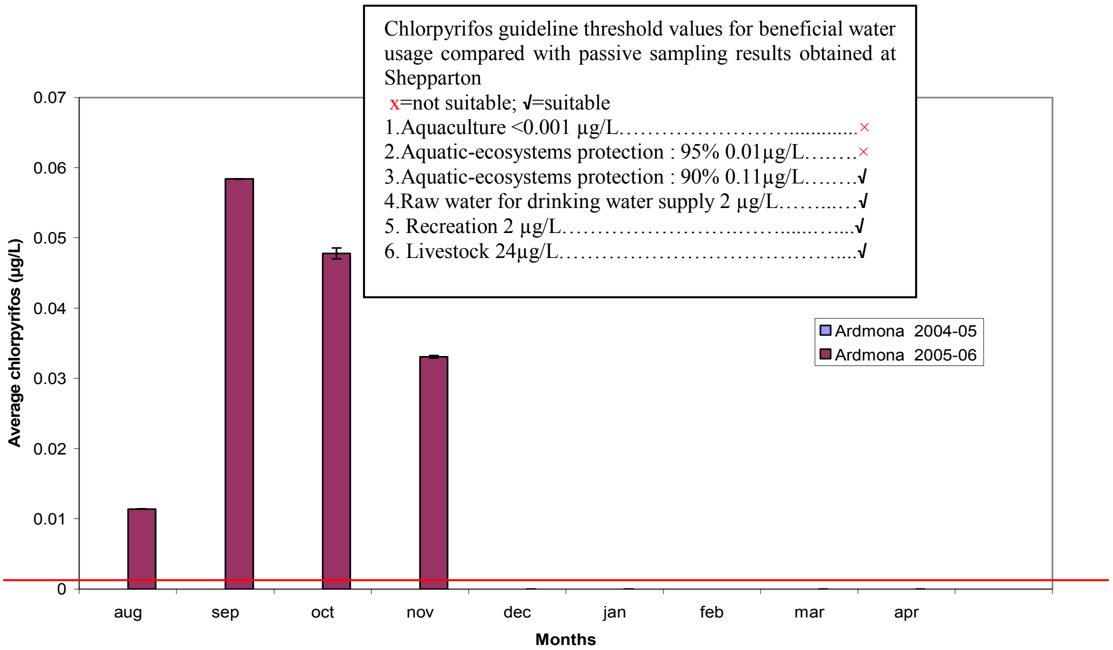

Figure 12 : Ardmona (site 6)

7.2 Passive Sampler solvent samples dodecanol and trimethylpentane

Fourteen site samples for 7 sampling periods during 2004-05 and fifteen sampling sites for 9 sampling periods during 2005-06, as listed in Table 1, were screened for the following pesticides at the limit of reporting (LOR) stated (see Table 5).

Table 5: Pesticides sampled by passive samplers with solvent mixture dodecanol : trimethylpentane (3:2) and their limit of reporting (LOR) after direct injection into the analytical instrument

Pesticides	2004-05 LOR, μg/L period 1-7	2004-05 LOR, μg/L period 6-7	2005-06 LOR, (μg/L) : period 1-9
ORGANOPHOSPHATES			
Azinphos methyl	30 (period 1-5)	20	100 (10μg/L period
Omethoate	20 (period 1-5)	5	4-9)
Phorate		100	5
Parathion methyl		100	100
Chlorpyrifos		100	100
			100
CARBAMATES			
Methomyl	10		5
Thiodicarb	10		3
HERBICIDES			
Atrazine	10		5
Molinate	10		5
SYNTHETIC PYRETHROIDS			
Esfenvalerate		50	50
Bifenthrin		50	50
Taufluvalinate		50	50
ORGANOCHLORINE			
α Endosulfan		5	5
β Endosulfan		5	5
Endosulfan sulfate		10	10
Pendimethalin		300	300
Chlorothalonil		300	300

In 2004-05 no pesticides were detected at or above the stated concentrations. In 2005-06 endosulfan, chlorpyrifos and parathion methyl were detected at some sites such as Mooroopna , Ardmona, Kyabram, Nagambie and Corop but on an irregular basis (see appendix 6,7,8). In addition, herbicides (Atrazine and molinate) and pyrethroids were detected at one occasion (see appendix 9,10)

Figures 13 and 14 shows the 4 week average parathion methyl (range measured 0.026-0.921 water concentration (± SE) at higher risk sites for each deployment period for dodecanol and TRIMPS mixture.

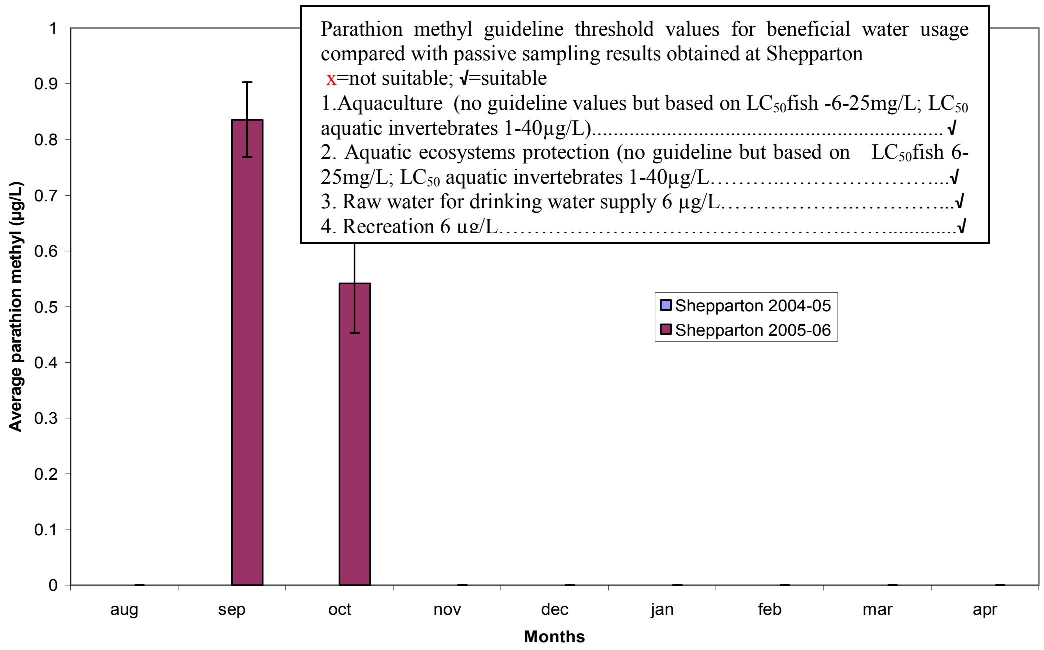

Figure 13 : Shepparton (site 4)

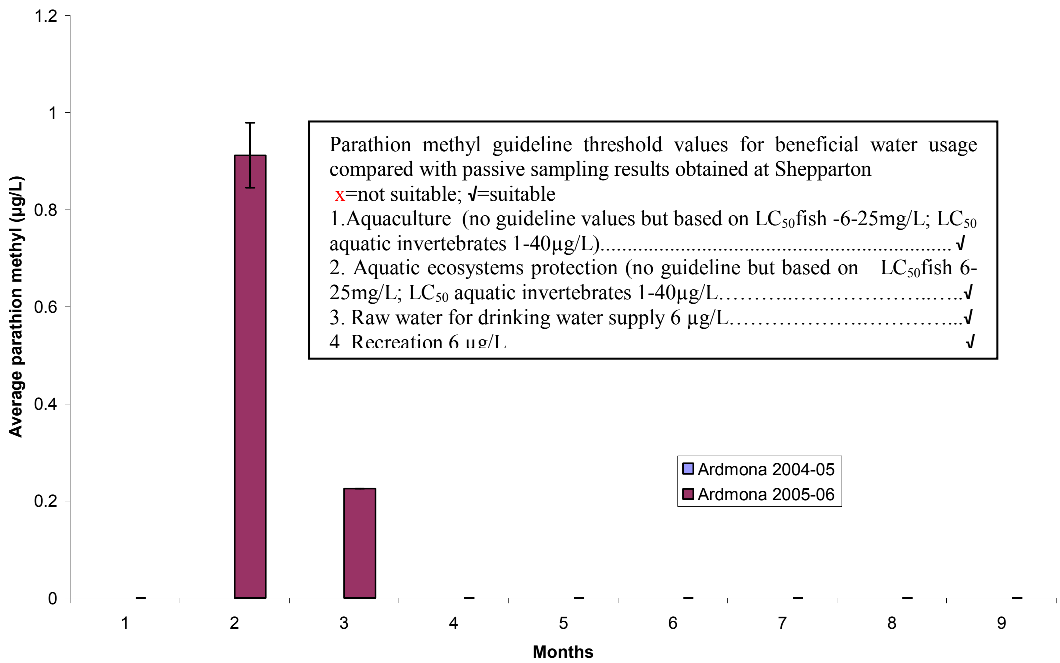

Figure 14 : Ardmona (site 6)

7.3 Spot Water Samples

Pesticides in spot water samples

Fourteen site samples for 7 sampling periods during 2004-05 and fifteen sampling sites for 9 sampling periods during 2005-06, as listed in Table 1 were screened for the following pesticides at the limit of reporting (LOR) stated (Table 6).

Table 6: Pesticides sampled in spot samples and their limit of reporting (LOR) in natural water pre concentration

Pesticides	LOR, µg/L 2004-05	LOR, µg/L 2005-06
ORGANOPHOSPHATES		
Azinphos methyl	0.02	0.02
Parathion methyl	0.02	0.02
Phorate	0.02	0.03
Chlorpyrifos	0.01	0.03
Omethoate	0.03	0.05
ORGANOCHLORINE		
α Endosulfan	0.005-0.01	0.01
β Endosulfan	0.005-0.01	0.01
Endosulfan sulfate	0.01-0.02	0.02
CARBAMATES		
Methomyl	0.05	0.05
Thiodicarb	0.04	0.04
PYRETHROIDS		
Esfenvalerate	0.02	0.02
Bifenthrin	0.02	0.02
Taufluvalinate	0.02	0.02
HERBICIDES/FUNGICIDES		
Molinate	0.05	0.1
Trifluralin	0.1	0.1
Pendimethalin	0.05	0.05
Atrazine	0.01	0.01
Chlorothalonil	0.1	0.1

In 2004-05 seasons atrazine was found on a regular basis at Mooroopna, Nagambie, West Boort and Appin, whereas in 2005-06 it was found on a regular basis at all the sites (see appendix 9). Ardmona is the site where both chlorpyrifos and parathion methyl were detected on few occasions during 2004-05 and 2005-06 seasons (see appendix 11,12). Appendix 13 provided an account of most frequently detected pesticides by different methods employed.

Metals in spot water samples in natural waters

Fourteen site samples for 7 sampling periods during 2004-05 and fifteen sampling sites for 9 sampling periods during 2005-06, as listed in the Table 7 were screened for the following metals at the limit of reporting (LOR) stated (Table 7).

Table 7: Heavy metals and their limit of reporting (LOR)

Heavy metals	LOR, μg/L
Copper	0.9
Zinc	1.2
Lead	0.21
Cadmium	0.4

The spot samples were tested for concentrations of copper, zinc, lead and cadmium and determined at the concentrations reported. Copper was detected on regular basis on most sites with higher concentrations detected at Torgannah, Mooroopna, Kyabram, West Boort, Appin, Kerang and Kangaroo Lake (Appendix 14). These sites are under intensive orchards and vegetable growing areas where copper is registered for use as a fungicide.

8. Discussion

8.1 Pesticides in passive samples

The analysis of passive samplers (trimethylpentane or TRIMPS) has revealed detection of endosulfan on a regular basis at 8 sites, of which elevated concentrations of endosulfan found at Shepparton, Mooroopna, Ardmona and Kyabram (2004-05 and 2005-06) where intensive horticulture (orchards, vineyards and Tomato growing) is being undertaken. The higher concentrations of endosulfan were found in passive samplers during the early part of the irrigation season (September-January). Endosulfan was also detected in passive sampler on 3 occasions at Nagambie in 2005-06 when it was not detected in 2004-05 (see Figure 9). The detection of endosulfan at Nagambie may be related with growing of vegetables (tomatoes) and fruit upstream of Nagambie. Endosulfan is registered and available for use on a range of horticultural crops (fruits and vegetables).

Endosulfan was not detected with passive samplers with solvent mixtures (dodecanol: trimethylpentane) in 2004-05 season but detected at 3 sites during 2005-06 seasons (see appendix 14). This suggests that passive samplers with TRIMPS are a reliable device for monitoring of pesticides in waterways when compared with dodecanol mixtures as used, in particular for endosulfan. Endosulfan was not detected in the matching spot water sample taken at the time solvent samples were removed from these three sites. This suggests that the endosulfan concentrations detected in TRIMPS were the result of transient spike concentrations of endosulfan. The detection of a range of isomer mixes of α endosulfan, β endosulfan and endosulfan sulfate may suggest sampling of these residues was from adjacent fields where passive samplers were deployed

Both chlorpyrifos and parathion methyl were also detected in passive samplers on several occasions at Shepparton and Ardmona (see Figures 10,11,12, 13) in 2005-06 season. Chlorpyrifos and parathion methyl are registered and available for use on a range of horticultural crops (fruits and vegetables). The reporting of chlorpyrifos and parathion methyl (trace amounts) at Ardmona and Shepparton sampling sites is expected to be associated with organophosphate insecticide usage in stone fruit orchards. Historically, DPI residue surveys reveal parathion methyl and chlorpyrifos applications in local stone fruit orchards.

8.2 G-MW Pesticides results and drinking & human health values

The results of two years pesticides and heavy metals monitoring were compared with Australian, New Zealand and USA drinking and human health values and found to be below the recommended threshold values (see Table 8).

Table 8: Drinking water (potable) and human health guideline values and most commonly detected pesticide concentrations in G-MW irrigation areas.

MCL =maximum contaminant concentration goal; HV= health values; HA = Health advisory values; DW=Drinking water guidelines

Compound	Australian drinking water guideline values (µg/L) (*Hamilton et al. 2003, NHMRC, 2006*))	New Zealand maximum acceptable values (MAV) for pesticides residues in drinking water (*Hamilton et al. 2003*)	United States (EPA) drinking water standards & life time health advisory values (µg/L) (USEPA 2006)	Raw water for drinking water supply (µg/L) (*ANZECC, 2000*)	Measured pesticides and heavy metals (in passive samples or spot samples) in G-MW irrigation areas (2004-2006) (µg/L) (range)	Comments
Endosulfan	GV[1] : 0.050 HV[2] : 30 DW=30	not available	Not available	40	0.0015-0.029 (see appendix 4 for details)	G-MW results below the guideline health values and health advisory values
Chlorpyrifos	GV:not available DW:10	70	HA : 20[3]	2	0.008-0.058 (see appendix 5 for details)	G-MW results below the guideline health values and health advisory values
Parathion methyl	GV : 0.5 HV : 100	not available	HA :2	6	0.226-0.921 (see appendix 9 for details)	G-MW results below the guideline health values and health advisory values (not always)
Atrazine	GV : 0.5 HV : 20 DW:40	2	MCL : 3 HA : 200	5	trace-0.050 (see appendix 12 for details)	G-MW results belowthe guideline health values and health advisory values
Copper	DW:2000	not available	MCL : 1300	1000	<0.9-4.2 (see appendix 15 for details)	G-MW results below the guideline health values and health advisory values

[1] *Guideline values (GV) is set at a concentration consistent with good management practice, which would not result any significant risk to health of the consumer over a life time of consumption. Exceeding the GV indicates that undesirable contamination of drinking water has occurred but it does not necessarily indicate a hazard to public health*

[2] *Health values (HV) are intended to manage health risks associated with inadvertent exposure resulting from spill or misuse of a pesticide. HV are calculated from the acceptable daily intake (ADI) (usually 10% for a 70-kg adult consuming 2l/day water*

[3] *The life time health advisory is 20% of the drinking water equivalent (DWEL) on the assumption that 80% of the consumers exposure to the pesticides is from other sources (eg. residues in food) with 20% from drinking water.*

Due to the pesticide concentration measured being in a concentrated solvent sample from a semi permeable membrane device, no direct comparison can be made with the national water quality guidelines. However, the concentrated endosulfan, chlorpyrifos and parathion methyl concentrations detected were converted into average water concentration (see Table 2) using the regression equations of Leonard, Hyne and Pablo (2002).

The average endosulfan, chlorpyrifos and parathion methyl concentration in water per day was then compared with the guideline values. The average concentrations for the four week deployment period showed that endosulfan, chlorpyrifos and parathion methyl concentration in water have not exceeded the guideline values for irrigation, raw water for drinking town supply, livestock and recreational uses and is of a good water quality for the above purposes. However, water at some sites, such as Mooroopna, Shepparton, Ardmona, Kyabram have exceeded the guideline values of both endosulfan and chlorpyrifos for aquaculture or fish farming.

8.3 Pesticides in spot water samples

Atrazine is highly persistent in soil and in the environment. It was detected on a regular basis at all 15 sites during 2005/06 season. It is likely that the atrazine detected was used to control weeds in forage legumes and orchards. The concentrations detected in spot water samples were in the range of trace-0.05 μg/L

By compassion with water quality guidelines of atrazine for irrigation, livestock and raw water for drinking water supply (ANZECC 2000; Hamilton et al. 2003) the atrazine concentration detected in spot samples did not exceed the recommended guideline values for the above water uses (see below, also appendix 12)

Atrazine guideline threshold values & beneficial water usage [Range measured in this study : trace-0.05μg/L)]
x=not suitable; √=suitable
1.Aquaculture- no guideline values……………………………………………….……......…..
2. Freshwater ecosystems protection : 95% - 13 μg/L; 90% - 45μg/L...…………….……..√
3.Raw water for drinking water supply 5 μg/L……………………………..…...……..√
4. Irrigation 10 μg/L…………………..……...……………………….……..………......√
5. Livestock 5 μg/L………………….……...………………………….…………..……..√
6. Human heath values 20 μg/L ……………………………………………...……….…√

8.4 Heavy metals in spot water samples

The results for copper reveals that water in the 15 sites was of good quality for most primary purposes including irrigation, livestock, drinking, and recreation (Table 15). However, there were some sites (Torgannah, Mooroopna, West Boort, Appin, Kerang and Kangaroo Lake) where higher concentrations of copper were detected. These sites are under intensive horticulture and copper use would be associated with fungal disease control in intensive orchards, vineyards and tomato crops. A considerable number of copper fungicides are registered by the APVMA for fungal disease control in fruit and vegetable crops. As there is no sample data to identify the origin of these concentrations, they are possibly attributable to natural or agriculture sources. No other heavy metals were found at elevated concentrations at any of the 15 sites investigated.

Copper guideline threshold values & beneficial water usage . Range measured in this study : 0.9-4.2μg/L
x=not suitable; √=suitable

1.Aquaculture <5 μg/L ……………. …………………………………………..…………….…..√

*2.Aquatic ecosystems protection : 95% - 1.4μg/L; 90% - 1.8μg/L; 80% - 2.5μg/L ………......√

3.Raw water for drinking water supply 1000 μg/L……………….…………………………..…√

4. Irrigation 200 μg/L…..………………………...…………………………………………….....√

5. Livestock 400-500 μg/L ………………….....…………………………………………......√

NOTE : : [a.] the origin of copper could be natural or agricultural, [b]. copper concentration measured in channel outfall sites will be much lower once it mixes with bulk of river water ; [c]. research carried out at RMIT University found that native fish are more tolerant to chemical toxicant than alien fish species. This includes copper (see Raymond et al. 2006)

9. Conclusions

Endosulfan has been detected on a regular basis in trimethylpentane solvent from passive samplers at eight sites during the two study seasons. In 2005-06 chlorpyrifos and parathion methyl were detected irregularly at Ardmona and Shepparton. These sites show associations with intensive orchards, vineyards, tomato production and forage production. Atrazine has been detected sporadically in spot samples at nine sites during 2004-05. Atrazine was detected at most sites and samplings in the 2005-06 season. Copper has been detected at a majority of sites on a regular basis. Reporting of endosulfan at Nagambie on three occasions in 2005-06 contrasted with no detections in 2004-05, suggesting increases in pesticide impacts in the Goulburn-Broken catchments.

Reported concentrations for endosulfan, and parathion methyl indicate concentrations below ANZECC guideline and international guideline values (Hamilton et al. 2003) for primary purposes (eg. raw water for drinking supplies, recreational and irrigation and stock and domestic supply and aquatic ecosystems protection) and potable/drinking and human health values. Chlorpyrifos concentrations were below the ANZECC guidelines for raw water for drinking, recreational, irrigation and stock and domestic supply. Chlorpyrifos concentrations exceeded the 95% protection (aquatic) ANZECC guideline at Shepparton and Ardmona on several occasion. The atrazine and copper concentration detected in spot water samples did not exceed the recommended guideline values for the above water uses including irrigation, livestock, drinking, and recreation and aquatic ecosystems protection. Similarly, the adverse impacts on aquatic ecosystems in receiving natural waters of high and medium risk pesticides at selected channel outfall are also unlikely

However, ANZECC guideline values for aquaculture have been reached or exceeded for 4-week average of endosulfan and chlorpyrifos concentrations at four G-MW monitoring sites (Shepparton, Mooroopna, Ardmona and Kyabram). There are no ANZECC aquaculture guideline values for parathion methyl but due to its higher fish toxicity threshold the reported concentrations are expected to safe for aquaculture.

Based on two years study of pesticides and metals in irrigation water in the Goulburn-Murray Water irrigation areas it is concluded that the water is suitable in relation to pesticide residues for current irrigation uses except aquaculture.

10. Recommendations

It is recommended that Goulburn Murray Water (G-MW) should consider to monitor pesticides in channels for at least another irrigation season where elevated concentrations of endosulfan and chlorpyrifos were detected. These sites are : Shepparton (SIA), Ardmona (CG), Mooroopna (CG), Kyabram (CG). In addition DPI can be requested to make a survey at these four higher risk sites in order to develop measures that would reduce the risk of contaminating G-MW channels.

11. Glossary

Analyte; component in sample targeted for determination and quantitation.

Guideline : Numerical concentration or narrative statements recommended to support and maintain a designated water use.

Limit of detection (LOD) : is defined as the concentration at which an analyte can identified but not quantified accurately

Limit of Reporting (LOR) : is the concentration at which the analyte can be identified and accurately quantified.

Kow (Octanol-water portioning coefficient) : a measurement of how a chemical is distributed at equilibrium between octanol and water. The parameter is used in the assessment of environmental fate and transport of organic chemicals

Hydrophobic or liphophilic : having a strong aversion for water (water hating/non-polar), fat soluble and water insoluble (eg. DDT)

Hydrophilic : strong affinity for water (water loving) water soluble and fat insoluble (eg. Phenol)

Partitioning co-efficient : measure of the sorption phenomenon, whereby a pesticide is divided between the soil and water phase

Organochlorine (OC) : organic compounds containing chlorine

Heavy metals : environmentally toxic metals of high atomic weight (having atomic weight between 63.546 and 200.595)

Synthetic Pyrethroids (SP) : usually synthetic pesticides related to pyrethrum

Organophosphates (OP) : compounds based on organophosphate structure

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13. Appendices

Appendix 1 Pesticides and their log K_{ow}

Main Group	Pesticides	K_{ow}
Organophosphates	Azinphos methyl	2.96
	Parathion methyl	3.0
	Omethoate	-0.74
	Phorate	3.92
	Chlorpyrifos	4.7
Organochlorines	Endosulfan	4.74
Carbamates	Methomyl	0.093
	Thiodicarb	1.4
Synthetic Pyrethroids	Esfenvalerate	6.22
	Bifenthrin	>6
	Tau-fluvalinate	4.26
Herbicides	Molinate	2.88
	Trifluralin	4.83
	Pendimethalin	5.18
	Atrazine	2.5
	Chlorothalonil	2.92
Fungicide/Heavy metals	Copper	
	Zinc	
	Lead	
	Cadmium	

Appendix 2 Surface water temperature (in °C) of 15 sites during 2005-06

(note:sampling made between 8 am and 1pm)

Site	16-18 Aug	13-15 Sept	11-13 Oct	8-10 Nov	6-8 Dec	3-5 Jan	31 Jan-2 Feb	28 Feb-2 Mar	28-30 Mar	25-27 Apr
1.Torgannah (MV)		12.3	13.9	14.7	20	22.6	27	22.6	20.2	14.5
2. Burramine MV)	10.5	14.9	16	17.6	20.5	23	25	23.8	24	15
3. Katamatite (MV)	11.2	14.6	16.6	17.4	22.8	23.6	27	25.1	23.4	14.2
4. Shepparton (S	11.5	14.3	16.8	18.8	22.8	24.5	22.5	24.2	24.9	13.5
5. Mooroopna (CG)	8.0	14.1	20.5	18.6	24	22.1	20.9	19	20.2	12.2
5. Ardmona (CG)	8.5	13.2	18	20	24.3	22.5	23	20.4	20.5	13.5
7. Kyabram (CG)	9.0	13.5	15	21.6	22.8	22.4	22.9	22.1	20.8	14.5
8. Tatura (CG)	12	10.5	16	23	21.5	24.5	29	23	14	17
9. Nagambie (GW)	10.5	13.5	15	21.8	19.5	26.5	23.9	23	13	14.3
10. Corop (R-C)	11	14	16	21	20	23	25.5	21.4	22.2	14.1
11. West Boort (P-B)	10.3	11.5	15.9	20.1	19.5	23.9	24.9	20.7	17.8	13
12. Appin (P-B)	10.6	13.5	14.9	20.9	18	26.1	24.4	22	18	13.2
13. Kerang town (T)	8.9	15	16.5	22.1	19.5	26.5	23.8	22.4	20.8	14.5
14. Kangaroo Lake (T)	10.0	13.7	15.8	22.6	17.9	24.8	23.9	23	19.6	15.2
15. Torrumbarry weir (T)	10.2	15	15.4	25.1	21.4	26.5	25.5	27	24	16.8

Appendix 3 Pesticides detected by different sampling methods

Pesticides	Log K_{ow}	1. Pesticides detected in passive samplers with solvent trimethylpentane (TRIMPS) 2004/05	1. Pesticides detected in passive samplers with solvent trimethylpentane (TRIMPS) 2005-06	2. Pesticides detected in passive samplers with solvent mixuture dodecanol : trimethylpentane (3:2)	3. Pesticides detected in spot water samplers 2004-05 &2005-06
Azinphos methyl Parathion methyl Omethoate Phorate Chlorpyrifos	2.96 3.0 -0.74 3.92 4.7	No (period 1-5), Yes (period 6-7) No (period 1-5), Yes (period 6-7) No (period 1-7)	Yes (1-9) Yes (1-9) No (1-9) Yes (1-9) Yes (1-9)	Yes No (period 1-5), Yes (period 6-7) Yes No (period 1-5), Yes (period 6-7) No (period 1-5), Yes (period 6-7)	Yes Yes Yes Yes Yes
Endosulfan	4.8	Yes	Yes(1-9)	No (period 1-5), Yes (period 6-7)	Yes
Methomyl Thiodicarb	0.093 1.4	No No		Yes Yes	Yes Yes
Esfenvalerate Bifenthrin Taufluvalinate	6.22 >6 4.26	Yes Yes Yes		No (period 1-5), Yes (period 6-7) No (period 1-5), Yes (period 6-7) No (period 1-5), Yes (period 6-7)	Yes Yes Yes
Copper	0.3	No		No	Yes
Molinate	2.88	No		Yes	Yes
Trifluralin Pendimethalin Atrazine Chlorothalonil	4.83 5.18 2.5 2.92	No No No No		No No (period 1-5), Yes (period 6-7) Yes No (period 1-5), Yes (period 6-7)	Yes Yes Yes Yes

Passive samples with TMP

Appendix 4 : Average endosulfan water concentration (in samplers with trimethylpentane) at different sites (2004/05 and 2005/06 irrigation season)

[ns=not sampled; ---- = <LOR]; [a]Regression equation used : see Table 2

[b]Guideline values for endosulfan : Aquaculture =<0.003µg/L ; Aquatic ecosystems protection (95%) 0.2µg/L; Raw water for drinking water supply=40µg/L; Recreational water 40µg/L; MV=Murray Valley Irrigation Area; S=Shepparton; CG=Central Goulburn; R_C=Rochester-Campaspe; P-B=Pyramid Boort; and T=Torrumbarry

Period-→ Site	1 Aug	2 Sep	3 Oct	4 Nov	5 Dec	6 Jan	7 Feb	8 Mar	9 Apr	Comments
1.Torgannah (MV)										1. Safe for all purposes
2004-05	ns	ns	0.0015	0.0015	0.0015	0.0015	0.0015	-	0.0015	
2005-06	-	0.0024	0.0007	0.0015	-	-	0.0007	0.0015	-	
2. Burramine MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	0.0007	-	0.0015	-	-	0.0007	0.0015	-	
3. Katamatite (MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	0.0007	-	-	-	-	-	-	-	
4. Shepparton (S)										1. Safe for all purposes except aquaculture
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	0.0015	-	**0.0052**	0.0015	-	-	-	-	
5. Mooroopna (CG)										1. Safe for all purposes except aquaculture
2004-05	ns	**ns**	**0.0260**	0.0033	0.0015	-	0.0015	0.0015	-	
2005-06	-	0.0015	**0.0046**	**0.0053**	-	0.0015	0.0007	0.0015	-	
6.. Ardmona (CG)										1. Safe for all purposes except aquaculture
2004-05	ns	**ns**	0.0042	0.0015	0.0021	-	-	-	-	
2005-06	-	**0.0291**	0.0062	0.0037	**0.0041**	-	-	0.0019	-	
7. Kyabram (CG)										1. Safe for all purposes except aquaculture
2004-05	ns	**ns**	**0.0025**	**0.0018**	**0.0087**	**0.0033**	0.0121	0.0015	-	
2005-06	-	0.0007	**0.0046**	**0.0032**	0.0015	0.0015	0.0007	0.0015	-	
8. Tatura (CG)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	0.0020	-	-	-	-	-	
9. Nagambie (GW)										1. Safe for all purposes except aquaculture
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	**0.0087**	**0.0186**	**0.0021**	-	-	-	-	
10. Corop (R-C)										1. Safe for all purposes
2004-05	ns	ns	0.0017	0.0015	0.0027	0.0020	0.0015	0.0015	0.0015	
2005-06	-	0.0024	-	0.0023	0.0017	0.0015	0.0015	-	-	
11. West Boort (P-B)										1. Safe for all purposes
2004-05	ns	ns	0.0015	0.0015	0.0015	0.0017	-	0.0015	0.0015	
2005-06	-	0.0015	-	-	0.0015	0.0015	0.0015	0.0015	-	
12. Appin (P-B)										1. Safe for all purposes
2004-05	ns	ns	0.0015	0.0015	0.0015	0.0015	-	0.0015	-	
2005-06	-	0.0015	-	0.0015	0.0015	0.0015	-	0.0007	0.0013	
13. Kerang town (T)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	0.0015	-	-	-	-	-	-	-	
14. Kangaroo Lake (T)										1. Safe for all purposes
2004-05	ns	ns	0.0015	0.0020	0.0026	0.0015	0.0015	0.0015	0.0015	
2005-06	-	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015		
15. Torrumbarry weir (T)										1. Safe for all purposes 2. No sampling during 2004-05
2005-06	ns -	ns 0.0015	ns 0.0015	ns 0.0015	ns -	ns -	ns -	ns -	ns -	

Appendix 5 Average chlorpyrifos (µg/L) water concentration (in samplers with trimethylpentane) at different sites estimated using the regression equation and the concentration factor during 2004-05 and 2005 06 irrigation seasons

a. Regression equation used : ***log10(y)=(0.95x(log10(x))+1.88 for chlorpyrifos***

b. Guideline values for chlorpyrifos : aquaculture =<0.001µg/L ; aquatic ecosystems protection (95%) 0.01µg/L; Raw water for drinking water supply=2µg/L; Recreation 2µg/L; Livestock=24µg/L

ns=not sampled; ---- = <LOR

Period-→ Site	1 Aug	2 Sep	3 Oct	4 Nov	5 Dec	6 Jan	7 Feb	8 Mar	9 Apr	Comments
1.Torgannah (MV) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
2. Burramine MV) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
3. Katamatite (MV) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- 0.0890	- -	- -	- -	1. Safe for all purposes
4. Shepparton (S) 2004-05 2005-06	**ns** **0.0260**	**ns** **0.0225**	**-** **0.0142**	**-** **0.0167**	**-** **-**	**-** **-**	**-** **0.0153**	**0.0333** **-**		1. Safe for all purposes except aquaculture, and 95% aquatic ecosystems protection
5. Mooroopna (CG) 2004-05 2005-06	ns -	ns -	- -	- 0.0100	- -	- -	- -	- -		1. Safe for all purposes except aquaculture, 95% aquatic ecosystems protection
5. Ardmona (CG) 2004-05 2005-06	**-** **0.0114**	**-** **0.0584**	**-** **0.0478**	**-** **0.033**	- -	- -	- -	- -		1. Safe for all purposes except aquaculture, 95% aquatic ecosystems protection
7. Kyabram (CG) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes 2. intensive tomatoes
8. Tatura (CG) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
9. Nagambie (GW) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
10. Corop (R-C) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
11. West Boort (P-B) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
12. Appin (P-B) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
13. Kerang town (T) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
14. Kangaroo Lake (T) 2004-05 2005-06	ns -	ns -	- -	- -	- -	- -	- -	- -	- -	1. Safe for all purposes
15. Torrumbarry weir (T) 2005-06	ns -	ns -	ns -	ns -	ns -	ns -	ns -	ns -	ns -	1. Safe for all purposes 2. No sampling during 04-05 (new site in 05-06)

Passive samples with dodecanol: TMP

Appendix 6: Average endosulfan (µg/L) water concentration (in samplers with dodecanol :trimethylpentane) at different sites estimated using the regression equation and the concentration factor during 2004-05 and 2005-06 irrigation seasons

a. Regression equation used : y=*21.882x for endosulfan sulfate*

b.Guidelines for endosulfan : Aquaculture =<0.003µg/L ; Raw water for drinking water supply=40µg/L; Recreational water 40µg/L

Period-→ Site	1	2	3	4	5	6	7	8	9	Comments
1.Torgannah (MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
2. Burramine MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
3. Katamatite (MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
4. Shepparton (S)										1. Safe for all purposes except
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
5. Mooroopna (CG)										1. Safe for all purposes except aquaculture
2004-05	ns	**ns**	**-**	**-**	**-**	-	-	-	-	
2005-06	-	**-**	**-**	**0.0081**	**-**	-	-	-	-	
5. Ardmona (CG)										1. Safe for all purposes except aquaculture
2004-05	ns	**ns**	**-**	**-**	**-**	-	-	-	-	
2005-06	-	**0.01305**	**-**	**0.0081**	**0.0061**	-	-	-	-	
7. Kyabram (CG)										1. Safe for all purposes except aquaculture
2004-05	ns	ns	**-**	**-**	**-**	-	-	-	-	
2005-06	-	-	**-**	**0.0081**	**-**	-	-	-	-	
8. Tatura (CG)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
9. Nagambie (GW)										1. Safe for all purposes except aquaculture
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	**0.0081**	-	-	-	-	-	
10. Corop (R-C)										1. Safe for all purposes except aquaculture
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	**0.0081**	-	-	-	
11. West Boort (P-B)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
12. Appin (P-B)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
13. Kerang town (T)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
14. Kangaroo Lake (T)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
15. Torrumbarry weir (T)										1. Safe for all purposes 2. No sampling during 04-05 (new site in 05-06)
2005-06	ns -	ns -	ns -	ns -	ns -	ns -	ns -	ns -	ns -	

Appendix 7 Average chlorpyrifos (µg/L) water concentration (in samplers with dodecanol :trimethylpentane) at different sites estimated using the regression equation and the concentration factor during 2004-05 and 2005-06 irrigation seasons

a. Regression equation used : y=*27.691x for chlorpyrifos;*b. Guidelines values for chlorpyrifos : Aquaculture =<0.001µg/L ; aquatic ecosystem protection 95%-0.01µg/L; Raw water for drinking water supply=40µg/L; Recreational water 40µg/L; livestock 24 µg/L

Period-→ Site	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Comments**
1.Torgannah (MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
2. Burramine MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
3. Katamatite (MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
4. Shepparton (S)										1. Safe for all purposes except aquaculture and exceeds 95% aquatic species protection guideline value
2004-05	ns	**ns**	-	-	-	-	-	-	-	
2005-06	-	**0.0645**	-	-	-	-	-	-	-	
5. Mooroopna (CG)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
6. Ardmona (CG)										1. Safe for all purposes except aquaculture and exceeds 95% aquatic species protection guideline value
2004-05	ns	**ns**	**-**	**-**	**-**	-	-	-	-	
2005-06	-	**0.1418**	**0.0645**	**-**	**0.0061**	-	-	-	-	
7. Kyabram (CG)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
8. Tatura (CG)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
9. Nagambie (GW)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
10. Corop (R-C)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
11. West Boort (P-B)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
12. Appin (P-B)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
13. Kerang town (T)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
14. Kangaroo Lake (T)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
15. Torrumbarry weir (T)										1. Safe for all purposes 2. No sampling during 04-05 (new site in 05-06)
2005-06	ns	ns	ns	ns	ns	ns	ns	ns	ns	
	-	-	-	-	-	-	-	-	-	

Appendix 8 Average parathion methyl (µg/L) water concentration (in samplers with dodecanol :trimethylpentane) at different sites estimated using the regression equation and the concentration factor during 2004-05 and 2005-06 irrigation seasons

a. Regression equation used : y=*7.905x for parathion methyl*

b.Guideline values for parathion methyl : Aquaculture =no guideline; Raw water for drinking water supply=6µg/L; Recreational water 6µg/L

Site / Period→	1	2	3	4	5	6	7	8	9	Comments
1.Torgannah (MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	0.3388	-	-	-	-	-	-	-	
2. Burramine MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
3. Katamatite (MV)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
4. Shepparton (S)										1. Safe for all purposes
2004-05	ns	**ns**	-	-	-	-	-	-	-	
2005-06	-	**0.8358**	0.5421	-	-	-	-	-	-	
5. Mooroopna (CG)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
6. Ardmona (CG)										1. Safe for all purposes
2004-05	ns	**ns**	**-**	**-**	**-**	-	-	-	-	
2005-06	-	**0.9213**	**0.2259**	**-**	**-**	-	-	-	-	
7. Kyabram (CG)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
8. Tatura (CG)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
9. Nagambie (GW)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
10. Corop (R-C)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
11. West Boort (P-B)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
12. Appin (P-B)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
13. Kerang town (T)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
14. Kangaroo Lake (T)										1. Safe for all purposes
2004-05	ns	ns	-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	-	
15. Torrumbarry weir (T)										1. Safe for all purposes 2. No sampling during 04-05 (new site in 05-06)
2005-06	ns	ns	ns	ns	ns	ns	ns	ns	ns	
	-	-	-	-	-	-	-	-	-	

Appendix 9 Average herbicides (Molinate (M) and Atrazine (A) Parathion Methyl (µg/L) water concentration (in samplers with dodecanol :trimethylpentane) at different sites estimated using the regression equation and the concentration factor during 2004-05 and 2005-06 irrigation seasons

- less than LOR

Site	Aug 1	Sept. 2	Oct. 3	Nov. 4	Dec. 5	Jan. 6	Feb. 7	Mar 8	Apr. 9
1.Torgannah (MV)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
2. Burramine MV)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
3. Katamatite (MV)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	Trace (A)	-	-	-			
4. Sheppaarton (S)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
5. Mooroopna (CG)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-		-	-	-			
5. Ardmona (CG)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
7. Kyabram (CG)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
8. Tatura (CG)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
9. Nagambie (GW)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
10. Corop (R-C)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
11. West Boort (P-B)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
12. Appin (P-B)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
13. Kerang town (T)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-			
14. Kangaroo Lake (T)									
2004-05		-	-	-	-	-	-	-	
2005-06	-	-	Trace (M)	-	-	-			
15. Torrumbarry weir (T)									
2005-06		-	-	-	-	-	-	-	
	-	-	-	-	-	-			

Appendix 10 Average synthetic pyrethroids (Bifenthrin (B), Esfenvalerate (E), Taufluvalinate (T)) (concentrated) detected (µg/L) in **dodecanol: trimethylpentane)** *samplers with dodecanol :trimethylpentane) at different sites estimated using the regression equation and the concentration factor during 2004-05 and 2005-06 irrigation seasons*

- less than LOR

Site	Aug 1	Sept. 2	Oct. 3	Nov. 4	Dec. 5	Jan. 6	Feb. 7	Mar 8	Apr. 9
1.Torgannah (MV) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
2. Burramine MV) 2004-05 2005-06	 -	 - -	 - -	 - -	 - -	 - -	 -	 -	
3. Katamatite (MV) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
4. Sheppaarton (S) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
5. Mooroopna (CG) 2004-05 2005-06	 -	 - -	 -	 -	 - -	 - -	 -	 -	
5. Ardmona (CG) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
7. Kyabram (CG) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
8. Tatura (CG) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
9. Nagambie (GW) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
10. Corop (R-C) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
11. West Boort (P-B) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
12. Appin (P-B) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
13. Kerang town (T) 2004-05 2005-06	 -	 - -	 - 100 (B), 65(E), 75(T)	 -	 - -	 - -	 -	 -	
14. Kangaroo Lake (T) 2004-05 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	
15. Torrumbarry weir (T) 2005-06	 -	 - -	 - -	 -	 - -	 - -	 -	 -	

Spot water samples :

Appendix 11: Herbicide - Atrazine detected (µg/L) in spot water samples during 2004-05 and 2005-06 irrigation season

a denotes less than LOR;

b. Guideline values for atrazine : Aquaculture =no guideline values; Raw water for drinking water supply=5µg/L; Recreational water 5µg/L; irrigation 10 **µg/L, livestock water 5 µg/L**

Site	Aug/05 1	Sept./05 2	Oct/05 3	Nov./05 4	Dec./05 5	Jan/06. 6	Feb/06. 7	Mar/06 8	Apr./06 9
1.Torgannah (MV)									
2004-05	ns	ns	-	-	-	-	-	-	-
2005-06	Trace	Trace	Trace	0.033	0.049	0.048	0.048	0.024	0.022
2. Burramine MV)									
2004-05	ns	ns	-	-	-	-	-	-	-
2005-06	Trace	0.014	0.034	0.039	0.062	0.038	0.048	0.027	trace
3. Katamatite (MV)									
2004-05	ns	ns	-	-	-	-	-	-	-
2005-06	Trace	0.017	0.031	0.030	0.056	0.038	0.045	0.030	trace
4. Sheppaarton (S)									
2004-05	ns	ns	-	-	-	0.01	-	0.02	0.02
2005-06	Trace	Trace	Trace	Trace	0.027	0.024	0.041	0.035	0.036
5. Mooroopna (CG)									
2004-05	ns	ns	-	-	0.01	0.01	-	0.017	trace
2005-06	trace	0.031	trace	-	0.021	0.034	0.047	0.034	0.035
5. Ardmona (CG)									
2004-05	ns	ns	-	-	-	0.01	-	0.014	0.020
2005-06	trace	-	trace	trace	0.026	0.021	0.038	0.030	0.036
7. Kyabram (CG)									
2004-05	ns	ns	-	-	-	-	0.01	-	0.01
2005-06	trace	0.021	trace	trace	-	trace	0.021	0.032	0.040
8. Tatura (CG)									
2004-05	ns	ns	-	-	-	0.01	-	-	0.02
2005-06	trace	-	trace	trace	0.025	0.040	0.041	0.040	0.042
9. Nagambie (GW)									
2004-05	ns	ns	-	-	-	0.02	0.01	0.019	0.02
2005-06	trace	-	trace	trace	0.042	0.033	0.044	0.048	0.039
10. Corop (R-C)									
2004-05	ns	ns	-	-	-	-	-	0.011	trace
2005-06	Trace	0.017	0.024	trace	-	trace	0.020	0.039	0.036
11. West Boort (P-B)									
2004-05	ns	ns	0.01	0.01	0.01	-	0.01	0.018	0.01
2005-06	trace	0.016	0.022	trace	trace	trace	Trace	0.032	0.033
12. Appin (P-B)									
2004-05	ns	ns	0.02	-	-	-	0.01	0.012	0.02
2005-06	trace	0.020	0.020	trace	-	-	Trace	0.032	0.030
13. Kerang town (T)									
2004-05	ns	ns	-	-	0.01	-	-	-	-
2005-06	trace	0.035	trace	0.022	trace	0.038	0.031	0.050	0.028
14. Kangaroo Lake (T)									
2004-05	-	-	-	-	-	-	-	-	-
2005-06	trace	0.012	trace	-	-	0.020	Trace	0.029	0.022
15. Torrumbarry weir (T)	ns	ns	ns	ns	ns	ns	ns	ns	ns
2005-06	0.01	0.016	0.022	0.032	0.045	0.038	0.030	0.030	0.020

Appendix 12 Organophosphate (Chlorpyrifos (C), Parathion Methyl (P), Azinphos Methyl (A) detected (µg/L) in spot water samples during 2004-05 and 2005-06 irrigation season

- less than LOR

Site	Aug 1	Sept. 2	Oct. 3	Nov. 4	Dec. 5	Jan. 6	Feb. 7	Mar 8	Apr. 9
1.Torgannah (MV)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	0.04 (P)	0.071 (P)	-	-	-	-	-	-	
2. Burramine MV)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	
3. Katamatite (MV)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	
4. Sheppaarton (S)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	0.056 C; trace (A)	0.97 (A)	-	-	-	-	
5. Mooroopna (CG)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	trace (A)	-	-	-	-	-	
5. Ardmona (CG)									
2004-05	ns	ns	-	-	trace-P,C	-	-	trace-P	-
2005-06	-	0.02 (P), trace (A)	0.20 (P)	trace C -	0.034 (P)	0.33 C	-	-	-
7. Kyabram (CG)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	
8. Tatura (CG)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	
9. Nagambie (GW)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	
10. Corop (R-C)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	
11. West Boort (P-B)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	
12. Appin (P-B)									
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-	-	-	-	-	-	-	
13. Kerang town (T)			-	-					
2004-05	ns	ns	-	-	-	-	-	-	
2005-06	-	-			-	-	-	-	
14. Kangaroo Lake (T)			-						
2004-05	ns	ns	-		-	-	-	-	
2005-06	-	-		trace C	-	-	-	-	
15. Torrumbarry weir (T)									
2005-06	ns -	ns -	ns -	ns -	ns -	ns -	ns -	ns -	ns -

Appendix 13 *Most frequently detected pesticides at the 15 monitoring sites during 2004-05 and 2005-06 irrigation season against different methods used for sampling (out of 9 periods)*

√=number of period detected; √=number of periods aquaculture guideline threshold values exceeded; - not detected or less than LOR

	Passive samplers with solvent trimethylpentane			**Passive samplers with solvent dodecanol:trimethylpentane mixtures**			**Spot water samples**		
Site	*endosulfan*	*chlorpyrifos*		*endosulfan*	*chlorpyrifos*	*parathion methyl*	*atrazine*	*Chlorpyrifos*	*Parathion methyl*
1.Torgannah (MV) 2004-05 2005-06	√√√√√√ √√√√√	- -		- -	- -	- √	- √√√√√√√√√	- -	- √√
2. Burramine MV) 2004-05 2005-06	- √√√√	- -		- -	- -	- -	- √√√√√√√√√	- -	- -
3. Katamatite (MV) 2004-05 2005-06	- √	- √		- -	- -	- -	- √√√√√√√√√	- -	- -
4. Shepparton (S) 2004-05 2005-06	√ √√√√	√√ √√√√√√		- -	- √	- √√	√√√ √√√√√√√√	- √	- -
5. Mooroopna (CG) 2004-05 2005-06	√ √ √√√ √√√ √√√	- √		- √	- -	- -	√√√√ √√√√√√√√	- -	- -
5. Ardmona (CG) 2004-05 2005-06	√ √ √ √√√ √ √	- √√√√		- √√√	- √√√	- √√	√√√ √√√√√√√√	√ √√	√√ √√√
7. Kyabram (CG) 2004-05 2005-06	√√√ √√√ √ √√√ √√√√	- -		- √	- -		√√ √√√√√√√√	- -	- -
8. Tatura (CG) 2004-05 2005-06	- √	- -		- -	- -	- -	√ √√√√√√√√	- -	- -
9. Nagambie (GW) 2004-05 2005-06	- √√√	- -		- √	- -	- -	√√√√ √√√√√√√√	- -	- -
10. Corop (R-C) 2004-05 2005-06	√√√√√√√ √√√√√	- -		- √	- -	- -	√√ √√√√√√ √	- -	- -
11. West Boort (P-B) 2004-05 2005-06	√√√√√√ √√√√√	- -		- -	- -	- -	√√√√√√ √√√√√√√√√√	- -	- -
12. Appin (P-B) 2004-05 2005-06	√√√√√ √√√√√√	- -		- -	- -	- -	√√√√ √√√√√√√√	- -	- -
13. Kerang town (T) 2004-05 2005-06	- √	- -		- -	- -	- -	√ √√√√√√√√√√	- -	- -
14. Kangaroo Lake (T) 2004-05 2005-06	√√√√√√√ √√√√√√	- -		- -	- -	- -	- √√√√√√√√	- √	- -
15. Torrumbarry weir (T) 2004-05 2005-06	ns √√√	ns -		ns -	ns -	ns -	ns √√√√√√√√√√	ns -	ns -

Appendix 14 Copper detected (µg/L) in spot water samples during 2004-05 and 2005-06 irrigation season

Guideline threshold values : Irrigation water : 200µg/L; livestock water : 400-500µg/L; recreation : 1000µg/L; raw water for drinking water supply 1000µg/L;aquaculture <5µg/L and aquatic ecosystems protection : 95% (1.4); 90% 1.8 and 80% 2.5

- denotes less than LOR; ns=not sampled

Site	Aug 1	Sept. 2	Oct. 3	Nov. 4	Dec. 5	Jan. 6	Feb. 7	Mar 8	Apr. 9
1.Torgannah (MV)									
2004-05	ns	ns	1.2	2.6	1.3	1.6	2.2	1.1	1.2
2005-06	3.6	3.6	2.3	1.8	1.4	1.7	1.4	1.1	1.5
2. Burramine MV)									
2004-05	ns	ns	-	-	-	-	-	-	-
2005-06	1.8	1.8	1.6	-	-	-	<0.9	<0.9	<0.9
3. Katamatite (MV)									
2004-05	ns	ns	1.6	-	-	-	1.0	-	-
2005-06	2.4	1.9	2.7	1.0	0.9	1.0	1.0	<0.9	<0.9
4. Sheppaarton (S)									
2004-05	ns	ns	-	3.6	1.1	1.1	1.3	-	-
2005-06	3.6	1.6	1.3	1.0	<0.9	-	<0.9	<0.9	<0.9
5. Mooroopna (CG)									
2004-05	ns	ns	1.2	1.4	1.4	1.3	2.2	1.0	1.6
2005-06	4.3	3.0	3.0	2.5	3.6	1.7	1.5	1.3	1.1
5. Ardmona (CG)									
2004-05	ns	ns	-	-	1.0	-	1.3	-	-
2005-06	2.5	1.5	2.2	0.9	<0.9	0.9	<0.9	<0.9	1.7
7. Kyabram (CG)									
2004-05	ns	ns	1.3	1.2	1.6	1.2	1.0	1.2	1.2
2005-06	2.6	1.8	2.4	1.8	1.7	2.2	1.4	1.0	1.4
8. Tatura (CG)									
2004-05	ns	ns	-	1.2	1.1	1.0	-	-	-
2005-06	3.5	1.0	2.6	<0.9	<0.9	-	<0.9	<0.9	-
9. Nagambie (GW)									
2004-05	ns	ns	-	-	-	-	-	-	-
2005-06	2.2	<0.9	1.3	<0.9	<0.9	-	<0.9	<0.9	-
10. Corop (R-C)									
2004-05	ns	ns	-	-	-	1.4	1.4	1.2	-
2005-06	1.2	1.3	1.2	1.2	1.3	1.1	1.0	2.1	1.2
11. West Boort (P-B)									
2004-05	ns	ns	1.8	1.3	1.4	1.8	1.3	1.5	1.8
2005-06	2.2	2.2	1.7	2.1	2.1	2.2	2.3	1.4	1.5
12. Appin (P-B)									
2004-05	ns	ns	1.9	1.1	1.1	1.9	1.3	1.7	1.7
2005-06	2.0	2.2	3.0	2.4	2.1	2.4	1.9	1.4	1.3
13. Kerang town (T)									
2004-05	ns	ns	-	-	-	-	-	-	-
2005-06	3.7	3.2	3.6	3.6	4.2	2.7	1.9	2.1	1.7
14. Kangaroo Lake (T)									
2004-05	ns	ns	1.9	1.9	2.4	3.9	2.3	2.4	2.4
2005-06	3.3	1.3	3.0	-	3.0	3.7	3.3	3.1	3.4
15. Torrumbarry weir (T)	ns	ns	ns	ns	ns	ns	ns	ns	Ns
2005-06	-	2.4	1.2	-	1.0	1.1	<0.9	<0.9	-

Appendix 15 Total (concentrated) endosulfan detected at higher risk sites (in samplers with trimethylpentane) at higher risk sites during 2004/05 and 2005/06 irrigation season) using (alpha edosulfan, + beta endosulfan + edndosulfan sulfate= total endosulfan)

Period→ Site	2 Sep	3 Oct	4 Nov	5 Dec	6 Jan	7 Feb	8 Mar
4. Shepparton (S) 2004-05 2005-06	ns (0+0+2) =2,(0+0+2)=2	- -	- (1.8+1+2)=4.8, .3+2.4+4.2)=11.9	- (0.5+0+2)=2.5, (0+0+2)=2	- -	- (0+0+2)=2;(0+0+2)=2	- -
5. Mooroopna (CG) 2004-05 2005-06	**ns** (0+0+2)=2,(0+0+2)=2	**(12+9+13) =34, (19+12+18)=49** **(0.5+1+6.7)=8.2, (1.6+1.9+9.8)=13.3**	(0+0.5+4)=4.5, (0+0.5+4)=4.5 **(0+0+4.3)=4.3, (0+0+5)= 5**	(0+0=2)=2 -	- (0+0+2)=2,(0+0+2)=2	(0+0+2)=2,(0+0+2)=2 (0+0+2)=2,(0+0+2)=2	(0+0+2)=2,(0+0+2)=2 (0+0+2)=2,(0+0+2)=2
6.. Ardmona (CG) 2004-05 2005-06	**n s** (15+14+18)=47,(14+14+17)=45	(4+2+2)=8, (3+1+2)=6 (2.1+2+4.4)=8.5,(2.5+2.4+5.4)= 10.3	(0+0+2)=2,(0+0+2)=2 (1.7+1.8+4.2)=7.7,(0.5+1+2)=3.5	(0.5+0.5+2)=3,(0.5+0.5+2)=3 **(10+0+2)=12, (0.5+0+2)=2.5**	- -	- -	- (0+0+2)=2,(0.5+0+0)=0
7. Kyabram (CG) 2004-05 2005-06	**ns** (0+0+0)=0, (0+0+2)=2	**(0.5+0.5+2)=3, (2+0.5+2)=4.5** **(4.8+1.4+2)=8.2, (5+1.4+2)=8.4**	**(0+0.5+2)=2.5, (0+0.5+2)=2.5** **(1.5+0.5+2)=4, (3.3+1.2+2)=6.5**	**(2+4+7)=13,(2+4+7)=13** (0+0+2)=2,(0+0+2)=2	**(3+2+2)=7, (1+0.5+2)=3.5** (0+0+2)=2,(0+0+2)=2	(6+9+2)=17, (9+14+2)=25 (0+0+0)=0,(0+0+2)=2	(0+0+2)=2,(0+0+2)=2 (0+0+2)=2,(0+0+2)=2
9. Nagambie 2004-05 2005-06	ns -	- **(18+11+2)=31,**	- (21+7.6+2)=30.6, (27+8+2)=37	- **(0.5+0+0)=0.5, 14+0.5+0)=14.5**	- -	- -	- -

Appendix 16 Total (concentrated) chlorpyrifos detected at higher risk sites (in samplers with trimethylpentane) at different sites during 2004/05 and 2005/06 irrigation season)

ns=not sampled

Period-→ Site	**1** **Aug**	**2** **Sep**	**3** **Oct**	**4** **Nov**	**5** **Dec**	**6** **Jan**	**7** **Feb**	**8** **Mar**	**9** **Apr**
4. Shepparton (S) 2004-05 2005-06	ns 48 , 48	ns 42 ,39	- 20 ,31	- 14,47	- -	- -	- 19 ,36	60;, 60 -	50 ,25 5 ,17 (
5. Mooroopna (CG) 2004-05 2005-06	**ns**		**18**						
6.. Ardmona (CG) 2004-05 2005-06	**ns** **22,19**	- 110,100	- 72,100	**-** **56,63**	- -	- -	- -	- -	- -