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Pesticide Monitoring in Goulburn-Murray Waters Irrigation Supply Channels Covering the Six Irrigation Areas [2004 -2005 Irrigation Season Study Report : Interim Report -1]

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Pesticide Monitoring in Goulburn-Murray Water's Irrigation Supply Channels Covering the Six Irrigation Areas (2004-2005 Irrigation Season Study Report)

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1. Executive Summary

During 2004-2005 irrigation seasons, a pesticide monitoring study was conducted at the 14 potential risk sites located within the six Goulburn-Murray Water irrigation areas in northern Victoria. The risk sites included intensive orchards (pome & stone) and vineyards, vegetable (intensive tomatoes), reference sites, channel outfall, stock & domestic and town supply, 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 are : endosulfan (an organochlorine insecticide), atrazine (herbicide) and copper (fungicide).

Endosulfan was detected at 8 of the 14 sites in passive samplers. The 8 sites where endosulfan was found on a regular basis are Torganah, Mooroopna, Ardmona, Kyabram, Corop, West Boort, Appin and Kangaroo lake. Atrazine was detected at 9 of the 14 sites (spot water samples); however it was found on a regular basis only at West Boort. Copper was detected at most sites, but at elevated levels at Torganah, Mooroopna, West Boort, Kerang Town, and Kangaroo Lakes. The three agriculture chemicals that were frequently detected were associated with intensive orchards (stone, pome fruit) and vineyards, vegetable (tomatoes) and pastures (legume plants).

By comparison with national water quality guidelines (ANZECC - drinking, recreational, irrigation, ecosystems protection 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 purposes. However, water endosulfan levels at Mooroopna, Ardmona, and Kyabram estimated from passive sampler's levels would have exceeded the recommended ANZECC guidelines for the purpose of aquaculture. 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 levels found were within the Canadian Guidelines for drinking, recreation, agriculture water uses and aquatic life protection but it is generally believed that the presence of atrazine in irrigation water may be hazardous to some agriculture crops. Copper levels detected in irrigation channel water were found to be safe for drinking, irrigation, and livestock. Copper exceeded the ANZECC guidelines trigger value of 1.4μg/L (95% protection of aquatic life) for slightly modified disturbed systems at all sites, except for the two reference sites (Nagambie and Burr-amine). As there are no sample data to identify the origin of these levels, these levels are possibly attributable to natural or agriculture sources.

It is recommended that Goulburn Murray Water (G-MW) should continue to monitor pesticides in channels for at least another irrigation season. This will help to validate the data collected and identify 'hot spots' to reduce risks from such sites.

The current report is the first of the two years monitoring results of pesticides and related heavy metals in the six irrigation areas.

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 levels of chemical contaminants (pesticides and related heavy metals) in G-MW's supply channels to establish risk levels 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 *et al* (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 level 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 *et al*. 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 , 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 pesticides concentrations in G-MW channels. The trial included the preparation of passive samplers, their deployment and retrieval of passive samplers in channels for pesticides 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 will run for two irrigation seasons.

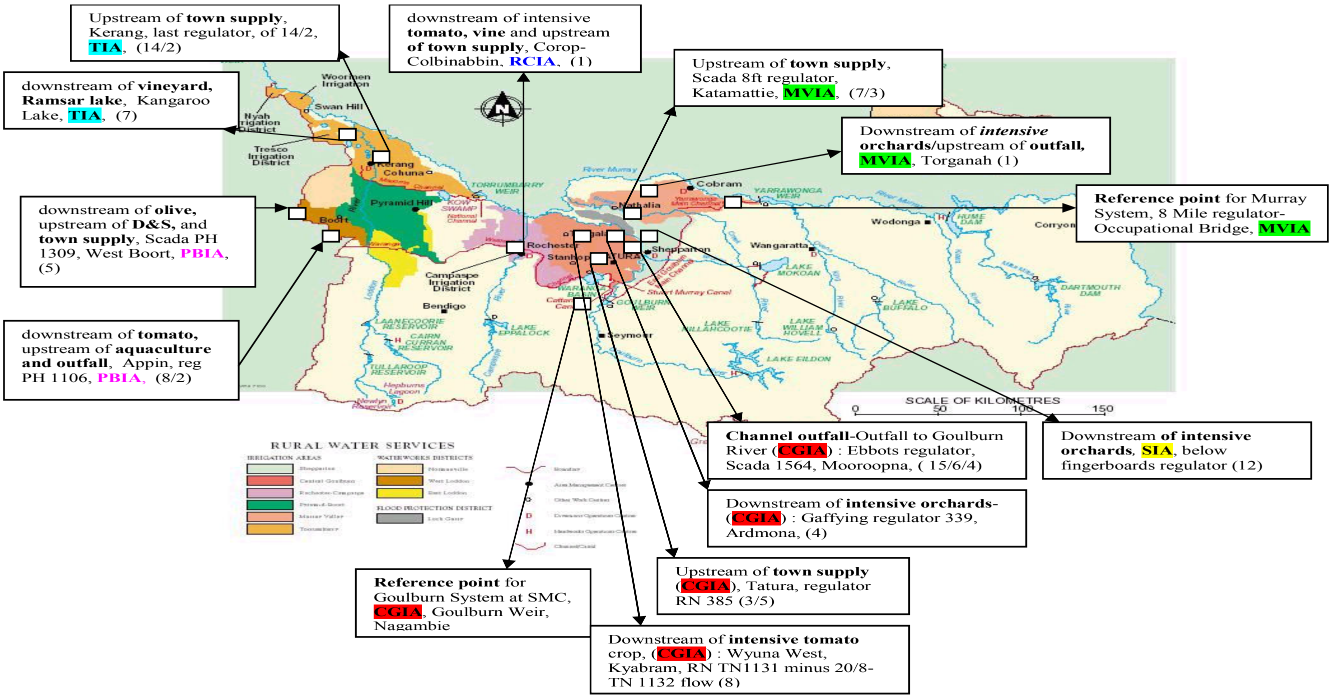
4. Scope of the work

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 2004-2005 and 2005-2006 irrigation seasons. The 2004-2005 analysis results reported here are from the 14 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 reference sites. 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 agriculture 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 I). 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 collaboration, the PIRVic (Werribee) developed methods for analysis of G-MW's samples appropriate for the project.

The highlight of 2004-2005 and 2005-2006 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)



Map showing pesticide passive sampling sites for the 2004-2006 irrigation seasons. Total 14 sites including town supply, aquaculture, orchards, vine, olive1, outfall and reference point

Table 1: **Pesticide monitoring sites in the six irrigation areas during 2004-2005 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	Reference point for Murray system	Channel offtake 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- CGIA	Nagambie	Stuart Murray Canal Goulburn Weir GPS 55-340603E; 59-63684N	Reference point for Goulburn System	Channel offtake 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 supply
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 and Loddon River
13. Torrumbarry Irrigation area (TIA)	Kerang town	Channel 14/2, regulator-last regulator of 14/2, 1 km upstream of Loddon-Murray Water channel offtake Access Rd : Collins Rd-Bendigo HW GPS 54-750149E; 60-61599N	Town supply	Upstream-pasture Downstream-townsupply
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 Downstream-vine, horticulture, pasture Downstream of Ramsar Lake Downstream of all Kerang Channels

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 the 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, (see Glossary).

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 factors curves which enable water concentrations to be predicted with reasonable accuracy from passive sampler concentrations. There is a good relationship between pesticides 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. The time integrated pesticide water concentrations determined facilitate to compare with the national and international water quality guideline values for drinking, recreation, irrigation, livestock, aquatic ecosystems protection and aquaculture. Hyne et al. (2004), Leonard, Hyne and Pablo (2002) . However, despite the advantages with 'passive samplers' they are generally limited to hydrophobic or liposoluble substances with high K_{ow} values. In order to monitor pesticides in G-MW supply channels (listed in Appendix I), 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 Monitoring sites

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

Number of pesticide monitoring sites : 14 (see Table 1, page 4)

6.3 Monitoring Schedule

Sampling frequency :

passive sampling - once per four weeks

Spot sampling - once per four weeks

Passive sampler's deployment & retrieval for the 2004-2005 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**
September/04	Missed out-delays in irrigation season, OHS procedures development			
1/October/04	• 4 October 2004 • 5-7 October 2004			
		2-4 November 2004	2-4 November 2004	2-4 November 2004
2/November/04	• 1 November 2004 • 2-4 November 2004			
		30 November-2 December 2004	30 November-2 December 2004	30 November-2 December 2004
3/December/04	• 29 November 2004 • 30 November-2 December 2004			
		28-30 December 2004	28-30 December 2004	28-30 December 2004
4/Januray/05	• 27 December 2004 • 28-30 December 2004			
		25-27 January 2005	25-27 January 2005	25-27 January 2005
5/February/05	• 24 January2005 • 25-27 January 2005			
		22-24 February 2005	22-24 February 2005	22-24 February 2005
6/March/05	• 21 February 2005 • 22-24 February 2005			
		22-24 March 2005	22-24 March 2005	22-24 March2005
7/April/05	• 21 March 2005 • 22-24 March 2005			
		19-21 April 2005	19-21 April 2005	19-21 April 2005

6.4 Duration of monitoring

For pesticides monitoring, 2004-2005 and 2005-2006 irrigation season was divided into the following :

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

6.5 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). 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 period 1-5 was discontinued after sample period 5. This was to allow for organophosphates residues to be determined without interference on GC from tributylphospate (see Table 2). Addition of monolinuron internal standard used in Dodecanol + TRIMPS for sample period 1-5 was discontinued after sample period 5. This was to allow for pesticides residues to be determined without interference on GC from monolinuron (see Table 7).

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). After 28 days, the passive samplers were retrieved, and the solvent from the deployed bags were collected into a glass vial (23x46mm) and dispatched off to DPI, State Chemistry Laboratory, Werribee for analysis via a courier.

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 were dispatched off to DPI for analysis via a courier.

6.6 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 subsample of water was extracted with 100mL of dichloromethane (DCM), then re-extracted twice with 50 mL of DCM. The DCM extracts are combined and dried through a sodium sulphate column. The extract is reduced and inverted into hexane which is reduced to 1mL. The final extract is 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. Organochlorines and synthetic pyrethroids are analysed by GC-ECD (electron capture detecto).

Taufluvalinate is extracted 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).

6.7 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 levels. The triplicate sample was retained as a confirmatory and alternative quality assurance sample. Normally two solvent samples tested and showing no residues would deem the triplicate sample as unnecessary.

6.8 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 14 sampling sites

7. Results

7.1 Passive Sampler solvent samples-TRIMPS

Fourteen site samples for seven separate sampling periods, as listed in the Table 1, were screened for the following pesticides at the limit of reporting (LORs) stated (see Table 2). The internal standard TBP was quantified in each sample but no correlation was found with documented flow rates in the sampling channel.

Table 2: Pesticides sampled by passive samplers with solvent trimethylpentane and their limit of reporting (LOR)

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

Passive samplers (with solvent trimethylpentane or TRIMPS) deployed at channels were able to pick up both organochlorine (endosulfan) and synthethic pyrethroids (bifenthrin, esfenvalerate, Taufluvalinate) pesticides. These pesticides, having a high log Kow (2.96-6.22) and hydrophobic in nature, are expected to be sampled by TRIMPS. Period 6 & 7 included additional pesticides as listed in Table 2. Endosulfan was detected at 8 of the 14 sites on a regular basis (see Table 3). Endosulfan was detected at elevated levels at 3 sites (Mooroopna, Ardmona and Kyabram). These sites are in proximity to intensive horticultural (orchards and tomato) industries. Endosulfan is registered for insect control on a number of crops including pome fruit, stone fruit and vegetables.

Chlorpyrifos was detected at elevated levels at Shepparton on two occasions (60 and 37.5µg/L respectively)

Table 3 : Total Endosulfan (concentrated) detected (µg/L) in trimethylpentane containing passive samplers (TRIMPS) retrieved during 2004-05 irrigation season

Site	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6	Period 7	Comments
1.Torgannah (MV)	trace	trace	trace	trace	trace	trace		intensive orchards
2.Burramine (MV)								reference point for Murray System
3.Katamatite (MV)								town supply & outfall to Booscy Creek-Broken creek
4.Shepparton (S)								intensive orchards
5.Mooroopna (CG)	41.5	4.5	trace		trace	trace		orchards, tomatoes & pastures outfall to Goulburn River
6.Ardmona (CG)	7	trace	trace					intensive orchards
7. Kyabram (CG)	3	trace	13	21	4	trace		intensive tomatoes
8.Tatura (CG)								town supply
9.Nagambie								reference point for Goulburn System
10.Corop (R-C)	1	trace	2	1	trace	trace	trace	tomatoes and vines downstream town supply
11.West Boort (P-B)	trace	trace	trace	trace		trace	trace	intensive orchards (olive) stock & domestic & town supply
12.Appin (P-B)	trace	trace	trace	trace		trace		intensive tomatoes outfall and aquaculture,
13.Kerang town (T)								town supply
14.Kangaroo Lake (T)	trace	trace	trace	3.5	trace	trace	trace	viticulure, pasture, horticulture & Ramsar Lake

Note: Total endosulfan is calculated by adding α-endosulfan, β-endosulfan and endosulfan sulfate. Trace levels are set at 50% of the LOR for summation.

The above analysis results (Table 3) is based on concentrated endosulfan sampled in passive samplers over a period of 28 days. This concentration was converted into time-integrated water concentrations using the concentration factor (CF) for α Endosulfan, β Endosulfan and Endosulfan sulfate following Leonard, Hyne and Pablo (2002). Table 4 shows an example of calculating α-endosulfan, β-endosulfan and endosulfan sulfate and total endosulfan (for site 5, period 1, where maximum endosulfan was detected). Table 5 shows an example of calculating chlorpyrifos (for site 4, period 7). Table 6 provides predicted water concentrations for all of the 14 sites.

Table 4 : Predicted average endosulfan water concentration at Site 5, from Period 1 TRIMPS extract.

Compound	Equations for Concentration Factors	Passive Sampler Concentration (µg/L)	Days Deployed	log10 (Days Deployed)	At day 28 log10 (Concentration Factor)	Concentration Factor (CF)	Predicted Concentration in water per day (µg/L)
α Endosulfan	y = 1.01x + 1.70	12 19 Average : 15.5	28	1.4471580	Y=1.01x1.4471580+1.70= 3.1616296	1958.276	0.007915127
β Endosulfan	y = 1.01x +1.61	9 12 Average : 10.5	28	1.4471580	Y=1.01x1.4471580+1.61= 3.0716296	1591.746	0.006596529
Endosulfan $S0_4$	y = 1.11x + 1.67	13 18 Average : 15.5	28	1.4471580	Y=1.01x1.4471580+1.67= 3.1316296	1354.034	0.011447274
Total endosulfan							0.0259589

Note (1)
NB : equations are based on the log 10 numbers
Where X= log 10 (day number)
Where Y= log 10 (concentration factor)
The levels of endosulfan are calculated from Leonard, Hyne and Pablo (2002)
Note (2)
The Centre for Ecotoxicology, NSW helped in using the equation and provided with lab based concentrated factor (CF) data for endosulfan
Note (3)
Endosulfan is normally applied as a mixture of alpha and beta isomers. The alpha isomer breaks down more rapidly to endosulfan sulphate than the beta isomer

Table 5 : Predicted average chlorpyrifos water concentration at Site 4, from Period 7 TRIMPS extract.

Compound	Equations for Concentration Factors	Passive Sampler Concentration (µg/L)	Days Deployed	log10 (Days Deployed)	At day 28 log10 (Concentration Factor)	Concentration Factor (CF)	Predicted Concentration in water per day (µg/L)
Chlorpyrifos	y = 0.95x + 1.88	50 25 Average : 37.5	28	1.4471580	Y=0.95x1.4471580+1.88= 3.25480	1798.04322	0.0208560

Table 6 : Predicted average endosulfan water concentration at different sites using the regression equation and the concentration factor (based on raw data)

Site	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6	Period 7	Comments
1.Torgannah (MV)	0.001477	0.001477	0.001477	0.001477	0.001477	0.001477		intensive orchards
2.Burramine (MV)								reference point for Murray System
3.Katamatite (MV)								town supply & outfall to Booscy Creek-Broken creek
4.Shepparton (S)								intensive orchards
5.Mooroopna (CG)	0.025959	0.003268	0.001477		0.001477	0.001477		orchards, tomatoes & pastures outfall to Goulburn River
6.Ardmona (CG)	0.004207	0.001477	0.002046					intensive orchards
7. Kyabram (CG)	0.002429	0.001791	0.008704	0.003284	0.012532	0.001477		intensive tomatoes
8.Tatura (CG)								town supply
9.Nagambie								reference point for Goulburn System
10.Corop (R-C)	0.001732	0.001477	0.002685	0.001987	0.001477	0.001477	0.001477	tomatoes and vines downstream town supply
11.West Boort (P-B)	0.001477	0.001477	0.001477	0.001732		0.001477	0.001477	intensive orchards (olive) stock & domestic & town supply
12.Appin (P-B)	0.001477	0.001477	0.001477	0.001477		0.001477		intensive tomatoes outfall and aquaculture,
13.Kerang town (T)								town supply
14.Kangaroo Lake (T)	0.001477	0.001477	0.002046	0.002585	0.001477	0.001477	0.001477	viticulure, pasture, horticulture & Ramsar Lake

7.2: Passive Sampler solvent samples dodecanol and trimethylpentane or polyethylene isooctane dodecanol (PID)

Fourteen site samples for seven separate sampling periods as listed in the Table 1 were screened for the following pesticides at the LORs stated (see Table 7). The internal standard monolinuron was quantified in each sample but no correlation was found with the documented flow rates

Table 7: Pesticides sampled by passive samplers with solvent mixture dodecanol : trimethylpentane (3:2) and their limit of reporting (LOR)

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

Passive samplers with dodecanol and trimethylpentane mixed solvent deployed at channels were able to extract organophosphates (azinphos methyl, omethoate), carbamates (methomyl, thiodicarb,) and herbicides (atrazine and molinate). These pesticides having lower Kow values (compared to pesticides extracted by TRIMPS were expected to be picked up by this type of sampler. No pesticides were detected at or above the stated levels. Period 6 & 7 included additional pesticides as listed in Table 7.

7.3 Spot Water Samples

Fourteen site samples for seven separate sampling periods as listed in the Table 1 above were screened for the following pesticides at the LORs stated (Table 8).

Table 8 : Pesticides sampled in spot samples and their limit of reporting (LOR)

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

The spot water samples were analysed for organophophates (phorate, parathion methyl, chlorpyriofos, omethoate, azinphos methyl), organochlorine (endosulfan), carbamates (methomyl, thiodicarb), synthetic pyrethroids (bifenthrin, esfenvalerate, tau-fluvalinate) and herbicides (trifluralin, pendimethlalin, atrazine and molinate) and the fungicide chlorothalonil, Out of 18 pesticides, four pesticides (endosulfan, chlorpyrifos, parathion methyl and atrazine) were detected above the LOR (see Table 9). Endosulfan was detected at two sites (Shepparton and Nagambie) whereas chlorpyrifos and parathion methyl was detected at one site (Ardmona). Atrazine was detected 9 out of 14 sites (no site showed at elevated levels). Atrazine was found on a regular basis at Mooroopna, Nagambie, West Boort and Appin.

Table 9: Pesticides detected in spot samples during 2004-05 irrigation season (µg/L)

Site	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6	Period 7	Comments
1.Torgannah (MV)								intensive orchards
2.Burramine (MV)								reference point for Murray System
3.Katamatite (MV)								town supply & outfall to Booscy Creek-Broken creek
4.Shepparton (S)	Endosulfan (trace)			Atrazine (0.01)		Atrazine (0.020)	Atrazine (0.020)	intensive orchards
5.Mooroopna (CG)			Atrazine (0.01)	Atrazine (0.01)		Atrazine (0.017)	Atrazine (trace)	orchards, tomatoes & pastures outfall to Goulburn River
6.Ardmona (CG)			Chlorpyrifos (trace), Parathion methyl (trace)	Atrazine (0.01)		Atrazine (0.014) Parathion methyl (trace)	Atrazine (0.02)	intensive orchards
7. Kyabram (CG)					Atrazine (0.01)		Atrazine (0.01)	intensive tomatoes
8.Tatura (CG)				Atrazine (0.01)		Atrazine (0.018)	Atrazine (0.02)	town supply
9.Nagambie	Endosulfan (trace)			Atrazine (0.02)	Atrazine (0.01)	Atrazine (0.019)	Atrazine (0.02)	reference point for Goulburn System
10.Corop (R-C)						Atrazine (0.011)	Atrazine (trace)	tomatoes and vines downstream town supply
11.West Boort (P-B)	Atrazine) (0.01)	Atrazine) (0.01)	Atrazine (0.01)		Atrazine (0.01)	Atrazine (0.018)	Atrazine (0.01)	intensive orchards (olive) stock & domestic & town supply
12.Appin (P-B)	Atrazine) (0.02)				Atrazine (0.01)	Atrazine (0.012)	Atrazine (0.02)	intensive tomatoes outfall and aquaculture,
13.Kerang town (T)			Atrazine (0.01)					town supply
14.Kangaroo Lake (T)								vineyard & Ramsar Lake

Fourteen site samples for seven separate sampling periods as listed in the Table 1 above were screened for the following heavy metals at the LORs stated (Table 10).

Table 10 : 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 levels of copper, zinc, lead and cadmium and determined at the levels reported. Cu was detected on regular basis at elevated levels (>1.4µg/L) at Torgannah, Mooroopna, Shepparton, West Boort, Appin, Kerang and Kangaroo Lake (Table 11). These sites are under intensive orchards and vegetables growing areas where copper is registered for use as a fungicide.

Table 11. **Copper µg/L detected in spot water samples above the LOR during 2004-05 irrigation season**

Site	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6	Period 7	Comments
1.Torgannah (MV)	1.2	2.6	1.3	1.6	2.2	1.1	1.2	intensive orchards
2.Burramine (MV)								reference point for Murray System
3.Katamatite (MV)	1.6				1.0			town supply & outfall to Booscy Creek-Broken creek
4.Shepparton (S)		3.6	1.1	1.6	1.3			intensive orchards
5.Mooroopna (CG)	1.2	1.4	1.4		2.2	1.0	1.6	orchards, tomatoes & pastures outfall to Goulburn River
6.Ardmona (CG)			1.0		1.3			intensive orchards
7. Kyabram (CG)	1.3	1.2	1.6	1.2	1.0	1.2	1.2	intensive tomatoes
8.Tatura (CG)			1.2	1.1	1.0			town supply
9.Nagambie								reference point for Goulburn System
10.Corop (R-C)				1.4	1.4	1.2		tomatoes and vines downstream town supply
11.West Boort (P-B)	1.8	1.3	1.4	1.8	1.3	1.5	1.8	intensive orchards (olive) stock & domestic & town supply
12.Appin (P-B)	1.9	1.1	1.1	1.9	1.3	1.7	1.7	intensive tomatoes outfall and aquaculture,
13.Kerang town (T)	1.9	1.9	2.4	3.9	2.3	2.4	2.0	town supply
14.Kangaroo Lake (T)	1.6	1.9	1.6	2.3	2.6	2.4	2.7	vineyard & Ramsar Lake

8. Discussion

8.1 :Pesticides in passive samples

The analysis of passive samplers (TRIMPS) has revealed elevated levels of endosulfan at Mooroopna, Ardmona and Kyabram, where intensive horticulture (orchards, vineyards and Tomato growing) is being practiced. Endosulfan is registered and available for use on a range of horticultural crops. Endosulfan was not detected in the matching spot water sample taken at the time solvent samples were removed from these three sites. Due to the level 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 levels detected were converted into water concentration (Table 12) using the regression equation of Leonard, Hyne and Pablo (2002).

Table 12: Predicted Endosulfan Concentration in TRIMPS & Guideline Values for Different Water Uses

Site	Predicted Maximum Endosulfan concentration in TRIMPS (µg/L)	Comments : Water Uses & Guideline Values A= Raw Water for **Drinking** (40 µg/L) ; B=**Recreation** (40 µg/L); C= Protection of **Aquatic Ecosystems** (99% protection) (0.03 µg/L); D=**Aquaculture** (<0.003 µg/L)
Site 1 (MV)	0.001477, 0.001477, 0.001477, 0.001477, 0.001477	Safe for all purposes (A,B,C,D) Upstream- Intensive orchards (stone & pome fruit)
Site 2 (Ref-Murray)		
Site 3 (MV)		
Site 4 (S)		
Site 5 (CG)	**0.025959**, **0.003268,** 0.001477, 0.001477, 0.001477, 0.001477	Safe for all purposes (A,B,C) except **Aquaculture** Upstream- Intensive orchards, tomatoes
Site 6 (CG)	**0.004207**, 0.002046, 0.001477	Safe for all purposes (A,B,C) except **Aquaculture** Upstream-Intensive orchards (stone & pome fruit)
Site 7 (CG)	**0.012531, 0.008704, 0.003268,** 0.002429, 0.001791	Safe for all purposes (A,B,C) except **Aquaculture** Upstream-Intensive tomatoes
Site 8 (CG)		
Site 9 (Ref -Goulburn)		
Site 10 (R-C)	0.002648, 0.001987, 0.001860, 0.001477, 0.001477	Safe for all purposes (A,B,C,D) Upstream-Vineyards and Intensive orchards
Site 11 (P-B)	0.001477, 0.001477, 0.001477	Safe for all purposes (A,B,C,D) Upstream-Intensive orchards (Olives)
Site 12 (P-B)	0.002585, 0.001477, 0.001477, 0.001477	Safe for all purposes (A,B,C,D) Upstream-Intensive tomatoes, crops
Site 13 (T)		
Site 14 (T)	0.0020465, 0.002585, 0.001477, 0.001477, 0.001477	Safe for all purposes (A,B,C,D) Upstream-vineyards

Note: Total endosulfan is calculated by adding α-endosulfan, β-endosulfan and endosulfan sulfate. Trace levels are set at 50% of the LOR for summation.

[1]ANZECC (1996), [2]ANZECC (2000)

The predicted endosulfan concentration in water per day was then compared with the guideline values. The estimated results showed that endosulfan concentration in water may not have been exceeded the guideline values for the protection of either freshwater ecosystems (95% or 99% protection), or raw water to be used for drinking water supply and recreational uses and is of a good water quality for the above purposes (see Table 10). However, water at some sites, such as Mooroopna (period-1,3), Ardmona (period 1), Kyabram (period 3,5), have exceeded the guideline values of endosulfan for aquaculture (See Table 10). The predicted endosulfan water concentration in Table 10 relate to the 28 day deployment. If the predicted levels were present for only 50% of the deployment then predicted values will approximately increase 100%. This will increase the predicted endosulfan concentration at Torganah, Corop, West Boort, Appin and Kangaroo Lake to ANZECC 'Aquaculture' guideline levels.

The predicted chlorpyrifos concentrations showed that water at Shepparton was safe for livestock and human drinking and recreational uses but have exceeded the guideline values for aquatic eco-systems protection and aquaculture (See Table 13).

Table 13 : Predicted Chlorpyrifos concentration in TRIMPS and Guideline Values for different Water uses

Site	Predicted maximum - minimum chlorpyrifos conc. in TRIMPS (µg/L) at different sites	Comments : Water Uses & Guideline Values A= Raw Water for **Drinking** (2.0 µg/L) ; B=**Recreation** (2.0 µg/L); C=**Livestock** ((24.0 µg/L); D= Protection of **Aquatic Ecosystems** (95% protection) (0.01 µg/L); E=**Aquaculture** (<0.001 µg/L)
Site 1 (MV)		
Site 2 (Ref-Murray)		
Site 3 (MV)		
Site 4 (S)		
Site 5 (CG)	**0.0333696, 0.020856**	Safe for all purposes (A, B) except aquatic system protection and aquaculture Upstream- Intensive orchards, tomatoes
Site 6 (CG)		
Site 7 (CG)		
Site 8 (CG)		
Site 9 (Ref.-Goulburn)		
Site 10 (R-C)		
Site 11 (P-B)		
Site 12 (P-B)		
Site 13 (T)		
Site 14 (T)		

[1]Canadian Environmental Quality Guidelines (2003); [2]ANZECC (1996),; [3]ANZECC (2000),

8.2 : Pesticides in spot water samples

The herbicide atrazine was detected at a number of sites including Shepparton, Mooroopna, Ardmona, Kyabram, Tatura, Nagambie, West Boort, Appin, Kerang town, which could of concern (see Table 14). It is likely that the atrazine detected was used to control weeds in forage legumes and orchards. The non detection of atrazine in dodecanol and trimethylpentane samplers (PID) is not inconsistent with spot sample levels as the sampler solvent LORs are higher.

The level detected in spot water samples was in the range of 0.01-0.02 µg/L. which is far below the ANZECC (2000) guideline values (13 µg/L) for the protection of freshwater aquatic ecosystems (95% protection). Since there are no ANZECC guidelines of atrazine for irrigation, livestock and drinking water therefore Canadian Environmental Guidelines values (2003) were used for comparison. Overall, the atrazine level detected in spot samples did not exceed the recommended guideline values for different water uses (see table 14 below). However, it is believed that the presence of atrazine in irrigation water may be hazardous to crops.

Table 14 : Atrazine concentration in spot water samples and guideline values for different water uses

Site	Atrazine concentration in spot water samples (µg/L)	Comments : Water Uses & Guideline Values A= Raw Water for **Drinking** (5 µg/L) ; B=I**rrigation** (10 µg/L); C=**Livestock** (5 µg/L), D= Protection of **Aquatic Ecosystems** (95% protection) (13 µg/L);
Site 1 (MV)		
Site 2 (Ref-Murray)		
Site 3 (MV)		
Site 4 (S)	0.01, 0.020	Safe for all purposes (A,B,C,D) Upstream-intensive orchards (stone & pome fruit)
Site 5 (CG)	0.01, 0.01, 0.017	Safe for all purposes (A,B,C,D) Upstream-Vineyards and Intensive orchards
Site 6 (CG)	0.01, 0.014	Safe for all purposes (A,B,C,D) Upstream-Intensive orchards (stone & pome fruit)
Site 7 (CG)	0.01	Safe for all purposes (A,B,C,D) Upstream-Intensive tomatoes
Site 8 (CG)	0.01, 0.018	Safe for all purposes (A,B,C,D) Upstream-pastures, crop
Site 9 (Ref.-Goulburn)	0.02, 0.01, 0.019	Safe for all purposes (A,B,C,D) Upstream-vine, tomatoes, pastures, aquaculture
Site 10 (R-C)	0.01	Safe for all purposes (A,B,C,D) Upstream-Vineyards and Intensive tomatoes
Site 11 (P-B)	0.01, 0.01, 0.01, 0.01, 0.018	Safe for all purposes (A,B,C,D) Upstream-Intensive orchards (Olives)
Site 12 (P-B)	0.02, 0.01, 0.012	Safe for all purposes (A,B,C,D) Upstream-Intensive tomatoes, crops
Site 13 (T)	0.01	Safe for all purposes (A,B,C,D) Upstream-pastures
Site 14 (T)		

[1]Canadian Environmental Quality Guidelines (2003); [2]ANZECC (2000)

The detection of endosulfan and atrazine at Nagambie (reference site for Goulburn system) may be attributed from upstream farming activities; pastures (lucerne), tomatoes, vineyards (see table 9)

The reporting of chlorpyrifos and parathion methyl (trace amounts) at Ardmona sampling site (spot sample) is expected to be associated with organophosphate insecticide usage in stone fruit orchards (see table 9). Historically, DPI residue surveys reveal parathion methyl and chlorpyrifos applications in local stone fruit orchards.

Heavy metals in spot water samples

The heavy metals results for copper reveals that water in the 14 sites was of good quality for most primary purposes including irrigation, livestock, drinking, and recreation (Table 15). However, there were 7 sites (Torganah, Shepparton, Mooroopna, West Boort, Appin, Kerang and Kangaroo Lake) where copper levels exceeded the recommended trigger value of 1.4µg/L for the protection of 95% aquatic species. Those sites are under intensive horticulture and copper use would be associated with fungal disease control in intensive orchards, vineyards and tomatoes. 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 levels, these levels are possibly attributable to natural or agriculture sources. No other heavy metals were found at elevated levels at any of the 14 sites investigated.

Table 15 : Copper concentration in spot water samples and guideline values for different water uses

Site	Copper concentration in spot water samples (µg/L)	Comments : Water Uses & Guideline Values A= Raw Water for **Drinking** (1000 µg/L) ; B=**Irrigation** (200 µg/L); C=**Livestock** (400-5000 µg/L), D=**Aquaculture** (<5 µg/L)
Site 1 (MV)	2.6, 2.2, 1.6, 1.3	Safe for all purposes (A,B,C,D) Upstream-intensive orchards (stone & pome fruit), pastures
Site 2 (Ref-Murray)		
Site 3 (MV)	1.6, 1.0	Safe for all purposes (A,B,C,D) Upstream-pastures, crops
Site 4 (S)	3.6, 1.6, 1.3, 1.1	Safe for all purposes (A,B,C,D) Upstream-intensive orchards (stone & pome fruit)
Site 5 (CG)	2.2, 1.9, 1.6, 1.4, 1.4, 1.2, 1.0	Safe for all purposes (A,B,C,D) Upstream-Vineyards and Intensive orchards
Site 6 (CG)	1.3, 1.0	Safe for all purposes (A,B,C,D) Upstream-Intensive orchards (stone & pome fruit)
Site 7 (CG)	1.6, 1.3, 1.2, 1.2, 1.2, 1.2, 1.0	Safe for all purposes (A,B,C,D) Upstream-Intensive tomatoes
Site 8 (CG)	1.2, 1.1, 1.0	Safe for all purposes (A,B,C,D) Upstream-pastures, crop
Site 9 (Ref.-Goulburn)		
Site 10 (R-C)	1.4, 1.4, 1.2	Safe for all purposes (A,B,C,D) Upstream-Vineyards and Intensive tomatoes
Site 11 (P-B)	1.8, 1.8, 1.8, 1.5, 1.4, 1.3, 1.3	Safe for all purposes (A,B,C,D) Upstream-Intensive orchards (Olives)
Site 12 (P-B)	1.9, 1.9, 1.7, 1.7, 1.3, 1.1, 1.1	Safe for all purposes (A,B,C,D) Upstream-Intensive tomatoes, crops
Site 13 (T)	3.9, 2.4, 2.4, 2.4, 2.3, 1.0, 1.9, 1.9	Safe for all purposes (A,B,C,D) Upstream-pastures
Site 14 (T)	2.7, 2.6, 2.4, 2.3, 1.9, 1.6, 1.6	Safe for all purposes (A,B,C,D) Upstream-vineyards

9. Conclusions

Endosulfan has been detected on a regular basis in trimetylpentane solvent from passive samplers at eight sites. These sites show associations with intensive orchards, vineyards, tomato production and forage production. Atrazine has been detected sporadically in spot samples at nine sites. Copper has been detected at 10 sites at elevated levels on a repeated basis. The chosen two reference sites have been validated by reporting minimal residues (Nagambie) or not detected (Burramine). Reported residues indicate levels below ANZECC guideline values for drinking, recreational, freshwater ecosystems and irrigation and livestock. ANZECC guideline values for aquaculture have been reached or exceeded for predicted endosulfan levels at a majority of monitoring sites. ANZECC guideline values for freshwater ecosystems for copper levels have been reached or exceeded at a majority of monitoring sites.

These findings are heavily constrained by the unavoidable absence of data from the early part of the season before November. With that important caveat in mind, it is concluded that the results for the first year's monitoring program do not indicate that the high and medium risk pesticides selected are likely to render water in Goulburn-Murray Water's irrigation channels unfit for irrigation or stock or human consumption. Similarly, adverse impacts on aquatic ecosystems in receiving natural waterways due to concentrations of the high and medium risk pesticides selected in channel outfalls are also unlikely.

Copper concentrations in a significant number of channels is likely to adversely impact on aquatic ecosystems. It is not clear whether these elevated copper concentrations are sourced from pesticides. More importantly, adverse impacts on aquatic ecosystems in receiving natural waterways due to copper concentrations in channel outfalls are unlikely.

However, it is concluded that elevated endosulfan levels in the water in G-MW channels is likely to render that water unfit for aquaculture at a significant number of locations.

For high risk sites identified after two years monitoring it is suggested that more intensive sampling on a seven to fourteen day passive sampler deployment period should be considered.

10. Recommendations

It is recommended that Goulburn Murray Water (G-MW) should continue to monitor pesticides in channels for at least another irrigation season. This will help to validate the data collected and identify 'hot spots' to reduce risks from such sites.

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 level at which an analyte can identified but not quantified accurately

Limit of Reporting (LOR) : is the level 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

12. References

Australian and New Zealand Environment and Conservation Council (ANZECC) and Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ), (2000*).*Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Volume 1, The Guidelines(Chapters1-7).

Australian and New Zealand Environment and Conservation Council (ANZECC) (1992). Australian Water Quality Guidelines for Fresh and Marine Water Quality. Chapter 1-4.

Canadian Environmental Quality Guidelines (2003) : Summary Table of Existing Canadian Environmental Quality Guidelines. Environment Canada.

EPA (2003) State Environment Protection policy (Waters of Victoria)

Hyne , R.V., Pablo, F., Aistrope, M., Leonard, A. W. and Ahmad, N (2004). Comparison of time integrated pesticide concentrations determined from field-deployed passive samplers with daily river-water extractions. *Environmental Toxicology and Chemistry*, 23 (9) : 2090-2098.

Kibria, G. (2003). Occupational and Health and Safety Procedures for Laboratory and Field based Works for EMPA2 (pesticides and Channels Contamination).. G-MW Docs Ref 1053172v2 .22p.

Kookana, R., Barnes, M., Correll, R. and Kibria, G. (2003). First tier assessment of the risks associated with pesticides used in Goulburn-Murray Irrigation Areas - A pesticide risk reduction program for G-MW Channels. Report prepared under a research collaboration agreement between G-MW & CSIRO. Goulburn-Murray Rural Water Authority (G-MW), Tatura and CSIRO, Adelaide.103p.

Krake, K and Breewel, L. and Kibria,G. (2001). Pesticide and Channel Contamination. Pesticide used in G-MW Irrigation Areas. G-MW Aquatic Plant Services. G-MW Docs Reference 704342. 25p.

Leonard, A W and Hyne, R V and Pablo, F. (2002). Trimethyl pentane-containing passive samplers for predicting time-integrated concentration s of pesticides in water; laboratory and field studies. *Environmental Toxicology and Chemistry*, 21 (12) : 2591-2599

Rose, G. and Kibria, G. (2004). Pesticide monitoring in Goulburn-Murray Waters Irrigation Supply Channels-Results of Pilot Study. Department of Primary Industries, State of Victoria and Goulburn-Murray Rural Water Authority (G-MW), Tatura. 22p.

Tomlin, C.D.S. (2000). The Pesticide Manual. 12th Edition. The British Crop Protection Council. Surrey, U.K. 1249p.

13. Appendices

Appendix I. 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	