Investigation of 10 herbicides in surface waters of a horticultural production catchment in south-eastern Australia

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Abstract

Herbicides are regularly applied in horticultural production systems and may migrate off-site, potentially posing an ecological risk to surface waterways. However, few studies have investigated the levels and potential ecotoxicological impact of herbicides in horticultural catchments in southern Australia. This study investigated the presence of 10 herbicides at 18 sites, over a five-month period in horticulturally important areas of the Yarra Valley in south-eastern Australia. Seven of the 10 herbicides were detected in the streams, in 39% of spot water samples, 25% of surface sediment samples, and more than 70% of the passive sampler systems deployed. Few samples contained residues of two or more herbicides. Simazine was the herbicide most frequently detected in water, sediment and passive sampler samples, and was found at the highest concentrations in the water (0.67 g/L), and sediment (up to 260 g/kg dry weight). Generally the concentrations of the herbicides detected were several orders of magnitude lower than reported ecotoxicological effect values, including those for aquatic plants and algae, suggesting that concentrations of individual chemicals in the catchment were unlikely to pose an ecological risk. However, little is known about the combined effects of simultaneous, low level exposure of multiple herbicides of the same mode of action on Australian aquatic organisms, nor their contribution when found in mixtures with other pesticides. Further research is required to adequately assess the risk of pesticides in Victorian aquatic environments.

Keywords: herbicides; horticultural catchment; surface water; sediment; environmental risk

1. Introduction

Herbicides are widely used in Australian agricultural productions systems for the suppression of unwanted plants (weeds) before and during crop growth. In monetary and volume terms, herbicides are the top ranked category of pesticides sold in Australia (based on 2010-11 data: 2130 products, A$1,252 million), more than twice that of insecticides (1098 products; A$362 million) and five times the sales of fungicides (619 products; A$231 million; APVMA 2012). The herbicide use regime employed by a farmer is largely influenced by the different weed threats faced by the crops being produced. For example, there are a greater number of herbicides registered for use on wheat (40) than potatoes (22), and a relatively low number of herbicides registered for use in some horticultural systems (e.g. lettuce (6), zucchini (3)) and on nut crops (e.g. almonds (9), walnuts (7)). Consequently, there is likely to be a substantial load of herbicides being applied in many agricultural production catchments. There are over 120 herbicides (active ingredients) registered for use in Victoria, although the number and amount of herbicides used by farmers in the state is unknown because, while farmers and other users must keep written records of pesticide use, there is currently no requirement to report pesticide use to either local or centralised authority (Wightwick and Allinson, 2007).

Despite the potential environmental risks, herbicides have received little attention in Australian waterways compared to other jurisdictions (Wightwick and Allinson, 2007). The presence of herbicides in the dissolved state in the aquatic environment has been extensively studied internationally and levels in the g/L and sub- g/L range reported in drinking and surface water. For instance, in North America the United States Geological Survey’s large, nation-wide surveys of pesticide residues in surface and ground waters produced a wealth of data for use in the environmental risk assessment of herbicides (Gillom et al., 2006). However, prior to this study, there had been no significant studies investigating herbicides in surface waters in Victoria since the 1990s, although in northern Australia a number of recent studies have detected residues of some herbicides, including atrazine, diuron, hexazinone, and simazine, in the water column in a relatively high percentage of samples (Shaw et al., 2010; Lewis et al., 2009; Bainbridge et al., 2009; Bengston Nash et al., 2006).

While the measurement of nutrients and salts in surface and groundwater is now routine and offered cheaply by many commercial laboratories, this is not so for other contaminants of concern, including many pesticides. Measurement of pesticides in waters and sediments can be expensive in Australia, which inhibits monitoring by water authorities (as providers of water), catchment management authorities (as custodians of the natural environment), and consumers (e.g. irrigators, industry and household and domestic water users), potentially resulting in increased risk to the natural environment. Grab (or spot) samples are commonly used to characterise pesticide residues in surface waters, although there are a number of modified or new approaches for sampling which facilitate cost-effective monitoring of pesticide concentrations in waterways, one of which is integrative sampling with passive samplers (or passive sampling). A 'passive sampler' can be defined as a device that is able to acquire a sample from discrete location without the active media transport induced by pumping or purge techniques (ITRC 2006). Hence, most passive samplers consist of a receiving phase with high affinity for organic contaminants, separated from the aquatic environment by a diffusion limiting membrane. Some of the most commonly used devices that rely on diffusion and sorption to accumulate analytes in the sampler are semi-permeable membrane devices (SPMDs) and passive in-situ samplers (such as the Chemcatcher™ system (CC)). One of the first studies in Victoria using passive samplers occurred during the 2004-05 and 2005-06 irrigation seasons, when Rose and Kibria (2007) deployed SPMDs containing trimethyl pentane at fifteen sites within six irrigation areas in northern Victoria. The monitoring found three insecticides (endosulfan, chlorpyrifos and parathion methyl) in the passive sampler solvents, but no herbicides. Elsewhere in Australia, a number of relatively recent studies have detected residues of some herbicides in rivers and estuaries on the eastern seaboard of Australia using CC passive sampling systems, including atrazine, diuron, hexazinone, and simazine (Escher et al., 2006; Lewis et al., 2009; Muller et al., 2008; O'Brien et al., 2011; Shaw et al., 2009, 2010; Stephens et al., 2009), but prior to this study, there had been no significant studies investigating herbicides in surface waters in Victoria using the CC system.

There has been less attention paid to levels of herbicides in sediment than in the water column, despite the potential effects they may have on benthic organisms. Noppe et al. (2007) were the first to report on the occurrence of triazines (e.g. atrazine, simazine) in suspended solids and sediment because up to that point, they contend, it had generally been assumed that these chemicals are mainly in the dissolved phase (as a group, the triazines are relatively polar (i.e. with an octanol-water partition coefficient, log Kow typically < 2.5) with good water solubility (up to 30 mg/L)). Chemical sorption, however, is also influenced by the organic carbon and clay content of sediments which may combine to increase the capacity of sediments to act as reservoirs for some chemicals. This in part may explain the wide variation in concentrations observed for compounds such as atrazine in sediments, e.g. up to 9.9 g/kg in Belgium and the Netherlands (Noppe et al. 2007), up to 170 g/kg in Pakistan (Maqbool et al. 2008) and up to 600 g/kg in the Fraser River valley in Canada (Wan et al. 2006). In Australia, Duke et al. (2005) reported atrazine, ametryn and diuron in mangrove sediments, with higher diuron concentrations in sediments where there were greater numbers of common mangrove (*Avicennia marina*) showing signs of toxicity.

To in part address the paucity of information on herbicides in Victorian waterways, in 2008 – 09 we examined the presence and concentration of 10 synthetic organic herbicide compounds plus a number of metabolites/breakdown products, in the water column and sediments at 18 surface water sites over a five month period within Victoria's Yarra River Catchment, in south-eastern Australia. The objective of this study was to generate new data on the environmental levels and possible ecological impact of herbicides used in horticultural production systems. The study included both intensive spot water and sediment sampling and time-integrated sampling via deployment of passive water samplers. To our knowledge this was the first study of its kind undertaken in horticultural catchments within Victoria.

2. Materials and methods

2.1 Study area

Eighteen sites were monitored in Victoria's Yarra River catchment for this study, which was conducted as part of a larger, multi-disciplinary study of waterways in and around Melbourne. In that context, this manuscript is a companion piece to the paper by Wightwick et al (2012), and Wightwick et al (2013) who reported the levels of 25 fungicides and trace metals in the surface waters and sediments, respectively, at the sites in the Middle and Upper Yarra catchment area used for this study (Figure S1). For full details of the study area, readers are directed to the Supplementary Information.

2.2 Water and sediment sampling

Water and sediment samples were collected from each of the 18 sampling sites every four weeks from September to December 2008 and again in February and March 2009. Water temperature, pH, and electrical conductivity (EC) were measured in-situ at the time of sampling using a field meter. The total organic carbon (TOC) content of water samples was determined according to American Public Health Association (APHA) method 5301B (APHA, 2005). Sediment samples were analysed for organic carbon (OC) using the Walkley and Black method (Rayment and Lyons, 2011, Method 6A1). The range and the mean of these water quality parameters for each of the monitoring sites was as follows: temperature (15.5 – 18.6^{o}C; mean 16.8 ^{o}C); pH (6.2 – 7.4; mean 6.7); EC (81 – 741 S; mean 300 S); TOC water (4.6 – 20 mg/L; mean 8.0 mg/L); sediment OC (2.0 – 7.3 %; mean 3.8 %). For full details of spot water and sediment sampling methods, readers are directed to the Supplementary Information.

2.3 Passive water sampling

Two types of passive sampler were used in this study, namely trimethyl pentane passive samplers (TRIMPs), a type of SPMD to target non-polar chemicals with log Kow > ~3.5, and the Chemcatcher™ passive sampler system (CC) fitted with an Empore™ SDB-XC disk (3M, MN, USA) as the receiving phase and a polyethersulfone (PES) membrane as the diffusion-limiting membrane, to target polar chemicals with log Kow < ~3.0. The two types of sampler were deployed for time-integrated monitoring to allow firstly a qualitative assessment (i.e. presence/absence) and then, where possible, a semi-quantitative assessment (i.e. based on estimated time-weighted average water concentrations) of herbicides in the catchment. For full details of the passive sampling methods, readers are directed to the Supplementary Information.

2.4 Analytical Testing Methods: Pesticides

Analysis included 10 different herbicides and selected associated degradates registered for use in Victoria (Table 1) from the following classes: benzamide, dinitroaniline, triazine/triazinone, and urea herbicides. No one analytical method is appropriate for the measurement of all of the herbicides investigated in this study. Several different methods based on solid-phase extraction (SPE) were used to prepare the different sample matrices and chemicals (see Supplementary Information). These SPE methodologies were validated and accredited by the National Association of Testing Authorities, Australia (NATA) to ISO 17025 standard. The final extracts from the SPE clean-ups were used in several different analysis programs: volatile nitrogen containing herbicides concentrations were measured using gas chromatography-nitrogen phosphorus detector (GC-NPD), triazines with liquid chromatography-tandem mass spectrometry (LC-MS/MS), and a range of other polar herbicides using a multi-residue LC-MS/MS screen (see Supplementary Information for details of extraction methods and instrument parameters, and the herbicides determined with each program). The results were not corrected for recovery, which was determined by spiking randomly selected samples of each analytical batch of water and sediment samples (typically the 24 sites) with each reported herbicide.

3. Results and Discussion

3.1 Herbicides in water, passive sampler, and sediment samples

Out of the 10 herbicides included in the analytical screens, 7 were detected in one or more water, passive sampler (TRIMPs or CC) and/or sediment samples (Table 2). Herbicides were not detected in any samples collected from the reference sites, but were detected in 39% of water samples (8 herbicides), 25% of the sediment samples (4 chemicals), 2% of the TRIMP solvents (2 chemicals), and 73% of CC disk eluates (3 chemicals) from the remaining sites. Simazine was the most frequently detected herbicide in water (47% samples), sediment (18% samples) and CC (73% samples). All other detected herbicides were present in no more than 10% and generally less than 5% of samples. Simazine was also found to have the highest concentrations in the water samples (0.67 g/L), with the majority of concentrations of the other herbicides detected in the water samples < 0.1 g/L. Simazine was also detected at relatively high concentrations in the sediment samples (up to 260 g/kg), and a high concentration of propyzamide was also observed on one occasion (180 g/kg).

Experimentally determined sampling rates for the herbicides detected in the TRIMPs are currently not available to derive time-weighted average water concentrations (TWAWCs). However, it was possible to estimate such TWAWCs based on predicted sampling rates (i.e. based on log K_{ow} values). These estimates provide semi-quantitative data for which to compare to the concentrations detected in water samples. In that context, the results for the TRIMPs do not agree with those of the water samples in that the TRIMP-derived TWAWCs of terbutryn were higher than those of pendimethalin, whereas measured pendimethalin water concentrations were much higher than the single observation of terbutryn (Table 2).

Sampling rates for the herbicides in the CCs were determined experimentally in a flow through system using a mixed dose of triazines at 1 g/L (see Supplementary Information). The sampling rates (Rs) were: atrazine, 12.0; cyanazine 14.8; metribuzin 6.8; prometryn 10.6; simazine 8.3 and terbutryn 10.1 mL/day. It is natural to wonder how the sampling rates derived experimentally in this study compare with published information. There appears to be some variability (factor of 10) in reported Rs depending on calibration conditions, including whether the receiving phases, i.e. the disk, are used ‘naked’ or with rate limiting membranes, length of exposure and the temperature and flow of the water in the calibration system. For instance, the sampling rates reported by Shaw et al (2009) for atrazine and simazine of 140 ml/day are an order of magnitude higher than those observed in this study, perhaps due to their use of a different disk (Empore SDB-RPS with a PES membrane). Vermeirssen et al. (2009) also reported sampling rates for a range of agrochemicals that were higher than observed in this study. In that case, including atrazine (Rs, 120 ml/day), DEA (Rs, 100 ml/day), and terbutryn (Rs, 110 ml/day) on Empore SDB-RPS disks plus PES membrane. As noted by Gunold et al. (2008) the SDB-RPS phase contains more sulphonic acid functional groups than the SCB-XC disk that may improve mass transfer compared to the SCB-XC disk. This in turn may explain the higher sampling rates. However, high sampling rates may result in a shorter linear uptake phase of the sampler. Thus the advantage of employing an Empore SDB-XC disk would be a longer exposure period until equilibrium is reached. Obviously, the best comparison is between sampling rates generated by groups using similar set ups. In that context, we can say that the sampling rates generated for the triazine herbicides for this study (Rs, 8-15 ml/day) are similar to those reported by Tran et al. (2007) who suggest that the uptake of five non-ionized polar herbicides (including simazine and atrazine) onto an Empore SDB-XC disk plus PES membrane, in a laboratory continuous-flow system was linear over a 21 day period, with Rs between 21 - 26 ml/day. Of the chemicals for which experimental sampling rates were generated, only atrazine and simazine were observed on the CC disks in this study. The TWAWCs generated using those experimentally determined sampling rates are about five times higher than those observed in water samples (Table 2), and, although the maximum estimated concentrations were an order of magnitude higher than observed in water samples, overall the TWAWCs broadly agree with those of the water samples in that the simazine and TWAWCs were much higher than those of atrazine (Table 2). Hexazinone was not included in the calibration experiment, so the average sampling rates for these triazine/triazone compounds was used to generate TWAWCs in agreement with those of the water samples (in that the hexazinone concentrations were lower than those of atrazine; Table 2).

The sampling rates of chemicals into passive samplers are dependent on a range of factors, both intrinsic to the passive samplers themselves, and extrinsic factors (Leonard et al 2002). Intrinsic factors that may affect uptake include the polarity of the contaminant (as measured by its log Kow), the diffusivity of the molecules that have to pass through the aqueous boundary layer, sampler design, exposure time, and concentrations of chemicals in the surrounding water. In the laboratory, a passive sampler is immersed in water spiked with the molecules of interest. The exposure media is typically controlled (temperature, agitation, contaminant concentrations, and physico-chemical parameters). All of these factors may change in the field, and one way to overcome some of the perceived issues with laboratory-derived uptake factors is to use field-derived sampling rates. By averaging the field spot water detections of simazine at deployment and retrieval across the monthly deployments, and using the relationship between the concentration of a chemical in the receiving phase and in the related waterbody after an exposure time during this linear sampling phase (see Supplementary Information for relevant equations), a field sampling rate was determined for each month of the survey (Table 3). Only simazine was observed in water samples sufficiently often to make this process appropriate, and although the field Rs contains significant variation, the mean sampling rate for simazine in field samples ranged from 43 to 63 mL per day, or a factor of five higher than the experimentally determined CC sampling rate. This is consistent with Ibrahim et al. (2013), who observed a four-fold difference between field- and laboratory-derived sampling rates derived for atrazine and simazine for the POCIS passive sampler system. The TWAWC for simazine (0.08 g/L) generated using the average field sampling rate (55 mL/day) was much closer to the actual mean simazine concentration (0.12 g/L; Table 2). This implies that elevated transient pulses of herbicides missed by the infrequent spot water samples may have been contributing to material sorbed onto the CC disks, producing the high TWAWCs from experimentally determined sampling rates, a possibility that has been previously reported for endosulfan in irrigation water (Rose and Kibria 2007).

Fewer herbicides were expected to be detected in sediments and TRIMPs than water and CC as the sediments and TRIMPs are suited to monitoring for non-polar chemicals (i.e. log $K_{ow} > 3.5$) and most of the herbicides included in this study have log $K_{ow} < 3.5$. Also, the limits of reporting in sediment samples are in the order of 100 times higher in sediment compared to water for most analytes. Interestingly however, around half of the herbicides that were detected in sediments were relatively non-polar (log $K_{ow} < 3.5$) (Table 2) indicating that this matrix is able to capture a wide range of chemicals. That said, the more polar herbicides detected were less prevalent in sediments and TRIMPs compared with water samples and CCs (Table 2), consistent with the theory that chemical accumulation in sediments and TRIMPs is based on log K_{ow} / log K_{oc} characteristics.

The preponderance of simazine detections across the study make it difficult to assess temporal changes in herbicide residue detections but overall the frequency at which the herbicides were detected in the waterways by both spot water and passive sampling was lowest in February and March 2008, and greatest in October to December 2009 (Table 4). An increase in the presence of herbicides in the Victorian Spring (October to December) was expected as this reflects the most intensive period of domestic, commercial and horticultural applications. Otherwise, there were no clear temporal trends in the concentrations of the herbicides detected in water, passive sampler or sediment samples.

This study was designed to provide an initial broad screening level investigation of herbicides in the study catchment. That simazine was detected in such a high proportion of the collected samples is a clear indication that simazine applied in the study catchment are migrating off-site. This is not to say farmers are using this chemical inappropriately, rather the results from this study suggest that the regular application of simazine can result in loading of these compounds in catchments where herbicides are a significant agricultural input. We did not target specific rain events or spray applications so it is not possible to elucidate whether or not the simazine and the other herbicides were entering the waterways diffusively or via episodic pulse events or to identify point sources of contamination. However, that the estimated TWAWCs of herbicides in CCs tended to be higher than in the spot water samples perhaps suggests that the CCs sampling may have integrated high pulse exposure concentrations of herbicides.

Our results are consistent with other Victorian data, albeit that until recently, there has again been very little monitoring of pesticides in receiving waters, e.g. rivers, streams, lakes, wetlands, in Victoria. For instance, as discussed in Radcliffe (2002), Chapman and Stranger (1993, 1994) observed atrazine, and metribuzin in surface water samples from sites within vegetable production areas of Gippsland between 1992 and 1994 but only at concentrations (3.2 and 0.28 g/L, respectively) below relevant ANZECC and ARMCANZ (2000) water quality guideline trigger values. The Gippsland studies did however highlight the potential for low level contamination of surface streams located in close proximity to areas of horticultural production, i.e. as in this study. Elsewhere in Australia, much of the focus of published studies of herbicide residues has been on chemicals in rivers draining the eastern seaboard of Queensland and with potential to impact on the Great Barrier Reef (Table 5). For instance, Lewis et al. (2009) found a range of triazine/triazone herbicides in the Tully-Murray, Burdekin-Townsville, and Mackay Whitsunday regions (atrazine up to 7.8 g/L; hexazinone, up to 5 g/L; and simazine, up to 0.18 g/L).

Our data is also consistent with levels reported internationally in the past 5 years. There have been a significant number of studies of herbicides in surface waters since the inception of this study, many of which have reported positive detects of one or more of the ten herbicides observed in the Yarra River and its tributaries (Table 5). While specific chemical targets reflect local land-use concerns and/or the research interests and technical capabilities of researchers, the most commonly reported herbicides are atrazine and simazine. Interestingly, in Europe, atrazine and simazine continue to be observed in water samples at concentrations similar to those observed in this study, despite the ban on their use in many countries (e.g. see Meyer et al. 2011; Silva et al. 2011; Thomatou et al. 2013; Table 5). There has been much less attention paid recently to levels of herbicides in sediment, despite the potential effects they may have on benthic primary producers. Although it is often assumed that polar chemicals such as the triazines are mainly found in the dissolved phase, chemical sorption to sediments is influenced by the type and amount of organic carbon and the clay content of sediments which may combine to increase the capacity of sediments to act as reservoirs for some chemicals. This, in part, may explain the wide variation in contaminant concentrations reported internationally in sediments for the ten herbicides screened in this study (Table 6). Sediment sampling methodology is another factor affecting reported concentrations, e.g. whether the whole sediment is extracted, or, as in this study, only the 64 m fraction, but despite this, our data is broadly consistent with the concentrations of herbicides reported internationally in sediments in the past 5 years (Table 6), where, again, the most commonly reported herbicides are atrazine and simazine.

Passive sampling has some advantages over grab water sampling in that the samplers need little attention apart from deployment and collection, and they also integrate and average exposures over time, thus enabling identification of events that may be missed by grab sampling. The major disadvantage of these methods is that the concentration data from the sampler may not be directly comparable to toxicity data based on water concentrations, and water concentrations may have to be extrapolated through the use of field or laboratory derived sampling rates, few of which are available (Gagnon et al., 2007). In addition, some chemicals may be missed, as may not readily partition into the sampler. From a practical perspective, in natural waterways samplers may be subject to periodic high-energy flows, which can wash away the samplers, and be the subject of human inquisitiveness, which may see the samplers removed from the waterway; both these externalities can reduce the integrity of a sampling program and both were experienced in this study. However, our data is also consistent with the concentrations of herbicides reported internationally using passive samplers in the past 5 years (Table 7); again the most commonly reported herbicides are atrazine and simazine.

Many studies investigating pesticides in surface waters where mixtures of chemicals are commonly detected at sampling sites (e.g. see Gillom et al. 2006; Gregoire et al. 2010), but in this study there were few instances of multiple herbicides in water samples, with three different herbicides the most detected at a single site. A similar trend was found in relation to the sediment samples, where only two samples contained residues of two different herbicides. The lack of multiple herbicide detections in the waterways was somewhat unexpected as different herbicidal compounds are likely to have been applied to control the different weed problems in the variety of crops present in the study catchment (Table 1). Indeed, Wightwick et al. (2012) reported that multiple fungicides were detected in Yarra Valley water sample (e.g. 31 % of the water samples contained residues of two or more fungicides, and 17 % containing residues of three or more fungicides). Whilst a relatively high number of common herbicides were included in this study it is recognised that there are many more herbicides registered for use in Victoria that were not included in the analytical screens, and that some of these chemicals are very commonly used in Victoria (such as glyphosate, paraquat and diquat, and some of the phenoxy acid and sulfonyl urea herbicides). Unfortunately, resource limitations prevented measurement of those chemical groups. Moreover, information on the type and quantities of herbicides being applied by the farmers was not available as it was outside the scope of this study to survey chemical use practices in this large catchment area. So it is not known how well the herbicides analysed corresponded with those being used in the catchment, and the lack of multiple residues detections may simply reflect the screening of a sub-set of the herbicides being used in the upper Yarra Valley.

3.2 Ecotoxicological risks of herbicides detected

Ecological risks of chemicals detected in the environment are often derived by comparisons with environmental quality values and reported ecotoxicological effects values for key sentinel aquatic species, and in Australia these are collated in the ANZECC and ARMCANZ (2000) water quality guidelines. In that context, only atrazine and simazine are in water quality guidelines, and no trigger values have been defined for any of the studied herbicides in sediments (ANZECC and ARMCANZ 2000). Because there are few formally recognised water quality guideline values available with which to compare data from this study, data on the ecotoxicological effects of herbicides has been taken from the IUPAC Pesticides Properties Database (University of Hertfordshire 2013; as summarised in Table 8). The ecological risk of pesticides is preferably quantified based on probabilistic methods using cumulative frequency distributions for effect and exposure concentrations. However, in the case of this study it was not necessary to go these lengths because the concentrations in water and sediment (exposure concentrations) were clearly lower than the most sensitive chronic ecotoxicological effect value for each of the herbicides (Table 8). Indeed, the concentrations detected in the waterways of this study were generally several orders of magnitude lower than ecotoxicological effect values and the few ANZECC and ARMCANZ (2000) trigger values.

Although few of the water samples in this study contained mixtures of herbicides, the presence of multiple pesticides in surface water is common in monitoring programs (Gillom et al., 2006; Gregoire et al., 2010). These mixtures of different chemicals have the potential for additive, synergistic or antagonistic effects on toxicity (ANZECC and ARMCANZ 2000). There is an increasing acknowledgement that toxic effects can occur at much lower concentrations where chemicals are present as mixtures (Baas et al., 2009). For example, a recent study has reported that the pyrethroid insecticide -cypermethrin was up to 12 times more toxic to *Daphnia magna* in the presence of the fungicides prochloraz, epoxiconazole and propiconazole (Nørgaard and Cedergreen, 2010). In this study most of the herbicides were photosystem II (PSII) inhibitors, and having the same mode of action, the mixtures of PSII herbicides are likely to have additive effects on algae and aquatic plants; however it is unclear what effect mixtures of herbicides with different modes of action will have on toxicity.

The study has shown the presence of residues of herbicidal compounds in the surface waters of a horticultural production catchment. Moreover, this study was conducted in a relatively dry season where total rainfall was approximately 40% lower than the long term mean in the catchment during the study period (BOM, 2010). Thus the risks may be greater in wetter seasons, as greater quantities of herbicides are likely to be applied and the frequency and extent of surface run-off events increased. Based on frequency of detection and concentrations, simazine is the priority herbicide of concern for the catchment studied, although we acknowledge that some commonly used herbicides (such as glyphosate, 2,4-D and MCPA) were not screened in this study. The detection of residues at so many of the surface water sites, and across sampling periods, indicates that the risks posed by this herbicide are more likely to be long-term (chronic) rather than short-term (acute). However, the concentrations detected were relatively low and mostly several orders of magnitude below reported ecotoxicological effect and hazardous concentration values (although there are some suggestions that herbicides may cause acute risks due to high pulse exposure concentrations and this should be examined in future studies). Whilst the findings from this study indicate that individually herbicides are likely to pose a low ecological risk, the toxicity of individual herbicides and herbicidal mixtures represents a significant research gap. This study provides valuable information for policy and decision-makers, both in Australia and other regions of the world, to assess the likely risks that the use of herbicidal compounds in horticultural production systems poses to aquatic ecosystems. To progress towards a more thorough assessment of the ecological risks posed, future research should focus on gaining a better understanding of the ecotoxicological effects of priority herbicides and herbicidal mixtures, particularly to the lower trophic levels of aquatic ecosystems.

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Tables

Table 1 Summary of partitioning properties of the herbicides investigated and their registered use in Victoria

Active	**Chemical Group**	**Log K_{ow}** [a]	**Log K_{oc}** [b]	**Half-life water (days)** [c]	**Number registered products** [d]	**Registered use** [d]
atrazine	triazine	2.7	2.0	86	73	Legumes (lupins), roots and tubers (potatoes), cereal grains (maize, sorghum, wheat), oilseeds (canola), pasture (grass pasture, lucerne), control of sedges and woody weeds in forestry
cyanazine	triazine	2.1	2.3	s	7	Bulb vegetables (onion), legumes (bean, chickpeas, field pea), roots and tubers (potatoes)
hexazinone	triazinone	1.2	1.7	56	27	Control of sedges and woody weeds in forestry, spot killing of weeds in pasture, commercial and industrial
linuron	urea	3.0	2.9	1460	5	Bulb vegetables (onion), cereal grains (barley, maize, oats, soybean, wheat), roots and tubers (potatoes, carrots, parsnips), coriander
metribuzin	triazinone	1.7	1.8	s	40	Asparagus, barley, chickpeas, faba beans, lentils, lupins, oats, pea, potatoes, soybeans, tomatoes, vetch, wheat
pendimethalin	dinitroaniline	5.2	4.2	s	32	Sunflowers, barley wheat, peas, chickpeas, faba beans, lupins and safflower, canola, carrots, avocadoes, bananas, citrus, deciduous fruits, grapevines, lychees, macadamia nut, mangoes, nuts, Eucalypt forestry plantation, turf
prometryn	triazine	3.3	2.6	s	14	Carrots, celery, pastures, perennial grass seed crops, potatoes
propyzamide	benzamide	3.3	2.9	s	46	Turf, lettuce, pasture (lucerne, clover), legume seed crops,
simazine	triazine	2.3	2.1	96	93	Algae (in swimming pools, ponds and aquaria), canola, fab beans, commercial and industrial, asparagus, berry fruits, citrus, gladioli, hops, roses, chickpeas, strawberry, lucerne pastures, lupins, apples and pears, vines, forestry
terbutryn	triazine	3.7	3.4	s	17	Barley, pastures, some varieties of oats and field peas, triticale, wheat

[a], log K_{ow}, logarithm of octanol-water partitioning co-efficient; [b], log K_{oc}, logarithm of organic carbon adsorption coefficient [c], data from Wightwick and Allinson (2008b), updated using University of Hertfordshire (2010); [d], products registered for use in Victoria, Australia, data from APVMA website; [e], includes cantaloupe, cucumber, honeydew and muskmelon, pumpkin, squash, rockmelon, watermelon; [f], includes chrysanthemums, geraniums, iris and other ornamental flowers; [g], brassica vegetables, includes broccoli, Brussels sprouts, cabbages, cauliflowers;, s, stable to hydrolytic degradation in water (University of Hertfordshire 2013); DEA, desethyl atrazine; DIA, desisopropyl atrazine

Table 2 The frequency of detection and concentrations of herbicides detected in water, sediment samples and passive sampler extracts

Active	Water (n = 106)					Sediment (n = 106)					TRIMPs (n = 127)[c]					CC (n = 89)[d]				
	FOD[a]	Mean[b]	Med	Min	Max	FOD[a]	Mean	Med	Min	Max	FOD[a]	Mean	Med	Min	Max	FOD[a]	Mean	Med	Min	Max
	(g/L)					(g/kg dry weight)					(g/L)					(L)				
atrazine	6	0.01	0.01	0.01	0.02	1	2				0					4	0.07	0.05	0.04	0.13
cyanazine	0					0					0					0				
hexazinone	1	0.01				0					0					10	0.03	0.03	0.02	0.05
linuron	1	0.003				1	3.5	3.5	2	5	0					nm				
metribuzin	0					0					0					0				
pendimethalin	5	0.03	0.02	0.01	0.04	0					1	0.002				nm				
prometryn	0					0					0					0				
propyzamide	0					1	180				0					nm				
simazine	47	0.12	0.05	0.01	0.67	18	19	4	2	260	0					73	0.52	0.20	0.03	3.20
terbutryn	1	0.001				0					2	0.005	0.005	0.005	0.005	0				
DEA	1	0.001				0					0					0				
DIA	1	1.3				0					0					0				
HA	0					0					0					0				

n, number of samples analysed; [a] FOD, frequency of detection (%) = (number of samples in which chemical detected / total number of samples analysed) x 100; [b], mean and other reported data is for detects only; [c], except for propyzamide, where n = 98; nm, not measured; [d], concentration data derived using laboratory generated uptake factors.

Table 3 Field determined sampling rates for simazine

	Field sampling rate			
	Oct-08	**Nov-08**	**Dec-08**	**Mar-09**
	(mL/day)			
mean	63	70	45	43
CV%	88	123	65	76
count [a]	10	8	9	4

[a] count, number of sites simazine detected in water samples at both deployment and retrieval of CC

Table 4 Temporal trends in the frequency in which three most commonly observed herbicides were detected in water samples

Active	**Frequency of Detection (%) [a]**					
	2008				**2009**	
	September	**October**	**November**	**December**	**February**	**March**
atrazine	0	0	0	6	17	0
pendimethalin	0	17	6	4	0	31
simazine	56	33	50	50	17	13

[a] FOD (%): (number of samples chemical detected / total number of samples collected) x 100

Table 5 Selected recent studies in Australia (post-1990) and overseas (post-2009) in which residues of one or more of the herbicides examined in this study have been reported in surface waters (freshwater wetlands, creeks, rivers and lakes).

Country	**Region**	**Herbicides concentration (max; g/L)**										**Reference**
		ATR	**CYN**	**HEX**	**LIN**	**MZN**	**PEN**	**PRM**	**PRO**	**SIM**	**TER**	
	Australia											
Victoria	**Yarra valley**	**0.02**		**0.01**	**0.003**		**0.04**			**0.67**	**0.001**	**This study**
	Gippsland	0.92										Chapman and Stranger (1993)
		3.2				0.28				0.61		Chapman and Stranger (1994)
New South Wales	South-west	4.4										Bowmer et al. (1998)
	Mcintyre, Namoi, Gwydir R	4.0					0.2	4.0		0.3		Muschal and Warne (2003)
Queensland	Mackay region	0.047		0.261						0.016		Duke et al. (2005)
	Hervey Bay basin	0.110								0.050		McMahon et al. (2005)
	Mackay Whitsunday	4.1		1.0								Mitchell et al. (2005)
	Brisbane R	0.009		0.002						0.043		Bengston Nash et al. (2006)
		1.0		3.6								Bainbridge et al. (2009)
	eastern	7.8		5.0						0.18		Lewis et al. (2009) *
Tasmania		53000	5.2	478		1.3			3.3			Davies et al. (1994)
	International											
Argentina		0.434										Bonansea et al. (2013)
Brazil	Santa Catarina						0.38					Freitas et al. (2012)
Canada	Québec	0.053	0.004							0.022		Garcia-Ac et al. (2009)
	British Columbia	0.053		0.017	1.050	0.002				0.896		Woudneh et al. (2009)
	Great Lakes	0.061										Kurt-Karakus et al. (2010)
	Ontario	3.91										Byer et al. (2011)
	Ontario	0.037			0.004	0.023	0.008					Kurt-Karakus et al. (2011)
	Maritime region				0.028	0.11						Xing et al. (2013)
China	Heilongjiang	0.4								0.1		Yu et al. (2010)

Table 5 (cont$^{\underline{d}}$)

Country	**Region**	**Herbicides concentration (max; g/L)**										**Reference**
		ATR	**CYN**	**HEX**	**LIN**	**MZN**	**PEN**	**PRM**	**PRO**	**SIM**	**TER**	
France	Midi-Pyrénées				0.9		0.2					Taghavi et al. (2010) *
	Save R, Gascogne	0.08	0.02	0.03	0.04		0.01			0.02		Polard et al. (2011)
	Gascogne				1.65							Taghavi et al. (2011)
	Rhone R, Gard	0.014								0.004		Ibrahim et al. (2013 *
Germany	R Leine, Göttingen	0.003										Nödler et al. (2010)
Greece	Evros R basin	0.6						0.05		0.6		Vryzas et al. (2009) *
	Lake Amvrakia	0.328					0.020	0.094		0.056		Thomatou et al. (2013)
Luxembourg		0.118			0.020					0.038		Meyer et al. (2011)
Kenya	River Kuywa	0.15		0.65								Muendo et al. (2011)
Japan	Kose R, Fukuoka									0.03		Phong et al. (2010)
Lebanon							0.010					Kouzayha et al. (2013)
Portugal	Alentejo									0.82		Silva et al. (2011)
Spain	Ebro R	0.039			0.015					0.667		Köck et al. (2010)
	Catalonia	0.017								0.013	0.054	Matamoros et al. (2010)
	Llobregat R, Barcelona	0.0001			0.327					0.0054		Ricart et al. (2010)
	Llobregat R, Catalonia	0.002								0.005		ck-Schulmeyer et al. (2011)
	Llobregat R, Catalonia	0.010	0.009							0.038		ck-Schulmeyer et al. (2012)
	Guadalquivir R basin	0.022								0.405	0.049	- . (2013)
	Guadalquivir R basin	2.1								6.7		Hermosin et al. (2013)
Thailand	Mae Sa R basin	0.4										Sangchan et al. (2012)

Table 5 (cont^{d})

Country	**Region**	**Herbicides concentration (max; g/L)**										**Reference**
		ATR	**CYN**	**HEX**	**LIN**	**MZN**	**PEN**	**PRM**	**PRO**	**SIM**	**TER**	
USA	IA, DC, MD, WY	26.2										Battaglin et al. (2009)
	California									0.004		Lavado et al. (2009)
	Cedar Ck, Indiana	90								30		Smiley et al. (2009)
	Choptank R	1.8								1.9		Whitall et al. (2010) *
	South Florida	12		1.3		0.071				7.3		Pfeuffer (2011)
	Nebraska	191										Vogel and Linard (2011)
	Texas						11.3					Anderson et al. (2013)
	California						1.02			0.10		Ensminger et al. (2013)
	upper Potomac R basin	0.071								0.053		Kolpin et al. (2013)

ATR, atrazine; CYN, cyanazine; HEX, hexazinone, LIN, linuron, MZN, metribuzin; PEN, pendimethalin; PRM, prometryn, PRO, propyzamide, SIM, simazine; TER, terbutryn; *, estimated from author figures; ‘up to’, used when method determination limit not definable because not clearly reported in paper; ^{I}nformation obtained by searching the Scopus database using the search terms “herbicide AND river OR lake” in article title, keywords or abstract; only positive detections of one or more of the herbicides screened for in this study in the citations reported, non-detects and other herbicides in the listed citations, and studies where no herbicides were examined/detected are not reported.

Table 6 Selected recent studies in Australia (post-1990) and overseas (post-2009) in which residues of one or more of the herbicides examined in this study have been reported in sediment (freshwater wetlands, creeks, lakes, rivers and estuaries).

Country	**Region**	**Herbicides concentration (max; g/kg)**										**Reference**
		ATR	**CYN**	**HEX**	**LIN**	**MZN**	**PEN**	**PRM**	**PRO**	**SIM**	**TER**	
	Australia											
Victoria	**Yarra valley**	**2**			**5**				**180**	**260**		**This study**
Queensland	Mackay region	0.2										Duke et al. (2005)
	Mackay region	1.3		1.5			4.5			0.6		Magnussen et al. (2013) *
	International											
China	Songhua River basin	42										Sun et al. (2013) *
France	s.w France		2651		73					201		Devault et al. (2009a)
	s.w. France	850	3620		3630					640		Devault et al. (2009b)
India	Delhi						53					Kumar et al. (2011)
Kenya		740		390								Muendo et al. (2011)
Spain	Llobregat R, Barcelona	0.86								0.81		Ricart et al. (2010)
Thailand	Nan Province	230										Thitiphuree et al. (2013)
USA	San Joaquin R, CA						3000					Hladik et al. (2009)
	Coldwater R, MS	921	6.3									Knight et al. (2009)
	Beasely Lake, MS	227	23.7				1.2					Lizzotte et al. (2010)
	South Florida	50										Pfeuffer (2011)
	Texas	37					900					Belden et al. (2012)

ATR, atrazine; CYN, cyanazine; HEX, hexazinone, LIN, linuron, MZN, metribuzin; PEN, pendimethalin; PRM, prometryn, PRO, propyzamide, SIM, simazine; TER, terbutryn; *, estimated from author figures/tabulated data; 'up to', used when method determination limit not definable because not clearly reported in paper; information obtained by searching the Scopus database using the search terms "herbicide AND sediment AND river OR lake" in article title, keywords or abstract; only positive detections in the citations reported, non-detects in the listed citations and studies where no herbicides were examined/detected are not reported.

Table 7 Selected recent peer-reviewed studies in Australia (post-2005) and overseas (post-2009) that have used passive samplers for the detection of one or more of the herbicides examined in this study in surface waters (freshwater wetlands, creeks, rivers, lakes and estuaries).

Country	**Region**	**Type of sampler**	**Reporting mode**	**Herbicide Concentrations (max; g/L or ng)**										**Reference**
				ATR	**CYN**	**HEX**	**LIN**	**MZN**	**PEN**	**PRM**	**PRO**	**SIM**	**TER**	
	Australia													
Victoria	**Yarra Valley**	**CC**	**TWAWC**	**0.13**		**0.05**						**3.2**		**This study**
	Yarra Valley	**SPMD**	**TWAWC**						**0.002**				**0.005**	**This study**
Queensland	Wet Tropics region	CC	TWAWC *	0.0003		0.00045						0.0025		Shaw et al. (2005)
	Noosa National Park	CC	TWAWC									0.015		Escher et al. (2006)
	Russell-Mulgrave R	CC	TWAWC *	0.035		0.004								Shaw et al. (2009)
	Moreton Bay	CC	ng/sampler	14								41		Stephens et al. (2009)
	Wet Tropics region	CC	TWAWC *	0.045		0.04								Shaw et al. (2010)
	South-east Qld	CC	TWAWC	0.03										O'Brien et al (2011)
New South Wales	Murrumbidgee Irrigation Area	SPMD	TWAWC *	0.1										Hyne and Aistrope (2008)
	International													
France	Ruiné and Charente R, west France	POCIS	TWAWC *	0.02								0.02		Mazzella et al (2010)
	Ruiné R, west France	POCIS	TWAWC *	0.012			0.005					0.042		Lissalde et al (2011)
	Ruiné R, west France	POCIS	TWAWC *	0.04								0.085		Pesce et al (2011)
	Rhone R, Gard	POCIS	TWAWC *	0.008								0.005		Ibrahim et al. (2013)

Table 7 (contd)

Country	Region	Type of sampler	Reporting mode	Herbicide Concentrations (max; g/L or ng)										Reference
				ATR	CYN	HEX	LIN	MZN	PEN	PRM	PRO	SIM	TER	
Spain	south east	POCIS	TWAWC	0.0015								0.0009	0.0001	Martínez Bueno et al (2009)
UK	Portsmouth Harbour	CC	ng/sampler	6.0										El-Shenawy et al (2010)
	River Thames estuary	PTF	TWAWC *	0.065				0.11	0.00004					St. George et al (2011)
	n.e. Scotland	SRS	ng/g sampler	2.7	1.5				25	1.6		2.4	6.4	Emelogu et al. (2013)
USA	Nebraska	POCIS	TWAWC *	0.98										Bartelt-Hunt et al (2011)

ATR, atrazine; CYN, cyanazine; HEX, hexazinone, LIN, linuron, MZN, metribuzin; PEN, pendimethalin; PRM, prometryn, PRO, propyzamide, SIM, simazine; TER, terbutryn; CC, Chemcatcher passive sampler system; POCIS, polar organic chemical integrative samplers; SPMD, semi-permeable membrane device; PTF, polymer thin film device; SRS, silicone rubber samplers; TWAWC, time weighted average concentrations obtained from passive samplers (g/L); N.D., not detected; *, estimated from author figures; Information obtained by searching the Scopus database using the search terms “passive sampler AND herbicide” in article title, keywords or abstract; only positive detections in the citations reported; non-detects in the listed citations and studies where no herbicides were examined/detected are not reported.

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Table 8 Summary of ecotoxicological effect data for the herbicides detected

Active	Mode of toxic action	Ecotoxicological effect value [a]				Maximum concentration in this study
		Fish	Aquatic invertebrates	Aquatic plants	Algae	
				(g/L)		
atrazine	PS II inhibitor	2000	250	19	100	0.02
hexazinone	PSII inhibitor	-	50000	72		0.005
linuron	PSII inhibitor	100	180	17	10	0.003
pendimethalin	Inhibits mitosis / cell division	6	15	12		0.04
simazine	PSII inhibitor	700	2500	300	600	0.67
terbutryn	PSII inhibitor	-	-	-	-	0.001

[a] Data from IUPAC Pesticide Properties Database (University of Hertfordshire 2013). Fish and aquatic invertebrates, 21 day NOEC; aquatic plants, 7 day EC$_{50}$ (biomass); algae, 96 hour NOEC (growth).

Figures

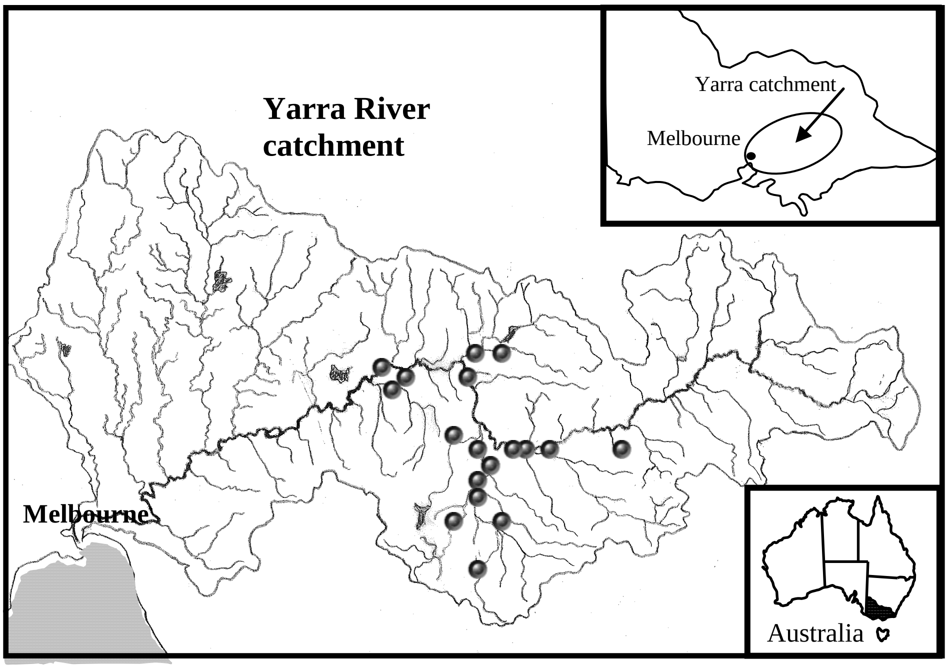

Figure 1 Approximate locations of the 18 monitoring sites (indicated by the circles) in the Yarra River catchment, Victoria, Australia