

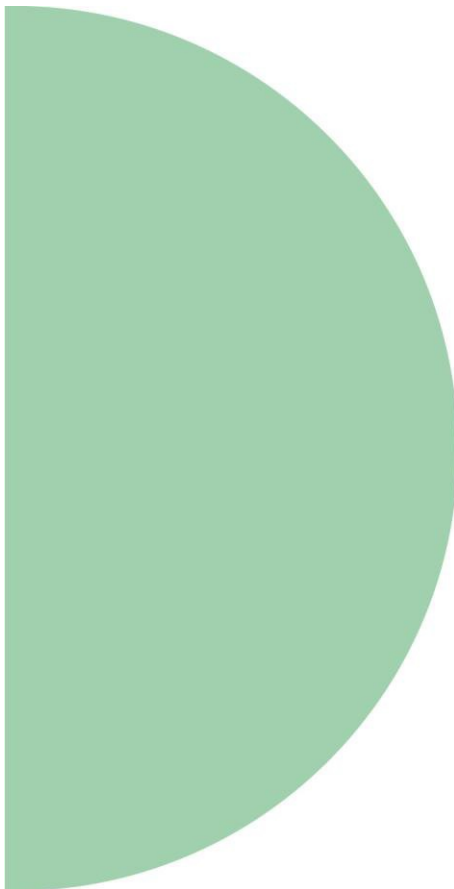
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A review of agrochemical uses and site monitoring to inform a water corporation's ambient water quality monitoring program

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Executive Summary

Pesticides are widely used to control pests that reduce agricultural productivity and cause damage to property. Following application, pesticides can be transported from the site of application to water bodies where they may cause adverse effects on the aquatic ecosystem and pose risks to human health. In instances of water use for potable and stock or irrigation, many of the currently available treatment processes do not adequately remove water-soluble pesticides, thus creating concern for water authorities and the public. Pesticides are often screened in surface water monitoring programs, especially in areas with intensive agricultural activities, to assess risks for the environment, recreation and for water re-use. One of the challenges in pesticide monitoring is the selection of the substances which are to be investigated, as a vast number of pesticides could potentially be present. Additionally, new pesticides are continuously being developed and used in agricultural and other activities. Therefore, regular reviews of new pesticides and their applications are needed to determine the pesticides likely to be present in surface waters of the monitoring area.

The Water Corporation is a regional water corporation that provide water service to over 160,000 residents and close to 7,000 businesses in Victoria. The water corporation also supplies rural water to some 1,300 farming and agricultural customers across its service region. Currently, the water corporation screens for 56 pesticides in their water monitoring program. However, approximately 50% of these are no longer permitted for use in Australia.

This report reviews the pesticides likely to be present in surface waters across the water corporation region and provides recommendations on the pesticides that should be included in the water corporation's ambient water quality monitoring program. Four criteria were applied to determine whether a pesticide was of priority for monitoring, including: solubility in water, likelihood of use in the region, potential threat posed to human health, and whether the pesticide has been identified in the international literature as a chemical of concern.

A total of 81 pesticides were identified and recommended for inclusion in water corporation's ambient water quality monitoring program. Among these, 72 are not included in the current monitoring program. The newly recommended pesticides are commonly used in the dominant agriculture activities across the region and have been detected in surface waters in Australia and worldwide. Its further recommended that the application of a continuous water sampling technique using passive samplers be incorporated into the water corporation's ambient water quality monitoring program. Passive samplers detect pesticides from intermittent pollution events at trace level concentrations that might be missed if relying on spot sampling methods only.

1 Introduction

Pesticides are chemicals used to kill or control pests. Pesticides play an important role in agriculture to protect crops and livestock from pest infestation and yield reductions. During and following application, pesticides can be transported offsite to water bodies through runoff, spray drift and atmospheric deposition and may cause adverse effects on the receiving aquatic ecosystem and human health. The fate of pesticides in the environment depends on their physicochemical properties and environmental conditions. The octanol/water partition coefficient (K_{ow}) is a measure of a compound's hydrophilicity/hydrophobicity and is commonly used to determine the fate of pesticides in aquatic environments (Cumming and R cker 2017; Jaff  1991). Pesticides with low log K_{ow} values (< 3), tend to be soluble in water and are described as hydrophilic chemicals, whereas those chemicals with high K_{ow} values (>3), are less soluble in water (hydrophobic) and tend to bind to organic matter (Solomon et al. 2008). Hydrophilic pesticides are difficult to remove from surface water during drinking water production and can be of concern for water management authorities and end users (Thuy et al. 2008).

Surface waters used for potable water supplies should be regularly monitored to identify any substances requiring removal during water treatment. In rural areas, pesticides would be of primary interest. Hundreds of pesticides are registered for use in Australia by the Australian Pesticides and Veterinary Pharmaceuticals Association (APVMA). New pesticides are continuously being developed and used in agricultural and other activities. Therefore, regular reviews of new and emerging pesticides are needed to ensure monitoring programs of raw water used for potable water supplies are assessing for pesticides most likely to be present. While it is not feasible to screen environmental samples for every single pesticide that may be present, a way to increase the feasibility of pesticide monitoring is to first determine what pesticides are most likely to be present based on surrounding land uses (Townsend and Pettigrove 2018).

Another challenge for monitoring programs is conducting a program that has the greatest chance of detecting pesticide presence in the environment. Most water quality monitoring programs collect a water sample every week or month. Only those contaminants present at that point in time when the water sample is collected will be detected. However, many other pesticides may be present at other times. For example, intermittent pollution can occur from spray drift and runoff during storm events. A single spot water sample may not be taken at the right point in time to capture this intermittent pollution. A more effective sampling method is to use passive samplers. These devices are deployed for several weeks or more in a waterbody, absorbing contaminants through a permeable membrane and storing them in a sorbent over the entire deployment period. This means that passive samplers can detect contaminants from intermittent pollution events.

This report reviews the pesticides likely to be present in surface waters across the water corporation's region and provides a list of pesticides recommended for consideration for inclusion in the water corporation's ambient water quality monitoring program. The criteria used to review which pesticides are to be recommended are:

1. solubility in water,
2. likelihood for use across the region,
3. potential threat posed to human health, and
4. identification in the international literature as chemicals of concern (COCs).

2 Method

The review was conducted in two parts: firstly, the pesticide active ingredients in registered products applied or used in the common commodities/activities that occur across the region were identified. Secondly, a review of scientific and grey literature on commonly detected pesticides in surface waters, together with a field survey of pesticides in surface waters at a site in the water corporation's region was undertaken. Based on the outcomes of these two stages a recommended list of pesticides for inclusion in routine monitoring was proposed.

2.1.1 Registered products identification

The identification of pesticide active ingredients used in registered pesticide products applied in the different commodities of the region was carried out using the Australian Pesticides and Veterinary Medicines Authority (APVMA) Public Chemical Registration Information System (PubCRIS) database (available at <https://portal.apvma.gov.au/pubcris>).

First product registration details for all pesticide products (herbicide/fungicide/insecticide) registered for use in Victoria was downloaded from the PubCRIS database. The downloaded data included information for each registered product (RP) including product name, active ingredients, host (applications the product was registered for use on) and pest targeted. A limitation of the PubCRIS database is that only the first 1000 results for each search are displayed downloadable. However, as results don't appear to be downloaded in any particular order (including alphabetically), it's assumed they provide a good representation of pesticide use across different commodities/activities.

The downloaded data was sorted by the main active ingredient in the RP. Log Kow values, for each active ingredient, were then obtained from the Pesticides Properties Database (PPD) (available at <https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>). If values were not attainable from the PPD, the log Kow were obtained from PubChem, a chemistry database (available at <https://pubchem.ncbi.nlm.nih.gov/>). The data was then sorted and refined to only include registered

products containing an active ingredient with a log Kow <3 (water-soluble pesticides) and that are registered for use in one of the commodities/activities occurring within the region.

The commodities/activities that occur within the region were determined based on the gross values (In Australian dollars) of agricultural commodities for the sub-state geographic area of Bendigo SA4 (Statistical Areas Level 4) downloaded from the Australian Bureau of Statistics (ABS) (available at <https://www.abs.gov.au/AUSSTATS/abs@.nsf/DetailsPage/7503.02016-17?OpenDocument>), hereafter referred to as ABS 2020. In addition to agricultural commodities defined in the ABS 2020 data, additional commodities/activities were added based on categories commonly found in the PubCRIS data. These included Urban/built up area activities (Ornamentals, Domestic/Residential, Commercial, Industrial/Processing, Public Area/Government Buildings, Green Spaces, Construction, Timber Treatment), Transport activities (Right of Way and Aviation/Shipping/Other Transport), Forestry/plantation, and Enclosed freshwaters (e.g., Swamps, Marshes, Ditches, Drains, Freshwater Lagoons, Water holding containers).

As no actual pesticide use data was available, the number of registered products for each pesticide was used as a surrogate measure to determine which pesticides were most commonly associated with an activity or a commodity. The pesticides with the most registered products for each dominant commodity and activity were added to the short-list of pesticides recommended to be monitored in the area.

2.1.2 Scientific and grey literature review

A review of scientific and grey literature reporting pesticide detections in surface waters of agricultural areas or identifying chemicals of concern was carried out to identify any pesticides likely to be present in surface water across the region that may not have been identified through the review of active ingredients in registered products. This review considered soluble pesticides with a small number of RP or some less soluble pesticides but identified as COCs or commonly reported in the literature to be present in agricultural areas. Relevant literature was identified through searches of “pesticides”, “surface water”, “water monitoring” and “agricultural areas” on Google.

Any additional pesticides identified were added to the recommended screen list.

2.1.3 Field survey

2.1.3.1 Surface water chemistry

Pesticides were assessed in surface waters using spot water samples and passive samplers. Two forms of passive samplers, Chemcatchers and Polar Organic Chemical Integrated Samplers (POCIS), were deployed for a period of 4 weeks at the Western Channel, on two occasions (November 2019 and March 2020). Spot water samples (500mL) were collected in amber glass bottles during the deployment of passive samplers. Spot water samples were analysed

immediately for 108 pesticides (see Appendix 1 for full screen details). Following retrieval, the POCIS were processed and analysed for over 20 pesticides (first round) by CSIRO (Adelaide) and 102 pesticides by NMI (Melbourne) (second round) (See Appendix 2 and 3 for full screen details). Chemcatchers were analysed for 201 pesticides by NMI (Melbourne) (first and second round) (See Appendix 4 for full screen details).

2.1.3.2 Sediment Chemistry

Sediment samples (<63µm fraction) were collected during the deployment of passive samples in November 2019 and March 2020 at the Western Channel site and analysed for 108 pesticides (see Appendix 1 for full screen details).

3 Results and Recommendations

3.1 Pesticides associated with common commodities in the water corporation Region

3.1.1 Major activities and commodities in the water corporation Region

The water corporation delivers drinking water, sewerage, trade waste and recycled water services to over 160,000 residents, 7,000 businesses, and 1,300 farming and agricultural customers across its service region (DELWP 2020). Agriculture is one of the major industries in the region (DELWP 2018) and is largely dominated by livestock and cropping, followed by hay, fruit, and vegetable production. The common commodities/activities and associated commodity values (derived from ABS 2020) across the region are shown in Table 1. Transport is also an important economic activity in the region (DELWP 2018), but the gross value of transport is not available.

Table 1. Common activities and commodities in the water corporation region based on commodity value.

Priority rank	Activity or commodity	Commodity value (\$) ^(a)
1	Livestock slaughtered and other disposals - sheep and lambs	142,735,528
2	Livestock slaughtered and other disposals - poultry	85,598,037
3	Livestock Products - wool	84,567,508
4	Livestock slaughtered and other disposals - pigs	74,551,733
5	Wheat	66,704,062
6	Barley	65,779,964
7	Cereal cut for hay	60,998,131
8	Livestock products - milk	50,669,608
9	Livestock slaughtered and other disposals - cattle and calves	39,674,013
10	Livestock slaughtered and other disposals - other	29,339,835
11	Canola	28,524,178
12	Oats	19,160,870
13	Livestock products - eggs	16,380,578
14	Other pasture cut for hay	11,891,576
15	Lucerne cut for hay	11,085,915
16	Pulses (chickpea, fava/broad bean, field pea, lentil, lupin, mung bean)	8,537,326
17	Apples	7,132,296
18	All other crops	5,775,511
19	Other crops cut for hay	5,087,960
20	Maize	2,629,377

21	Grapes	2,548,163
22	Tomatoes - Fresh market	1,465,595
23	Tomatoes - Processing	1,188,350
24	Cherries	895,223
25	Nurseries	854,655
26	All other nuts	513,089
27	Mushrooms	260,273
28	Cut flowers	77,936
29	All other vegetables	66,759
30	Pears	50,841
31	All other orchard fruit	6,005
32	Urban/built up area*	NA
33	Transport*	NA
34	Forestry/plantation *	NA
35	Enclosed freshwaters*	NA

^a Commodity values derived from ABS; (*) Gross value is not available, order was not ranked

3.1.2 Fungicides associated with common commodities in the water corporation region

There are 509 fungicide products registered for use in Victoria, of which all contain at least one of the 31 registered soluble fungicide active ingredients. The number of registered fungicide products associated with dominant commodities and activities in region are presented in Table 2. The most common fungicide active ingredients registered for use in dominant activities across the area are: imazalil, didecyl dimethyl ammonium chloride, flutriafol, azoxystrobin, prothioconazole, imidacloprid, iprodione, mancozeb, carbendazim, thiram, metalaxyl-M, captan, chlorothalonil, thiabendazole. These fungicides have different applications across several activities (Table 3) and would be included in the routine screen list.

Table 2. Fungicides associated with common commodities in the water corporation region

Priority rank	Activity or commodity	#registered products	Most common fungicides
1	Livestock slaughtered and other disposals - sheep and lambs	1	didecyl dimethyl ammonium chloride
2	Livestock slaughtered and other disposals - poultry	3	imazalil, didecyl dimethyl ammonium chloride
3	Livestock Products - wool	0	
4	Livestock slaughtered and other disposals - pigs	1	didecyl dimethyl ammonium chloride
5	Wheat	94	flutriafol, azoxystrobin, prothioconazole, imidacloprid
6	Barley	38	azoxystrobin, prothioconazole, imidacloprid
7	Cereal cut for hay	0	
8	Livestock products - milk	0	
9	Livestock slaughtered and other disposals - cattle and calves	1	didecyl dimethyl ammonium chloride
10	Livestock slaughtered and other disposals - other	3	imazalil, didecyl dimethyl ammonium chloride
11	Canola	87	flutriafol, iprodione, prothioconazole
12	Oats	24	prothioconazole, imidacloprid
13	Livestock products - eggs	2	imazalil
14	Other pasture cut for hay	50	mancozeb, carbendazim, thiram
15	Lucerne cut for hay	6	metalaxyl-M

16	Pulses	146	chlorothalonil, mancozeb, thiram, carbendazim
17	Apples	103	mancozeb, captan, iprodione
18	All other crops	139	chlorothalonil, captan, thiram, prothioconazole, mancozeb
19	Other crops cut for hay	0	
20	Maize	14	imidacloprid, metalaxyl-M
21	Grapes	259	chlorothalonil, mancozeb, azoxystrobin, iprodione, captan
22	Tomatoes - Fresh market	182	chlorothalonil, azoxystrobin, iprodione
23	Tomatoes - Processing	0	
24	Cherries	142	chlorothalonil, mancozeb, iprodione, captan
25	Nurseries	23	azoxystrobin
26	All other nuts	190	chlorothalonil, mancozeb, iprodione, carbendazim
27	Mushrooms	3	thiabendazole
28	Cut flowers	69	mancozeb, captan
29	All other vegetables	266	chlorothalonil, mancozeb, azoxystrobin, iprodione
30	Pears	87	mancozeb, captan, iprodione
31	All other orchard fruit	250	chlorothalonil, azoxystrobin, mancozeb, iprodione
32	Ornamental*	153	chlorothalonil, iprodione, captan, mancozeb, fosetyl aluminium
33	Domestic/residential*	41	chlorothalonil
34	Green spaces*	150	chlorothalonil, iprodione, captan, thiram, azoxystrobin
35	Timber treatment*	4	chlorothalonil
36	Commercial*	3	chlorothalonil, azoxystrobin
37	Industrial/manufacturing/factory*	2	chlorothalonil
38	Public area/government building*	2	chlorothalonil
39	Building/construction*	0	
40	Right of way*	0	
41	Aviation/shipping/transport*	0	
42	Forestry/plantation*	0	
43	Enclosed freshwaters*	0	

(*) Gross value is not available, order was not ranked.

Table 3. Summary of the different registered applications and products for commonly fungicides used across the region.

Fungicide	#activities/ commodities registered for use in	Commodity/activity	# registered products
Chlorothalonil	16	Grapes	78
		Fresh tomatoes	78
		Ornamental	78
		Nuts	77
		Vegetables	77
		Orchard Fruits	77
		Pulses	75
		All other crops	75
		Cherries	74
		Green spaces	71
		Domestic/residential	37

		Timber treatment	4
		Commercial	3
		Industrial/manufacturing/factory	2
		Public area/government building	2
		Cut flowers	1
Thiram	16	Pulses	21
		All other crops	17
		Green spaces	13
		Pasture cut for hay	9
		Wheat	1
		Barley	1
		Oats	1
		Apples	1
		Maize	1
		Grapes	1
		Cherries	1
		Pears	1
		Cut flowers	1
		Vegetables	1
		All other orchard fruits	1
		Domestic/residential	1
Azoxystrobin	14	Vegetables	50
		Fresh tomatoes	48
		Grapes	46
		All other orchard fruits	46
		Nurseries	19
		Wheat	12
		Barley	12
		Green spaces	11
		All other nuts	8
		Ornamental	5
		Pulses	2
		Canola	1
		Pasture cut for hay	1
		Commercial	1
Mancozeb	13	Grapes	53
		All other vegetables	53
		Apples	44
		All Other orchard fruits	43
		Cut flowers	42
		Pears	40
		All other nuts	38
		Cherries	34
		Pulses	27
		Pasture cut for hay	25
		All other crops	11
		Ornamental	11

		Domestic/residential	2
Iprodione	11	Canola	23
		Apple	16
		Grapes	39
		Tomatoes	39
		Cherries	31
		All other nuts	38
		All other vegetables	45
		Pears	13
		All other orchard fruit	33
		Ornamental	25
		Green space	18

Metalaxyl-M	9	Lucerne cut for hay	5
		Maize	5
		Wheat	4
		Barley	4
		Oats	2
		Maize	5
		All other crops	3
		All other vegetables	6
		Green spaces	4
Captan	8	Grapes	19
		Cherries	19
		Crops	18
		Cut flowers	18
		Pears	18
		Ornamental	18
		Green spaces	18
		Apples	17
Imazalil	8	Livestock slaughtering activities poultry	2
		Livestock products- eggs	2
		Livestock slaughtered and other disposals - other	2
		Apples	4
		Tomatoes	1
		All other vegetables	5
		All other orchard fruits	9
		Pears	4
Didecyl dimethyl ammonium chloride	7	Livestock slaughtering activities sheep and lamb	1
		Livestock slaughtering activities poultry	1
		Livestock slaughtering activities pigs	1
		Livestock slaughtering activities cattle and calves	1
		Livestock slaughtered and other disposals - other	1
		Other orchard fruits	1
		Cut flowers	1
Prothioconazole	6	Canola	12
		Oats	12
		Wheat	11
		Barley	11
		Other crops	11
		All other nuts	2
Thiabendazole	6	Mushroom	3
		Apples	3
		All other vegetables	4
		Pears	1
		All other orchard fruits	4
		Green spaces	3
Imidacloprid*	4	Wheat	7
		Barley	7
		Maize	7

		Oats	7
Flutriafol	4	Wheat	56
		Canola	51
		Oats	1
		All other crops	1
Carbendazim	3	Pasture cut for hay	15
		Pulses	15
		All other nuts	14

* Insecticide component commonly used in fungicide products.

3.1.3 Insecticides associated with common commodities in the water corporation region

At least one of the 36 registered soluble insecticide active ingredients are present in the 275 insecticide products registered for use in Victoria. The number of registered insecticide products associated with the dominant commodities and activities across the region are presented in Table 4. The most common insecticides registered for use in dominant activities across the area include: imidacloprid, azamethiphos, cyromazine, methomyl, pirimicarb, carbaryl, dimethoate, chlorantraniliprole, sulfoxaflor, thiacloprid, dichlorvos, malathion, bendiocarb, dinotefuran, hydramethylnon, chloropicrin, 1,3-dichloropropene. These insecticides have different applications across several activities (Table 5) and would be included in the routine screen list.

Table 4. Insecticides associated with common commodities in the water corporation region

Priority rank	Activity or commodity	#registered products	Most common insecticides
1	Livestock slaughtered and other disposals - sheep and lambs	7	imidacloprid, bendiocarb
2	Livestock slaughtered and other disposals - poultry	13	imidacloprid, azamethiphos, cyromazine
3	Livestock Products - wool	0	
4	Livestock slaughtered and other disposals - pigs	13	imidacloprid, azamethiphos, cyromazine
5	Wheat	87	imidacloprid, methomyl, pirimicarb, dimethoate
6	Barley	87	imidacloprid, methomyl, pirimicarb, dimethoate
7	Cereal cut for hay	1	carbaryl
8	Livestock products - milk	7	imidacloprid
9	Livestock slaughtered and other disposals - cattle and calves	9	imidacloprid, cyromazine
10	Livestock slaughtered and other disposals - other	7	imidacloprid
11	Canola	89	imidacloprid, methomyl, pirimicarb, dimethoate
12	Oats	86	imidacloprid, methomyl, pirimicarb, dimethoate
13	Livestock products - eggs	11	imidacloprid, azamethiphos, cyromazine
14	Other pasture cut for hay	50	methomyl, dimethoate, pirimicarb
15	Lucerne cut for hay	50	methomyl, pirimicarb, dimethoate

16	Pulses	86	imidacloprid, methomyl, pirimicarb, dimethoate
17	Apples	82	imidacloprid, methomyl, pirimicarb
18	All other crops	51	imidacloprid, dimethoate
19	Other crops cut for hay	35	imidacloprid
20	Maize	79	imidacloprid, methomyl, dimethoate
21	Grapes	9	carbaryl, chlorantraniliprole
22	Tomatoes - Fresh market	133	imidacloprid, methomyl, pirimicarb, dimethoate
23	Tomatoes - Processing	0	
24	Cherries	96	imidacloprid, methomyl, pirimicarb
25	Nurseries	81	imidacloprid, pirimicarb, dimethoate
26	All other nuts	7	sulfoxaflor, carbaryl, malathion, carbaryl, dichlorvos, 1,3-dichloropropene
27	Mushrooms	3	1,3-dichloropropene, chloropicrin, cyromazine
28	Cut flowers	27	pirimicarb, dimethoate
29	All other vegetables	128	imidacloprid, methomyl, pirimicarb, dimethoate
30	Pears	42	methomyl, carbaryl, chlorantraniliprole, thiacloprid
31	All other orchard fruit	5	1,3-dichloropropene, carbaryl, chloropicrin, dichlorvos, malathion
32	Ornamental*	86	imidacloprid, pirimicarb, dimethoate
33	Domestic/residential*	64	imidacloprid, dinotefuran, hydramethylnon
34	Green spaces*	12	hydramethylnon, chlorantraniliprole, imidacloprid
35	Timber treatment*	16	imidacloprid
36	Commercial*	44	imidacloprid, dinotefuran, hydramethylnon
37	Industrial/manufacturing/factory*	42	imidacloprid, dinotefuran
38	Public area/government building*	37	imidacloprid, dinotefuran, hydramethylnon
39	Building/construction*	13	imidacloprid
40	Right of way*	2	bendiocarb, carbaryl
41	Aviation/shipping/transport*	6	imidacloprid
42	Forestry/plantation*	38	imidacloprid, dimethoate
43	Enclosed freshwaters*	1	malathion

(*) Gross value is not available, order was not ranked.

Table 5. Summary of the different registered applications and products for commonly insecticides used across the region

Insecticide	#activities/ commodities registered for use in	Commodity/activity	# registered products
Imidacloprid	30	Livestock products (sheep and lambs, poultry, pigs, milk, cattle and calves, eggs, other livestock products)	6*
		Crops (wheat, barley, canola, oats, pulses, maize, other crops)	39*
		Crops cut for hay	35
		Apples	25
		Cherries	43

		Tomatoes and vegetables	73
		Nurseries	47
		Ornamental	46
		Domestic/residential	36
		Green spaces	2
		Timber treatment	15
		Commercial	27
		Industrial/manufacturing/factory	29
		Public area/government building	29
		Construction	12
		Aviation/shipping/transport	5
		Forestry	22
		Pasture cut for hay	1
Dimethoate	15	Crops (wheat, barley, oats)	8*
		Crops (canola and pulses)	10*
		All other crops	10
		Maize	11
		Hay (pasture and lucerne cut for hay)	11*
		Tomatoes	9
		All other vegetables	9
		Nurseries	8
		Cut flowers	11
		Ornamental	11
		Forestry	11
Methomyl	13	Crops (wheat, barley, canola, oats, maize, pulses)	21*
		Hay (pasture and lucerne cut for hay)	21*
		Fruit (apples, cherries, pears)	21*
		Tomatoes	21
		Vegetables	21
Carbaryl	21	Crops (wheat, barley, oats, maize)	2*
		Cereals cut for hay	1
		Pasture cut for hay	2
		Lucerne cut for hay	3
		Apples	3
		Grapes	2
		Cherries	2
		Pears	3
		Other orchard fruits	1
		Tomatoes	1
		All other vegetable	3
		Ornamental	2
		Domestic/residential	3
		Right of way	1
		Green spaces	1
		Commercial	2
		Industrial/manufacturing/factory	2
		Public area/government building	1
Cyromazine	5	Livestock products (poultry, pigs, cattle and calves, eggs)	2*
		Mushroom	1
Dinotefuran	7	Livestock product (poultry, pigs, eggs)	1*
		Domestic/residential	5
		Commercial	5
		Industrial/manufacturing/factory	5
		Public area/government building	5
Hydramethylnon	7	Nurseries	4
		Domestic/residential	5
		Green spaces	4
		Commercial	5
		Public area/government building	4

		Industrial/manufacturing/factory	1
		Forestry	3
1,3-dichloropropene	18	Crops (wheat, barley, canola, oats, pulses, maize, all other crops)	1*
		Fruits (apples, grapes, cherries, pears, all other orchard fruit)	1*
		Tomatoes	1
		Nurseries	1
		All other vegetable	1
		Cut flowers	1
		All other nuts	1
		Mushroom	1
Azamethiphos	4	Livestock products (poultry, pigs, and eggs)	2*
		Livestock products - milk	1
Malathion	20	Crops (wheat, barley, canola, oats, maize)	1*
		Hay (lucerne and pasture cut for hay)	1*
		Apples	3
		Tomatoes	1
		Cherries	2
		Pears	2
		All other nuts	1
		Cut flowers	1
		All other vegetable	1
		All other orchard fruit	1
		Ornamental	1
		Domestic/residential	1
		Green space	1
		Industrial/manufacturing/factory	1
		Enclosed freshwaters	1
Bendiocarb	16	Livestock products (sheep and lambs, poultry, pigs, milk, cattle and calves, eggs, other livestock products)	1*
		Hay (lucerne and pasture cut for hay)	1*
		Domestic/residential	1
		Right of way	1
		Green space	1
		Commercial	1
		Industrial/manufacturing/factory	1
		Public area/government building	1
Chloropicrin	18	Crops (wheat, barley, canola, oats, maize, all other crops)	1*
		Fruits (apples, grapes, cherries, pears, all other orchard fruit)	1*
		Tomatoes	1
		Nurseries	1
		All other nuts	1
		Mushroom	1
		All other vegetables	1
		Cut flowers	1
Chlorantraniliprole	14	Pulses and all other crops	1*
		Apples and pears	3*
		Grapes and cherries	2*
		Tomatoes	2
		All other vegetables	2
		Domestic/residential	2
		Green space	2
		Commercial	1
		Industrial/manufacturing/factory	1
		Public area/government building	1
		Building/construction	1

Dichlorvos	6	Fruits (apples, grapes, cherries, pears, all other orchard fruit)	1*
		All other nut	1
Sulfoxaflor	12	Crops (wheat, canola, and all other crops)	2*
		Crops (barley, oats and maize)	1*
		Fruits (apples, cherries, pears)	2*
		All other nuts	2
		Tomatoes	2
		All other vegetables	
Pirimicarb	14	Crops (wheat, barley, oats, canola, pulses, all other crops)	12*
		Pasture cut for hay	11
		Lucerne cut for hay	12
		Apples	12
		Tomatoes	12
		Cherries	11
		Nurseries	12
		Cut flowers	12
		All other vegetable	12
		Ornamental	12
Thiacloprid	5	Apples	3
		Cherries	3
		Nurseries	2
		Pears	3
		Ornamental	2

(*) # registered products for each activity/commodity.

3.1.4 Herbicides associated with common commodities in the water corporation Region

There were 65 registered soluble herbicide active ingredients for use in 407 products registered for use in Victoria. The number of registered herbicide products associated with dominant commodities and activities in the region are presented in Table 6. The most common herbicides registered for use in dominant regional activities are: glyphosate, glufosinate, isoxaflutol, atrazine, diuron, MCPA, diquat, metribuzin, sulfosulfuron, simazine, paraquat dichloride, hexazinone, tebuthiuron, 2,4 D acid, 2,4 D B, imazethapyr, metsulfuron-methyl, halosulfuron-methyl. These herbicides have different applications cross several activities (Table 7) and would be included in the routine screen list.

Table 6. Herbicides associated with common commodities in the water corporation region

Priority rank	Activity or commodity	#registered products	Most common herbicides
1	Livestock slaughtered and other disposals - sheep and lambs	0	
2	Livestock slaughtered and other disposals - poultry	0	
3	Livestock Products - wool	0	
4	Livestock slaughtered and other disposals - pigs	0	
5	Wheat	187	paraquat dichloride, glyphosate isopropylamine salt, diuron, MCPA, diquat, metribuzin, sulfosulfuron

6	Barley	172	paraquat dichloride, glyphosate isopropylamine salt, diuron, MCPA, metribuzin
7	Cereal cut for hay	64	MCPA, paraquat dichloride, diquat, atrazine, 2,4 D B, metsulfuron methyl, diuron
8	Livestock products - milk	0	
9	Livestock slaughtered and other disposals - cattle and calves	0	
10	Livestock slaughtered and other disposals - other	0	
11	Canola	105	glyphosate isopropylamine salt, atrazine, diquat, simazine.
12	Oats	154	glyphosate isopropylamine salt, paraquat dichloride, diuron, MCPA, diquat, metribuzin
13	Livestock products - eggs	0	
14	Other pasture cut for hay	158	paraquat dichloride, hexazinone, MCPA, diquat, metribuzin, simazine, tebuthiuron, 2,4 D B
15	Lucerne cut for hay	92	atrazine, simazine, 2,4 D B
16	Pulses	189	glyphosate isopropylamine salt, paraquat dichloride, isoxaflutole, atrazine, diuron, MCPA, diquat, metribuzin, simazine
17	Apples	26	glyphosate isopropylamine salt, simazine
18	All other crops	297	glyphosate isopropylamine salt, glufosinate, paraquat dichloride, isoxaflutole, atrazine, diuron, MCPA, diquat, metribuzin, sulfosulfuron
19	Other crops cut for hay	34	glyphosate isopropylamine salt, atrazine
20	Maize	89	glyphosate isopropylamine salt, paraquat dichloride, atrazine, diquat, halosulfuron methyl
21	Grapes	106	glyphosate isopropylamine salt, glufosinate, paraquat dichloride, diquat, simazine
22	Tomatoes - Fresh market	40	glufosinate, diquat, metribuzin
23	Tomatoes - Processing	0	
24	Cherries	1	2,4 D Acid
25	Nurseries	25	diquat, paraquat dichloride
26	All other nuts	108	glyphosate isopropylamine salt, paraquat dichloride, simazine, 2,4 D B
27	Mushrooms	0	
28	Cut flowers	10	simazine
29	All other vegetables	126	glyphosate isopropylamine salt, paraquat dichloride, atrazine, diuron, diquat, simazine, metribuzin
30	Pears	9	simazine
31	All other orchard fruit	111	glyphosate isopropylamine salt, glufosinate, paraquat dichloride, simazine
32	Ornamental*	10	halosulfuron methyl
33	Domestic/residential*	52	glyphosate isopropylamine salt, metsulfuron methyl, halosulfuron methyl
34	Green spaces*	60	glufosinate, MCPA, halosulfuron methyl
35	Timber treatment*	0	
36	Commercial*	123	glyphosate isopropylamine salt, glufosinate, hexazinone, MCPA, metsulfuron methyl, imazethapyr
37	Industrial/manufacturing/factory*	121	glyphosate isopropylamine salt, glufosinate, hexazinone, MCPA, metsulfuron methyl, imazethapyr

38	Public area/government building*	61	glyphosate isopropylamine salt, simazine, metsulfuron methyl, imazethapyr, diquat
39	Building/construction*	24	glyphosate isopropylamine salt
40	Right of way*	142	glyphosate isopropylamine salt, glufosinate, paraquat dichloride, hexazinone, MCPA, atrazine, metsulfuron methyl, diquat
41	Aviation/transport*	0	
42	Forestry/plantation*	112	glyphosate isopropylamine salt, glufosinate, atrazine, hexazinone, tebuthiuron, simazine
43	Enclosed freshwaters*	57	glyphosate isopropylamine salt, diuron, diquat, simazine

(*) Gross value is not available, order was not ranked.

Table 7. Summary of the different registered applications and products for commonly herbicides used across the REGION

Herbicides	#activities/ commodities registered for use in	Commodity/activity	# registered products
Glyphosate	20	Crops (wheat, barley, canola, oats, maize, pulses)	15*
		All other crops	47
		Apples	13
		Grapes	25
		All other nuts	38
		All other vegetables	16
		All other orchard fruit	27
		Domestic/residential	18
		Right of way	9
		Commercial	19
		Industrial/manufacturing/factory	19
		Public area/government	21
		Building/construction	20
		Forestry/plantation	9
Enclosed freshwaters	15		
Simazine	19	Wheat and barley	1*
		Canola	11
		Hay (lucerne and pasture cut for hay)	10*
		Pulses	10
		Apples and Pears	9*
		Grapes	11
		All other nuts	10
		Cut flowers	10
		All other vegetables	10
		All other orchard fruit	9
		Right of way	5
		Commercial	1
		Industrial/manufacturing/factory	1
		Public area/government	5
Forestry/plantation	9		
Enclosed freshwaters	10		
Diquat	17	Crops (wheat, canola, oats)	10*
		Barley and maize	5*
		Pulses	8
		All other crops	12
		Cereal cut for hay	5
		Pasture cut for hay	10

		Lucerne cut for hay	3
		Grapes	10
		Nurseries	10
		All other vegetables	10
		Right of way	5
		Public area/government	5
		Forestry/plantation	3
		Enclosed freshwaters	7
Paraquat dichloride	14	Crops (wheat, barley, oats, maize, pulses)	21*
		All other crops	23
		Cereal cut for hay	8
		Pasture cut for hay	23
		Grapes	19
		Nurseries	14
		All other nuts	21
		All other vegetables	23
		All other orchard fruit	23
		Right of way	6
Glufosinate	13	Crops (wheat, barley, oats, maize, pulses)	2*
		Canola	3
		Grapes	29
		Tomatoes	29
		All other orchard fruit	31
		Green spaces	19
		Right of way	28
		Commercial	25
		Industrial/manufacturing/factory	25
		Forestry/plantation	31
2,4 D Acid	12	Wheat and barley	2*
		Canola and oats	1*
		Maize	3
		All other crops	3
		Cereal cut for hay	2
		Cherries	1
		All other nuts	3
		All other vegetables	2
		Right of way	2
		Industrial/manufacturing/factory	2
MCPA dimethylamine salt	11	Crops (wheat, barley, oats, pulses, all other crops)	13*
		Cereal cut for hay	12
		Pasture cut for hay	13
		Right of way	13
		Green space	13
		Commercial	13
		Industrial/manufacturing/factory	13
Metsulfuron methyl	11	Crops (wheat, barley, all other crops)	8*
		Cereal cut for hay	8
		Pasture cut for hay	8
		Domestic/residential	8
		Right of way	8
		Commercial	8
		Industrial/manufacturing/factory	8
		Public area/government building	8
		Forestry/plantation	3
Atrazine	10	Crops (canola, maize, pulses, all other crops)	18*
		Cereal cut for hay	13
		Lucerne cut for hay	18
		Other crops cut for hay	18
		All other vegetables	18
		Right of way	16

Metribuzin	8	Forestry/plantation	18
		Crops (wheat, barley, oats, pulses, all other crops)	11*
		Pasture cut for hay	11
		Tomatoes	11
		All other vegetables	11
Diuron	9	Crops (wheat, barley, oats, pulses, all other crops)	13*
		Cereal cut for hay	
		Lucerne cut for hay	2
		All other vegetables	13
		Enclosed freshwaters	13
2,4 D B	8	Crops (wheat, barley, oats, all other crops)	8*
		Hay (cereal, lucerne and pasture cut for hay)	8*
		All other nuts	8
Isoxaflutole	5	Crops (wheat, barley, and oats)	1*
		Pulses	23
		All other crops	21
Hexazinone	5	Pasture cut for hay	13
		Right of way	10
		Commercial	16
		Industrial/manufacturing/factory	16
		Forestry/plantation	15
Halosulfuron methyl	5	Maize	5
		All other crops	5
		Ornamental	6
		Domestic/residential	6
		Green spaces	6
Imazethapyr	4	Right of way	5
		Commercial	7
		Industrial/manufacturing/factory	7
		Public area/government building	7
Tebuthiuron	2	Pasture cut for hay	11
		Forestry/plantation	11
Sulfosulfuron	2	Wheat	10
		All other crops	10

3.2 Review of pesticides commonly detected in surface waters

A review of the scientific and grey literature on pesticides commonly detected in surface waters or chemicals of concern identified several pesticides missed during the review of active ingredients in registered pesticide products used across the region. These are outlined further below.

3.2.1 Identified chemicals of concern (COCs)

Synthetic pyrethroids

Synthetic pyrethroids are a class of synthetic organic insecticides derived from pyrethrins. They've been used worldwide since the 1980s due to their high level of effectiveness and low toxicity in comparison to other insecticides (Tang et al. 2018). Synthetic pyrethroids are applied in nearly all agricultural crops, nurseries, various urban structural and landscaping sites, construction sites, the home/garden environment, and many other sites (Spurlock and Lee 2008).

Synthetic pyrethroid insecticides are highly hydrophobic compounds with very low water solubility and high adsorption capacities, which means they tend to bind to sediments, making them immobile following application, and less likely to be found dissolved in surface waters. However,

recent studies show that irrigation or stormwater runoff can result in the transport of synthetic pyrethroids from sites of application to surface waters (Liu et al. 2004). In natural surface waters, synthetic pyrethroids exist in three phases:

1. adsorbed to suspended solids,
2. adsorbed to dissolved organic matter, and
3. freely dissolved in the water.

Synthetic pyrethroids that are adsorbed to suspended solids tend to settle quickly out of the water column, but the freely dissolved fraction may be much more mobile (Liu et al. 2004). Synthetic pyrethroid insecticides have been identified as emerging compounds of concern (Stehle and Schulz 2015; Marshall et al. 2016) with increasing detections in surface waters across Australia (Allinson et al. 2015) and worldwide (Tang et al. 2018) Thus, synthetic pyrethroids are strongly recommended for inclusion in the water corporation's routine screen list. In particular, the synthetic pyrethroids: alpha- cypermethrin, bifenthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin should be included. These pyrethroids are registered for use in many of the dominant commodities across the region, such as livestock, crops, fruits, vegetables, and urban/built up activities.

High risk pesticides used in Goulbourn – Murray Irrigation Areas

In 2003, The Commonwealth Scientific Industrial & Research Organisation (CSIRO) was engaged by Goulburn Murray Rural Water Corporation (G-MW) to undertake a first-tier assessment of the potential risks associated with pesticides used in G-MW Irrigation Areas to water quality and through water quality changes to humans, stock, aquaculture, food industries, pastures, aquatic flora and fauna and aquatic ecosystems. The assessment identified seventeen pesticides pose a potential threat to human health. Among these, five pesticides were already identified by our assessment of active ingredients in registered pesticide products and two are no longer used in Australia (parathion methyl and endosulfan). The remaining pesticides included azinphos-methyl, omethoate, phorate, trifluralin, molinate, pendimethalin, phosmet, thiobencarb, ziram and thiodicarb. These pesticides are used in various farming practices and thus are recommended for inclusion in the screen list.

3.2.2 Pesticides commonly detected in surface waters of agricultural areas

A number of pesticides were identified for inclusion in the recommended screen list following review of the literature on pesticides commonly detected in surface waters nationally and internationally. These pesticides are the active ingredients in a low number of registered products for use in common commodities across the region, which is why they were likely to have been excluded from the search of active ingredients in registered products. Soluble pesticides identified include the fungicides boscalid, myclobutanil, and pyrimethanil and herbicide linuron (Rose et al. 2009; Phillips and Bode 2004; Reilly et al. 2012; Wightwick et al. 2012). There were several

pesticides, while less soluble and thus not usually considered to be frequently detected in surface waters, that have been commonly reported in literature on surface water monitoring and could be applied in the dominant commodities of the region including the fungicides tebuconazole, penconazole, prochloraz, pyraclostrobin, trifloxystrobin, difenoconazole and cyprodinil; insecticide chlorpyrifos, and herbicides S-metolachlor and prometryn, (Rose et al. 2009; Moschet et al. 2014; Reilly et al. 2012; Pfeuffer and Rand 2004; Myers et al. 2014; Banks, Hunter, and Wachal 2005).

3.3 Pesticides detected in the water corporation Catchment Area

Five herbicides and one insecticide were detected in POCIS and Chemcatcher passive samplers in two deployment rounds (Table 8). The herbicides atrazine and simazine were detected in both type of passive samplers in both deployment rounds. The insecticide imidacloprid was detected in both types of passive sampler in round two. No pesticides were detected in spot water samples. Additionally, no pesticides were detected in sediment samples collected in either sampling round.

As a part of another project carried by AQUEST for the water corporation, pesticides were monitored in a nearby river using POCIS. Several herbicides and two insecticides were detected across the study area. The herbicides detected included diuron, simazine, atrazine, MCPA and triclopyr. Two insecticides, imidacloprid and carbaryl, were detected. The most frequently detected, occurring at all sites, was triclopyr (Myers et al. 2019).

Table 8. Herbicides and insecticides detected in surface waters using POCIS ($\mu\text{g}/0.2\text{ g sorbent}$) and Chemcatcher ($\mu\text{g}/\text{filter}$) passive samplers

Herbicide (H) and Insecticide (I)	POCIS		Chemcatcher	
	Round 1	Round 2	Round 1	Round 2
Atrazine (H)	19.80	4.75	0.066	0.03
Simazine (H)	80.97	4.15	0.068	0.023
2,4 D (H)	69.45			
Metolachlor (H)		1.7	0.022	
Propyzamide (H)		1.3		
Imidacloprid (I)		5.25		0.014

3.4 Recommendations for routine monitoring

Based on the identification of active ingredients in registered products applied across the region; a review of the wider literature on pesticides commonly detected in surface waters or identified as chemicals of concern and field surveys of pesticides in surface waters in the region, recommendations for both the types of pesticides that should be prioritised for inclusion in routine screening lists and sampling methods for routine monitoring are provided.

3.4.1 Pesticide screening

The water corporation currently screen for 56 pesticides in their routine monitoring program (Table 9). Many of these are no longer registered or permitted for use in Australia, including all the listed organochlorine pesticides, four of the organophosphate pesticides (fenthion, parathion, stirofos,ronnel), and 5 herbicides (silvex, hexachlorobenzene, prometon, pichloram, dinoseb).

Based on the identification of active ingredients in registered products used across the region, the literature review and field survey outcomes, 81 pesticides are recommended for inclusion in the water corporation's routine pesticide monitoring screen for surface waters (Table 10). Nine of the pesticides listed in the water corporation's current pesticide screen are included in the recommended screen list (Table 9). The recommended screen includes 24 fungicides, 27 herbicides, and 30 insecticides all of which occur in the commonly used registered products across the region, have been commonly detected in surface waters across Australia and/or within the region or are knownchemicals of concern (Table 10).

Table 9. Currently screened pesticides. Those in bold are no longer registered or permitted for use in Australia. Pesticides highlighted in grey are included in the recommended list.

Organochlorine pesticides (OCPs)	Organophosphate pesticides (OPPs)	Herbicides and other chemicals
Aldrin	Chlorpyrifos	Dicamba
Chlordane	Diazinon	Mecoprop
Total Aldrin Dieldrin	Dichlorvos	Hexachlorobenzene
BHC Beta Isomer	Mevinphos	Prometon
DDT	Ethion	Bentazon
BHC Delta Isomer	Fenthion	Glyphosate
Dieldrin	Malathion	Bromoxynil
Cis-Chlordane	Parathion	Clopyralid
Total DDT	Ronnel (Fenchlorfos)	Dichlorprop
Methoxychlor	Stirofos	Pichloram
Endosulfan I		Triclopyr
Endosulfan II		Fluroxypyr
BHC Alpha Isomer		Prometryn
Endosulfan Sulphate		Silvex
Endrin Aldehyde		Epoxide
Endrin Ketone		Dinoseb
Endrin		MCPB
Oxy-Chlordane		MCPA
Trans-chlordane		Terbutylazine
Heptachlor		Ametryn
Lindane		Atrazine
		Terbutryn
		Propazine
		Simazine
		Simetryn

Table 10. Pesticides recommended for surface water monitoring in the water corporation Region

Fungicides	Herbicides	Insecticides
Azoxystrobin	2,4 D Acid	1,3-dichloropropene
Boscalid	2,4 D B	Alpha cypermethrin
Captan	Atrazine	Azamethiphos
Carbendazim	Diquat	Azinphos-methyl
Chlorothalonil	Diuron	Bendiocarb
Cyprodinil	Glufosinate	Bifenthrin
Didecyl dimethyl ammonium chloride	Glyphosate	Carbaryl
Difenoconazole	Halosulfuron methyl	Chlorantraniliprole
Flutriafol	Hexazinone	Chloropicrin
Imazalil	Imazethapyr	Chlorpyrifos
Iprodione	Isoxaflutole	Cypermethrin
Mancozeb	Linuron	Cyromazine
Metalaxyl-M	MCPA	Deltamethrin
Myclobutanil	Metribuzin	Dichlorvos
Penconazole	Metsulfuron methyl	Dimethoate
Prochloraz	Molinate	Dinotefuran
Prothioconazole	Paraquat dichloride	Esfenvalerate
Pyraclostrobin	Pendimethalin	Hydramethylnon
Pyrimethanil	Prometryn	Imidacloprid
Tebuconazole	Simazine	Lambda-cyhalothrin
Thiabendazole	Triclopyr	Malathion
Thiram	Sulfosulfuron	Methomyl
Trifloxystrobin	Tebuthiuron	Omethoate
Ziram	Thiobencarb	Permethrin
	Trifluralin	Phorate
	S-metolachlor	Phosmet
	Propyzamide	Pirimicarb
		Sulfoxaflor
		Thiacloprid
		Thiodicarb

3.4.2 Sampling Methods: Passive Sampling

Most traditional surface water monitoring programs rely on spot sampling, which involves the collection of a water sample at a site on a single occasion. Spot sampling is considered a cheap and commonly encountered sampling methodology, but it has several limitations, in particular, regarding its representativeness. A grab sample reflects the water composition only at the point in time the sample is collected. Thus, intermittent pollution events (e.g., runoff events or accidental spills) are often missed when relying on spot sampling only. Pesticides entering waterways following intermittent events, such as rainfall or accidental spills, generally result in an initial spike in concentrations immediately following the event, thereafter, are broken down or diluted within hours to a few days (Schäfer et al. 2008). To determine trace amounts of pesticides in spot samples, large volumes of water are required. Monitoring techniques are thus needed that allow for detection of episodically occurring pollutants and trace concentrations.

Continuous water sampling using passive samplers represents an alternative to spot sampling that meets both a need for assessment of episodic pollution events and the ability to assess trace concentrations. Passive sampling methods sequester contaminants over their entire deployment period, which can be up to a month or more, thus detecting pollutants from episodic events

commonly not detected with spot sampling. They can be used in situations of variable water concentrations, permitting measurement of trace contaminant concentrations over extended time periods (Allan et al. 2006).

Passive sampling devices have been employed successfully for continuous monitoring of pesticides in surface waters across Australia (Schäfer et al. 2011; Rose et al. 2009; Myers et al. 2014) and worldwide (Schäfer et al. 2008; Alvarez et al. 2008; Muenze et al. 2015; Thomatou et al. 2011).

Often, passive sampling is conducted in conjunction with spot water sampling, however, not all pesticides are detected in passive samplers are also detected in spot samples, as was observed during field sampling in the current investigations. Two types of passive samplers: Chemcatcher and polar organic chemical integrative samples (POCIS) are commonly used to monitor pesticides in surface waters. It is recommended that future pesticide monitoring programs across the REGION employ both POCIS and Chemcatcher together with traditional spot sampling (as different compounds are detectable from each).

4 References

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Appendices

Appendix 1 - List of pesticides in water and sediment screens. Units are in µg/L for waters and mg/kg for sediment.

Analyte	Limit of Reporting	Analyte	Limit of Reporting
Atrazine	0.1	Tebufenpyrad	0.1
Diuron	0.1	Tetradifon	0.1
Hexazinone	0.1	Chlorfenvinphos (Z)	0.1
Linuron	0.1	Parathion (ethyl)	0.1
Metolachlor	0.1	Parathion methyl	0.1
Molinate	0.1	Pirimiphos methyl	0.1
Oxyfluorfen	0.1	Pirimiphos ethyl	0.1
Pendimethalin	0.1	Azinphos methyl	0.1
Simazine	0.1	Azinphos ethyl	0.1
Trifluralin	0.1	Bromophos ethyl	0.1
HCB	0.1	Carbophenothion	0.1
Heptachlor	0.1	Coumaphos	0.1
Heptachlor epoxide	0.1	Dioxathion	0.1
Aldrin	0.1	Fenamiphos	0.1
gamma-BHC(Lindane)	0.1	Fenchlorphos	0.1
alpha-BHC	0.1	Formothion	0.1
beta-BHC	0.1	Methacrifos	0.1
delta-BHC	0.1	Methidathion	0.1
trans-Chlordane	0.1	Mevinphos	0.1
cis-Chlordane	0.1	Phorate	0.1
Oxychlordane	0.1	Phosalone	0.1
Dieldrin	0.1	Profenophos	0.1
p,p-DDE	0.1	Prothiofos	0.1

p,p-DDD	0.1	Thiometon	0.1
p,p-DDT	0.1	Triazophos	0.1
Endrin	0.1	Bifenthrin	0.1
Endrin aldehyde	0.1	Bioresmethrin	0.1
Endrin Ketone	0.1	Cyfluthrin	0.1
alpha-Endosulfan	0.1	Cyhalothrin	0.1
beta-Endosulfan	0.1	Cypermethrin	0.1
Endosulfan sulfate	0.1	Deltamethrin	0.1
Methoxychlor	0.1	Fenvalerate	0.1
Dicofol	0.1	Permethrin	0.1
Carbaryl	0.1	Phenothrin	0.1
Fenoxycarb	0.1	Bupirimate	0.1
Pirimicarb	0.1	Chlorothalonil	0.1
Dichlorvos	0.1	Cyprodinil	0.1
Demeton-S-methyl	0.1	Dichlofluanid	0.1
Diazinon	0.1	Dicloran	0.1
Dimethoate	0.1	Difenoconazole	0.1
Chlorpyrifos	0.1	Dimethomorph	0.1
Chlorpyrifos methyl	0.1	Diphenylamine	0.1
Malathion	0.1	Fenarimol	0.1
Fenthion	0.1	Flusilazole	0.1
Ethion	0.1	Hexaconazole	0.1
Fenitrothion	0.1	Iprodione	0.1
Chlorfenvinphos (E)	0.1	Imazalil	0.1
Pyrimethanil	0.1	Metalaxyl	0.1
Tebuconazole	0.1	Penconazole	0.1
Vinclozolin	0.1	o-Phenylphenol	0.1
Buprofezin	0.1	Prochloraz	0.1
Methoprene	0.1	Procymidone	0.1
Piperonyl Butoxide	0.1	Propiconazole I	0.1
Propargite	0.1	Propiconazole II	0.1

Appendix 2 - List of pesticides in POCIS screens round 1. Units are in µg/0.2 g sorbent

Analyte	Limit of Detection
Pirimicarb	<1
Simazine	<1
Metalaxyl	<1
Atrazine	<1
Carbaryl	<1
Diuron	<1
Pyrimethanil	<2
indoxacarb	<5
Metolachlor	<1
Pyraclostrobin	<1
Trifloxystrobin	<1
Prochloraz	<1
MCPA	<1
2,4-D	<5
Dicamba	<5
Myclobutanil	<5
Difenconazole	<2
Benzotriazole	<2
Imidacloprid	<1
Triclopyr	<2.5

Appendix 3 - List of pesticides in POCIS screens round 2. Units are in µg/0.2g sorbent

Analyte	Limit of detection	Analyte	Limit of detection
Acephate	<1	Paclobutrazol	<1
Temephos	<1	Penconazole	<1
Fenamiphos	<1	Piperonyl butoxide	<1
Methamidophos	<1	Prochloraz	<1
Monocrotophos	<1	Propiconazole	<1
Cadusafos	<1	Propamocarb	<1
Atrazine	<1	Pyraclostrobin	<1
Carfentrazone Ethyl	<1	Pyrimethanil	<1
Linuron	<1	Tebuconazole	<1
Isoxaben	<1	Tolclophos methyl	<1
Ethofumesate	<1	Triadimefon	<1
Bromacil	<1	Triadimenol	<1
Metolachlor	<1	Quinoxifen	<1
Metribuzin	<1	Spiroxamine	<1
Methabenzthiazuron	<1	Forchlorfenuron	<1
Norflurazon	<1	Aldicarb (incl sulfoxide & sulfone)	<1
Pendimethalin	<1	Bendiocarb	<1
Napropamide	<1	Carbaryl	<1
Ametryn	<1	Methiocarb	<1
Butafenacil	<1	Pirimicarb	<1
Cyanazine	<1	Thiodicarb	<1
Diflufenican	<1	Acetamiprid	<1
Hexazinone	<1	Chlorantaniliprole	<1
Prometryn	<1	Clothianidin	<1
Propyzamide	<1	Fenoxycarb	<1
Simazine	<1	Emamectin	<1
Buprofezin	<1	Flubendiamide	<1
Clofentezine	<1	Indoxacarb	<1
Etoxazole	<1	Novaluron	<1
Hexythiazox	<1	Pyriproxyfen	<1
Propargite	<1	Methoxyfenozide	<1
Tebufenpyrad	<1	Spinetoram	<1
Benalaxyl	<1	Spirotetramat	<1
Bitertanol	<1	Thiamethoxam	<1
Boscalid	<1	Triflumuron	<1
Cyproconazole	<1	Azoxystrobin	<1
Cyprodinil	<1	Vamidothion	<1
Difenoconazole	<1	Benomyl	<1
Dimethomorph	<1	Benzyladenine	<1
Epoxiconazole	<1	Carbendazim	<1
Fenarimol	<1	Diuron	<1
Fenpyrazamine	<1	Fenhexamid	<1
Flusilazole	<1	Fenpyroximate	<1
Hexaconazole	<1	Imidacloprid	<1
Imazalil	<1	Methomyl	<1
Kresoxim methyl	<1	Pymetrozine	<1
Metalaxyl	<1	Spinosad	<1
Mandipropamid	<1	Tebufenozide	<1
Metrafenone	<1	Thiabendazole	<1
Myclobutanil	<1	Thiacloprid	<1
Oxycarboxin	<1	Trifloxystrobin	<1

Appendix 4 - List of pesticides in Chemcatcher screens round 1 and 2. Units are in µg/filter

Analyte	Limit of detection	Analyte	Limit of detection
Aldrin	<0.01	Bitertanol	<0.01
BHC - alpha	<0.01	Boscalid	<0.01
BHC - beta	<0.01	Captan	<0.01
BHC - delta	<0.01	Chlorothalonil	<0.01
BHC - Total	<0.01	Cyproconazole	<0.01
Chlordane	<0.01	Cyprodinil	<0.01
DDD - o.p.	<0.01	Diclofluanid	<0.01
DDD - p.p.	<0.01	Dicloran	<0.01
DDE - o.p.	<0.01	Difenoconazole	<0.01
DDE - p.p.	<0.01	Dimethomorph	<0.01
DDT - o.p.	<0.01	Diphenylamine	<0.01
DDT - p.p.	<0.01	Epoxiconazole	<0.01
DDT - Total	<0.01	Fenarimol	<0.01
Dicofol	<0.01	Fludioxonil	<0.01
Dieldrin	<0.01	Fenpyrazamine	<0.01
Endosulfan - a.	<0.01	Flusilazole	<0.01
Endosulfan - b.	<0.01	Hexaconazole	<0.01
Endosulfan - Sulphate	<0.01	Imazalil	<0.01
Endosulfan - Total	<0.01	Iprodione	<0.01
Endrin	<0.01	Kresoxim methyl	<0.01
HCB	<0.01	Metalaxyl	<0.01
Heptachlor	<0.01	Mandipropamid	<0.01
Heptachlor-Epoxyde	<0.01	Metrafenone	<0.01
Lindane	<0.01	Myclobutanil	<0.01
Methoxychlor	<0.01	Oxadixyl	<0.01
Nonachlor	<0.01	Oxycarboxin	<0.01
Trichlorfon	<0.01	Paclobutrazol	<0.01
Acephate	<0.01	Penconazole	<0.01
Temephos	<0.01	Piperonyl butoxide	<0.01
Azinphos ethyl	<0.01	Prochloraz	<0.01
Azinphos methyl	<0.01	Procymidone	<0.01
Bromophos ethyl	<0.01	Propiconazole	<0.01
Carbophenothion	<0.01	Propamocarb	<0.01
Chlorfenvinphos	<0.01	Pyraclostrobin	<0.01
Chlorpyrifos	<0.01	Pyrimethanil	<0.01
Chlorpyrifos methyl	<0.01	Quintozene	<0.01
Chlorthal dimethyl	<0.01	Tebuconazole	<0.01
Coumaphos	<0.01	Tolclophos methyl	<0.01
Demeton-S-Methyl	<0.01	Tolyfluanid	<0.01
Diazinon	<0.01	Triadimefon	<0.01
Dioxathion	<0.01	Triadimenol	<0.01
Dichlorvos	<0.01	Vinclozolin	<0.01
Dimethoate	<0.01	Quinoxifen	<0.01
Ethion	<0.01	Spiroxamine	<0.01
Fenamiphos	<0.01	Bupirimate	<0.01
Fenchlorphos	<0.01	Forchlorfenuron	<0.01
Fenitrothion	<0.01	Chlorfenapyr	<0.01
Fenthion	<0.01	O-Phenylphenol	<0.01
Formothion	<0.01	Aldicarb (incl sulfoxide & sulfone)	<0.01
Malathion	<0.01	Bendiocarb	<0.01
Methacrifos	<0.01	Carbaryl	<0.01
Methamidophos	<0.01	Methiocarb	<0.01
Methidathion	<0.01	Pirimicarb	<0.01
Mevinphos	<0.01	Thiodicarb	<0.01
Monocrotophos	<0.01	Bifenthrin	<0.01
Omethoate	<0.01	Bioresmethrin	<0.01

Parathion ethyl	<0.01	Cyfluthrin	<0.01
Parathion methyl	<0.01	Cyfluthrin - b.	<0.01
Phorate	<0.01	Cyhalothrin	<0.01
Phosalone	<0.01	Cyhalothrin - l.	<0.01
Phosmet	<0.01	Cypermethrin	<0.01
Phosphamidon	<0.01	Cypermethrin - a.	<0.01
Pirimiphos methyl	<0.01	Deltamethrin	<0.01
Profenofos	<0.01	Esfenvalerate	<0.01
Prothiofos	<0.01	Fenvalerate	<0.01
Terbufos	<0.01	Fluvalinate	<0.01
Triazophos	<0.01	tau-Fluvalinate	<0.01
Cadusafos	<0.01	Permethrin	<0.01
Ethofumesate	<0.01	Phenothrin	<0.01
Bromacil	<0.01	Acetamiprid	<0.01
Carfentrazone Ethyl	<0.01	Fipronil	<0.01
Isoxaben	<0.01	Chlorantaniliprole	<0.01
Linuron	<0.01	Clothianidin	<0.01
Atrazine	<0.01	Fenoxycarb	<0.01
Metribuzin	<0.01	Emamectin	<0.01
Metolachlor	<0.01	Flubendiamide	<0.01
Methabenzthiazuron	<0.01	Indoxacarb	<0.01
Molinate	<0.01	Pyriproxyfen	<0.01
Oxyfluorfen	<0.01	Novaluron	<0.01
Pendimethalin	<0.01	Methoxyfenozide	<0.01
Norflurazon	<0.01	Spinetoram	<0.01
Napropamide	<0.01	Spirotetramat	<0.01
Propachlor	<0.01	Thiamethoxam	<0.01
Trifluralin	<0.01	Triflumuron	<0.01
Ametryn	<0.01	Vamidotion	<0.01
Butafenacil	<0.01	Azoxystrobin	<0.01
Cyanazine	<0.01	Benomyl	<0.01
Diflufenican	<0.01	Benzyladenine	<0.01
Hexazinone	<0.01	Carbendazim	<0.01
Prometryn	<0.01	Diuron	<0.01
Propyzamide	<0.01	Fenhexamid	<0.01
Simazine	<0.01	Fenpyroximate	<0.01
Buprofezin	<0.01	Imidacloprid	<0.01
Clofentezine	<0.01	Methomyl	<0.01
Disulphoton	<0.01	Pymetrozine	<0.01
Etoxazole	<0.01	Spinosad	<0.01
Hexythiazox	<0.01	Tebufenozide	<0.01
Propargite	<0.01	Thiabendazole	<0.01
Tebufenpyrad	<0.01	Thiacloprid	<0.01
Tetradifon	<0.01	Trifloxystrobin	<0.01
Benalaxyl	<0.01		