Environmental/Ecological Risk Assessment (ERA) Model for Assessing Risks in Irrigation Areas (River, Creeks, Channels, Drains) of Toxicants (Pesticides, Herbicides and Trace Metals) to Various Receptors

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CORESPEONDEDNCE ABOUT THE TECHNICAL REPORT AND R&D

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G-MW R&D WEB SITES

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Summary

The Environmental/Ecological Risk assessment (ERA) model was developed in collaboration with federal, state and regional government departments (CSIRO, Australia; The Department of Primary Industries, Victoria, Australia; Centre for Ecotoxicology, Department of Environment, and Climate Change and Water (DECCW), NSW; North Central catchment management Authority, Victoria, Australia; and Universities (the University of Technology, Sydney, Australia; RMIT University, Australia; University of Hong Kong and City University of Hong Kong) and Rho Environmetrics (Adelaide, Australia). The model helped G-MW to analyze and evaluate the possibility of adverse effects that can be caused by toxicants such as pesticides, herbicides and trace metals on various ecological receptors including humans. Though the model developed principally for pesticides, herbicides and metals but can also be used for assessing risks to other harmful chemicals group such as endocrine disrupting chemicals (EDCs), dioxins and pharmaceuticals. The ERA model has eight steps as listed below:

1. An inventory of pesticides, herbicides in use and trace metals sources in the region.

2. A preliminary hazard identification of pesticides, herbicides and trace metals using toxicity values (LC50, LD50 and EC50) to different receptors.

3. A survey to identify the potential and possible risk sites (high, medium and low and least risk sites) for assessing risks level in the whole G-MW catchment.

4. Innovation or development or use of novel technology to accurately measure and improve risk assessment of micro-pollutants (pesticides, herbicides and trace metals) at µg/l to ng/L.

5. Use of a multiple sampling strategy (novel technology, and use of native biota (fish, mussels) and spot sampling)).

6. A pilot trial to evaluate the effectiveness of the novel technology in environmental/ecological risk assessment.

7. A two years continuous monitoring using novel technology, and other sampling strategies (step 5) to assess spatial and temporal variation of pollutants, long term environmental conditions in the catchment and impacts from climate variability on inputs, transport and bioavailability of pollutants.

8. An assessment of the effects of most frequently detected pollutants (endosulfan and copper) on Australian native biota (fish) living in the Goulburn Murray River region

The ERA model helped G-MW in assessing risks posed from harmful chemicals (pesticides, herbicides, and trace metals) to various receptors (drinking water, raw town supply, biodiversity (fish), flora and fauna, stock and domestic supply, food security, water security, recreation, aquatic ecosystems and humans.

Table of Contents

List of Tables

List of Figures

Appendix

Acronyms and glossary

Acute toxicity: Adverse effects occurring within a short time of administration of a single dose of a chemical or immediately following short or continuous exposure, or multiple doses over 24 hours or less.

Antimicrobials: Antimicrobial" refers to a group of drugs that includes antibiotics, antifungals, antiprotozoals, and antivirals.

Antibiotics: An antibiotic is a substance or compound (also called chemotherapeutic agent) that kills or inhibits the growth of bacteria. Antibiotics belong to the group of antimicrobial compounds used to treat infections caused by micro-organisms, including fungi and protozoa. Antibiotic and antimicrobial, these two terms are now regarded as synonymous to each other.

ANZECC: Australia and New Zealand Environment Conservation Council.

ARMCANZ: Agriculture and Resource Management Council of Australia and New Zealand.

Artificial mussels (AM): The 'Artificial Mussel (AM)' is passive sampler device that collects or accumulates metals through a diffusion barrier onto a sorbent medium.

Bio-accumulative: Substances which are actually or potentially very bio-accumulative are those substances with a BCF >10,000 or a log K_{ow} >3; Log K_{ow} > 5 (greatest concern) (unless BCF <50,000). Log K_{ow} >4 (high concern) (unless BCF <500) [BCF= Bio-concentration factor].

BCF (Bio-concentration factor): 1. A unit less value describing the degree to which a chemical can be concentrated in the tissues of an organism in the aquatic environment. 2. Bioconcentration factor (BCF) is the concentration of a particular chemical in a biological tissue per concentration of that chemical in water surrounding that tissue. That is, a dimensionless number representing how much of a chemical is in a tissue relative to how much of that chemical exists in the environment. BCF= Concentration in organism/ Concentration in Environment. 3. Bioconcentration refers to uptake of chemical from water via respiratory surface and/or skin. In contrast, Biomagnification refers to uptake from food, whereas Bioaccumulation refers to total uptake (water plus food) process (combination of bioconcentration & biomagnifications) (Arnot and Gobas 2006).

Biodiversity: The number and variety of organisms found within a specified geographic region. Biodiversity is a measure of the health of ecosystems.

Blue-green algae: Primitive single or multi-celled algae, characterized by the absence of a nucleus and other membrane bound organelles and often by their blue-green colour.

Carcinogenic: The term carcinogen refers to any substance, radionuclide or radiation that is an agent directly involved in the promotion of cancer or in the increase of its propagation. This may be due to the ability to damage the genome or to the disruption of cellular metabolic processes.

Contaminant: Any biological, chemical, physical and radiological substance or matter that has an adverse response (effect) on air, water, soil or living things.

Concentration: The amount of active ingredient or pesticide equivalent in a quantity of diluents.

Cyanobacteria: Also known as blue-green algae, blue-green bacteria or Cyanophyta, is a phylum of bacteria that obtain their energy through photosynthesis. The name 'cyanobacteria' comes from the colour of the bacteria (Greek: κυανός (kyanós) = blue).

Domestic & stock water (D&S): This is a small water entitlement, for supplying households, watering of cattle and other stock, water of animals kept as pets. D&S water is untreated and are not to be used for human consumption or drinking.

EC_{50}: The concentration of material in water that is estimated (median effective concentration) to be effective in producing some lethal (toxic) response in 50% of the test organisms.

Ecological/environmental risk assessment: see ERA

Ecosystem: Community of organisms interacting with each other and the chemical and physical factors making up their environment.

EDCs: Endocrine disrupting chemicals such as 17β-estradiol, 17α-ethynylestradiol, atrazine, endosulfan, cadmium,

ERA: Environmental/ecological risk assessment. It is an estimation of risk (high, medium, low or nil) (quantity or quality) and is a process for analyzing and evaluating the possibility of adverse ecological effects caused by environmental pollutants or toxicants or stressors such as pesticides and metals on ecological receptors. The concept of ecological risk assessment can be best defined as "a way of examining risks so that they may be better avoided, reduced, or otherwise managed" (Wilson and Crouch 1987).

Exposure: Risk= hazard x exposure including time and pathways

Food security: Refers to a household's physical and economic access to sufficient, safe, and nutritious food that fulfills the dietary needs and food preferences of that household for living an active and healthy life.

G-MW: Goulburn Murray Rural Water Corporation

Goulburn River: The Goulburn River is a major inland river in Victoria, Australia. The headwaters of the Goulburn River rise in the western end of the Victoria Alps, near Mount Buller. The Eildon Dam (on the upper Goulburn River) creates Lake Eildon, a major storage of water for irrigation. From Lake Eildon, most of the irrigation water goes to Goulburn Weir and Waranga Basin. North of Eildon the Goulburn River enters the northern plains of Victoria and eventually flows into the Murray River near Echuca. This area is a very productive irrigated agricultural area.

Guideline trigger values: These are the concentrations (or loads) of the key performance indicators measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur. They indicate a risk of impact if exceeded and should 'trigger' some action, either further ecosystems specific investigations or implementation of management /remedial actions.

Half-life (T ½): The time required for half of the residue to lose its analytical identity whether through dissipation, decomposition, metabolic alteration or other factors.

Harm: Potential adverse effect of an event.

Harmful chemicals: Harmful chemicals define here are those chemicals which are persistent, bio-accumulative and toxic or produce chronic effects in nature that may pose a threat to water security, food security, biodiversity and can be carcinogenic to humans.

Hazard: (1) Likelihood that exposure to a chemical will cause an injury or adverse effect under the conditions of its production, use or disposal; (2) The potential or capacity of a known or potential environmental contaminant to cause adverse ecological effects.

Heavy metals: are a group of metallic elements with an atomic weight greater than 20 such as copper, mercury, chromium, nickel, zinc.

Hydrophobic: Lacking affinity for water (non-polar).

Irrigation: Irrigation is the deliberate application of water to land for the purpose of agricultural production. Effective irrigation will influence the entire growth process from seedbed preparation, germination, root growth, nutrient utilisation, plant growth and regrowth, yield and quality.

LC_{50}: The concentration of material in water that is estimated to be lethal to 50% of the test organisms. The LC_{50} is usually expressed as a time-dependent value, e.g. 24 hour or 96 hour; LC_{50}, the concentration estimated to be lethal to 50% of the test organisms after 24 or 96 hours of exposure.

LD_{50}: The dose of material that is estimated to be lethal to 50% of the test organisms. Appropriate to use with test animals such as rats, mice and dogs. It is rarely applicable to aquatic organisms because it indicates the quantity of a material introduced directly into the body by injection or ingestion rather than the concentration of the material in water in which aquatic organisms are exposed during toxicity tests.

Log Kow: Logarithm of the octanol/water partitioning coefficient. It quantifies the liphophilicity of a substance and is assumed to be an index of the ability to pass through biological membranes and to bio-accumulate in living organisms. It is utilized as a measure of the affinity of a pesticide for the biota. Bio-accumulating pesticides have a Log K_{ow} >3.

LOEC: Lowest observable effect concentration.

Microcystin: One of the groups of toxins produced and released by cyanobacteria is called microcystin named from the species *Microcystis aeruginosa*. The microcystins are a group of cyclic heptapeptide hepatotoxins produced by a number of cyanobacterial genera. The peptide ring is made up of two protein amino acids and five non-protein amino acids. It is the two protein amino acids that distinguish microcystin types from each other, while the other amino acids are relatively constant. By using amino acid single letter code classification, each microcystin is designated a name depending on the variable amino acids which complete their structure. For instance, one of the most common toxins found in water supplies around the world, microcystin-LR contains the amino acids Leucine (L) and Arginine (R) in these variable positions.

ML: megalitres. 1 ML= one million litres.

Murray River: The Murray River, or River Murray, is Australia's second-longest river in its own right (the longest being its tributary the Darling).

NOEC: No observed effect concentration. NOEC is a hazard assessment parameter that represents the concentration of a pollutant that will not harm the species involved, with respect to the effect that is studied. It is often the starting point for environmental policy.

NOEL: No observed effect level, the highest tested concentration at which no adverse effect was observed.

Octanol-water partition coefficient (K_{ow}): see Log K_{ow}

Outfall: Regulating structure located at the downstream end, or intermediate points, of a supply channel to allow safe discharge of surplus flows arising in the system due to the effects of rainfall inflow, planned channel shutdown or operational error. An outfall can also be used to drain water from the channel at the end of the irrigation season.

Passive sampling: A device that collects or accumulates pollutants (e.g. pesticides) independently through
a diffusion barrier onto a sorbent medium without use of a vacuum source or energy.

Persistent (P): a substance is persistent if it does not decay to half of its original quantity within two months (if in water) or six months (if in soil or sediment).

Pesticides: A chemical used to kill pests. They are broadly used to protect crops, livestock and other animals and plants from insect-pests and diseases. They are classified as herbicides, insecticides and fungicides (e.g. glyphosate, endosulfan, ziram).

PNEC: Predicted no effect concentration.

Pollutant: It is a general term for a chemical or non-chemical agent present at an elevated level in the environment and can cause adverse effects (see also contaminant).

Receptors: (a) The organisms of concern or ecosystem component(s) that are being investigated or threatened or endangered animals, or local populations of a single spices or communities consisting of multiple species. This is a general term referring to a species, a group of species, an ecosystem function or characteristic, or a specific habitat or biome, people, environmentally sensitive zone; (b) environmental resources, including plant and animal species, humans, sensitive environments and habitats, water supply wells, and locations that have the potential to be, or have actually been, exposed to contamination. In exposure assessment, an organism that receives, may receive, or has received environmental exposure to a chemical.

Residue: That quantity of pesticide, its degradation products, and/or its metabolites remaining on or in the soil, plant parts, animal tissues, whole organisms, and surfaces

Risk: 1. A statistical concept defined as the expected likelihood or probability of undesirable effects resulting from a specified exposure to known or potential hazardous environmental concentrations of a material. A material is considered safe if the risks associated with its exposure are judged to be acceptable. If the hazard= O there is no risk; no exposure= no risk. 2. The product of the likelihood event multiplied by the potential harm.

Risk assessment: A qualitative or quantitative evaluation of the environmental and/ or health risk resulting from exposure to a chemical or physical hazardous agent (pollutant). Risk assessment or "site-specific risk assessment" means a site-specific characterization of the current or potential threats that may be posed to human health and the environment by contamination migrating to or in groundwater or surface water, discharging to the air, leaching through or remaining in soil, bio-accumulating in the food chain, or other complete and significant exposure pathways identified in the Site Conceptual Exposure Model (SCEM). ***Key components of a risk assessment*** are the ***identification of hazard*** (i.e., identifying site-related chemicals and their concentrations in the exposure media), ***exposure assessment*** (identifying complete and significant exposure pathways (air, water and food) and quantifying intake, ***toxicity assessment*** (identifying the toxic effects and dose-response [toxicity value]), risk characterization, and discussion of uncertainties. For the purposes of these regulations, a Tier 3 Risk Assessment is considered a "site-specific risk assessment."

River: A river is a large natural waterway. The source of a river may be a lake, a spring, or a collection of small streams, known as headwaters. From their source, all rivers flow downhill, typically terminating in the ocean.

Run-off: That portion of precipitation which is not absorbed into the soil, but flows into surface streams

Sub-lethal: Having an effect less severe than death.

Surface water: Water in open bodies such as streams, rivers, ponds, lakes and oceans.

Trace metals: Trace metals are metals in extremely small quantities typically in the ppm range (μg to ng/l), almost at the molecular level, that reside in or are present in animal and plant cells and tissue. They are a necessary part of good nutrition, although they can be toxic if ingested in excess quantities. Trace metals may come from industrial contamination or natural deposits. They can cause increased cancer risk, damage to organs and changes in blood chemistry.

Toxicant: A substance or material capable of producing an adverse response (effect) in a biological system, seriously injuring structure and/or function or producing death.

Toxicity: The degree to which a substance can harm humans or animals. Toxicity can be acute, subchronic or chronic. *Acute toxicity* involves harmful effects in an organism through a single or short-term exposure. *Subchronic toxicity* is the ability of a toxic substance to cause effects for more than one year but less than the life time of the exposed organism. *Chronic toxicity* is the ability of a substance or mixture of substances to cause harmful effects over an extended period, usually upon repeated or continuous exposure, sometimes lasting for the entire life of the exposed organism. According to UK Department for Environment, Food and Rural Affairs (Defra) toxicity= LC_{50}/EC_{50} < 1mg/l or NOEC <0.11 mg/L. A substance can be classed as being of concern if it is lethal to at least 50% of test aquatic organisms of a concentration of 0.1 mg/l or less (http://www.defra.gov.au/environment/chemicals/csf/concern/index.htm).

Toxicity test: A procedure to measure of the degree of response of an organism exposed to a particular concentration of a chemical or a particular level of some other environmental variable.

TRIMPS: passive samplers. i.e., .2,2,4-trimethylpentane containing passive samplers or TRIMPS

Uptake: A process by which materials are absorbed and incorporated into a living organism

Water security: Water security is the capacity of a population to ensure that they continue to have access to pure drinking water and other beneficial water usage including irrigation, farming, recreation, and healthy functioning of the ecosystem service.

Water quality: Water quality refers to the physical, chemical and biological characteristics of water. It is a measure of the condition of water relative to the requirements of one or more biotic species and or to any human need or purpose.

Waterways: River, creeks, channels, drains, lakes, wetlands.

1. Introduction

Goulburn Murray Rural Water Corporation, Tatura, Victoria, Australia (G-MW) carried out a number of environmental or ecological risk assessments of harmful chemicals commencing in 2001 via various research and investigations and literature reviews as part of environmental and natural resources management programmes (called here as "ERA"). *Harmful chemicals define here are those chemicals which are persistent, bio-accumulative and toxic in nature that may pose a threat to water security, food security, biodiversity and can be carcinogenic to humans- see Tables 1 to 6.* It has been identified that at least six group of chemicals or toxicants can cause a threat to G-MW business as listed in Tables 1 to 6. They are likely to originate from a number of sources or causes within the G-MWs catchment such as agriculture, livestock and aquaculture or old and new mining or natural origin (mineralization of rocks) or climate change/climate variability impacts. They are pesticides, trace metals, endocrine disrupting chemicals, dioxins, livestock pharmaceuticals, and algal biotoxins. G-MW suspected that water contaminated with the above harmful chemicals can be unsuitable for irrigation, stock and domestic supply, raw town supply, recreation, aquatic ecosystems protection, biodiversity, fish farming/aquaculture, and human health (see Rose and Kibria 2006; Kibria et al. 2010a). G-MWs ERA cover the risk to all ecosystems (water security, food security, biodiversity, flora and fauna, aquatic ecosystems protection and human health) that is supported by water, including humans.

In order to assess the risks and minimize or reduce the risks from the identified chemicals (Tables 1 to 6), G-MW cooperated and collaborated with the Australia's federal government departments (e.g. The Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia); and state government departments (e.g. Department of Primary Industries, Victoria (DPI); Centre for Ecotoxicology, NSW Department of Environment, Climate change and Water (DECCW)) and Universities (RMIT University, Melbourne, Australia; University of Technology, Sydney, Australia; and City University of Hong Kong and the University of Hong Kong).

The present document is a synthesis of information of ERA model developed over the years and is based on actual risk assessment carried out on toxicants (pesticides, herbicides and trace metals- the two common group of chemicals found in the G-MW region; Tables 1 and 2)). However, the preliminary risks of other four identified chemicals group (e.g. endocrine disrupting chemicals, dioxins, livestock pharmaceuticals, and cyanobacterial toxins) are also included (Tables 3-6) for the purpose of reference, and prioritization for future work. The ERA model developed highlights the rational for G-MWs ERA, the main steps undertaken in the ERA and results or outcomes of ERA conducted on pesticides, herbicides and trace metals. The author led all of these ERA (as G-MWs project manager in collaboration with federal, state and regional government departments and Universities) and the document is based on his involvement and practical experiences gained.

Table 1: *Hazards identified (pesticides, herbicides and fungicides) in G-MW catchment and their possible threats to environmental ecosystems, food security, water security, biodiversity, and human health* *[note: B= Bio-accumulative, EDC= endocrine disrupting chemicals; H= herbicides; I= insecticide; IARC= International Agency for Research on Cancer; F= fungicide; LOEC= Lowest tested concentration at which noted effect occurred; NA= not available T= Toxic; PNEC= predicted no effect concentration; NOEC= no observed effect concentration; pg=picogram (one trillionth of a gram)].*

Chemicals group and examples	Possible source(s) in the catchment	Physicochemical characteristics (Log K_{ow}, half life, bioconcentration) and toxicity and guideline values	Listed hazards and their effect to environment, biodiversity, water security, food security (examples)	Specific effects to humans (hazardous or carcinogenic or EDCs) * *Bold== detected in G-MW region*
1.Pesticides *(e.g. Atrazine (H), Azinphos methyl (I), Chlorpyrifos (I), Copper hydroxide (F), Endosulfan (I), Molinate (H), Parathion methyl (I)).*	Agriculture (vegetables including tomatoes; pasture; orchards including stone & pome fruit and viticulture; cereals (oats, wheat, rice, & barely) and livestock (beef cattle, dairy, sheep, goat, poultry, piggery and aquaculture).	***Log K_{ow}*:**Atrazine: 2.5; Azinphos methyl: 2.96; Chlorpyrifos: 4.7; Copper hydroxide: 0.44; Endosulfan including α, β and endo sulphate: 4.74 to 4.9; Molinate: 2.88; Parathion methyl: 3 (Tomlin 2006). ***Half-life:*** Atrazine: 16-77 days; Azinphos methyl: several weeks; Chlorpyrifos: 33-56 days; Endosulfan: 30-70 days; Molinate: 8-25 days; Parathion methyl: 14 days (Tomlin 2006). ***Bioconcentration factors:*** Atrazine: (86, based on water solubility) (USEPA 2003a); Endosulfan sulphate: (2263 to 2936, mosquito fish (Hoang et al. 2011); Molinate: (25 to 31, catfish) (Martin et al.1992). ***Toxicity-LC_{50} (freshwater fish)*:** Atrazine: 4.5 to 11 mg/L; Azinphos methyl: 0.02 mg/L; Chlorpyrifos: 0.007 mg/L; Copper hydroxide: 10 mg/L; Endosulfan: 0.002 µg/L; Molinate: 13 mg/L; Parathion methyl: 0.04 µg/L (Tomlin 2006). ***Freshwater trigger value (99% or 95% aquatic species protection):*** Atrazine: 13 µg/L; Azinphos methyl: 0.01 µg/L; Chlorpyrifos: 0.01 µg/L; Endosulfan: 0.03 µg/L; Molinate: 3.4 µg/L; Parathion methyl: 0.004 µg/L (ANZECC & ARMCANZ 2000). ***Australia drinking water guideline values:*** Atrazine : 0.0001 mg/L; Azinphos methyl: 0.002 mg/L; Chlorpyrifos:NA; Endosulfan: 0.00005 mg/L; Molinate: 0.0005 mg/L; Parathion methyl:0.0003 mg/L (NHMRC, NRMMC 2011).	- water contaminated with pesticides can be unfit for human consumption, irrigation, food processing, livestock drinking, recreation use, aquatic ecosystems protection and aquaculture (Rose and Kibria 2007). - pesticides can kill fish, tad poles, birds and bees (pollinators) (Helfrich 1996; Ralof et al 1998; Cornell University 2007; Palmer et al. 2007). -copper sulphate (uses to kill aquatic plants) is very toxic to fish and other aquatic organisms (Helfrich 1996). -endosulfan may cause behavioural and growth abnormalities in frogs (tadpoles) (Science Daily 2006). - exposure of endosulfan (I) to Murray cod decreased in the length of fish larvae and affected larval behaviour but didn't result in any deaths in Murray cod larvae; exposure of acrolein (H) caused in reduction in fish length, yolk sac length and heart rate (Raymond et al. 2006). -Murray river rainbow fish were found very sensitive to both endosulfan and acrolein as low as 1 µg/L (Raymond et al. 2006). - Carbaryl (15 mg/L) caused reduced survival and reduced swimming ability in Gray tree frog*, Hyla versicolor* (tadpoles) (Mann et al. 2009). - DDT caused thinning of egg shells and reduction in the reproductive success of carnivorous birds such as, peregrine falcon (Vos et al. 2000).	***Atrazine** (evidence of carcinogenic; evidence of endocrine disrupting) *Amitrol* (carcinogenic to animals but not humans; priority EDC in Germany) ***Azinphos methyl** (extremely hazardous) *Bifenthrin* (possible human carcinogenic) *Chlorothalonil* (may cause cancer) *Carbaryl* (likely to be carcinogenic; suspected to be EDC by EU) ***Chlorpyrifos** (moderately hazardous) ***Copper** *DDT/DDD* (probably human carcinogenic; priority EDC in Germany) ***Endoulfan**, (moderately hazardous; evidence of endocrine disrupting) *Esfenvalerate* (moderately hazardous) *Mancozeb* (carcinogenic to animals but not to humans) ***Parathion methyl** (extremely hazardous, evidence of carcinogenic) ***Metiram*** (carcinogenic to animals but not to humans) *Methomyl* (highly hazardous) ***Molinate** (moderately hazardous, evidence of carcinogenic) *Omeothate* (moderately hazardous) ***Parathion methyl** (extremely hazardous, not classifiable to carcinogenicity to humans; potential for endocrine disruption) *Pendimethalin* (possible human carcinogenic) *Thiodicarb* (carcinogenic to animals but not to humans) *Thiram* (not carcinogenic to humans; endocrine disrupting substance) *Phosphmet* (not carcinogenic) *Ziram* (likely to be carcinogenic; potential for endocrine disruption) (PAN 2005; IARC 2006; Rose and Kibria 2006; Rose and Kibria 2007). - pesticide residues can enter into human body via food chains or drinking water & may cause cancer and other tumours; brain and nervous system damages; birth defects; miscarriages, infertility, male sterility and other reproductive problems. It may also cause damage to liver, kidneys, lungs and other body organs (WHO/UNEP 1999).

Table 2: ***Hazards identified(heavy metals/trace metals) in G-MW catchment and their possible threats to environmental ecosystems, food security, water security, biodiversity, and human health*** *[note: B= Bio-accumulative, EDC= endocrine disrupting chemicals; H= herbicides; I= insecticide; IARC= International Agency for Research on Cancer; F= fungicide; LOEC= Lowest tested concentration at which noted effect occurred; NA= not available T= Toxic; PNEC= predicted no effect concentration; NOEC= no observed effect concentration; pg=picogram (one trillionth of a gram)].*

Chemicals group and examples	Possible source(s) in the catchment	Physicochemical characteristics (Log K_{ow}, half life, bioconcentration) and toxicity and guideline values	Listed hazards and their effect to environment, biodiversity, water security, food security (examples)	Specific effects to humans (hazardous or carcinogenic or EDCs) * == *detected in G-MW region*
Heavy metals/trace metals *(e.g. Copper (Cu), Cadmium (Cd), Lead (Pb), Mercury (Hg), Nickel (Ni), and Zinc (Zn)).*	- Cadmium (phosphate fertilizers; farmyard manures; fossil fuel combustion; sewage sludge; incineration; mine tailings; natural such as parental rock material) (Marcotullio 2007). - Copper (copper fungicide; fertilizers; farmyard manures; sewage sludge; copper dust; natural such as parental rock material; old mine) (Marcotullio 2007). - Lead (farmyard manures; mining; sewage sludge; natural such as parental rock material) (Marcotullio 2007). - Mercury (fertilizers; pesticides; lime; manures; sewage sludge; natural such as parental rock materials) (Marcotullio 2007). - Zinc (fertilizers; pesticides; fossil fuel combustion; sewage sludge; natural such as parental rock) (Marcotullio 2007).	***Bio-concentration factors:*** Cd: (10,000 to 20,000, mussel); Cu: (100 to 26,000, various aquatic species); Hg- (MeHg): (1,000,000 to 100, 000,000, fish); Pb: (499 to 1700, invertebrates and fish); Zn: (50 to 1130, freshwater animals) (ANZECC & ARMCANZ 2000; Spear & Pierce 1979; Cossa 1988; USEPA 1985; USEPA 1987). ***Toxicity to freshwater*:** Hg>Cu> Cd> Pb> Zn (Brown 1968). ***Toxicity values for freshwater fish (NOEC)*:** Cd: 0.49 µg /L to 767 µg /L; Cu: 2.6 µg /L to 131 µg /L; Pb: 5.65 µg/L to 43 µg/L; Hg: 0.14 µg/L to 1271 µg/L; Zn: 24 µg/L to 1316 µg/L (ANZECC & ARMCANZ 2000). ***Freshwater trigger value (99% or 95% aquatic species protection):*** Cd: 0.2 µg/L; Cu: 1.4 µg/L; Pb: 3.4 µg/L; Hg: 0.06 µg/L; Zn: 8.0 µg/L (ANZECC & ARMCANZ 2000). ***Australian drinking water quality guidelines****:* Cd: 0.002 mg/L; Cu: 2 mg/L; Pb: 0.01 mg/L; Hg: 0.001 mg/L; Zn: <3mg/L (NHMRC 2004).	- water contaminated with metals can be unfit for human consumption, irrigation, food processing, livestock drinking, recreation use, aquatic ecosystems protection and aquaculture (Kibria et al. 2010b). - higher levels of cadmium, copper, lead, mercury can affect survival and growth of aquatic organisms (e.g. fish) (ANZECC & ARMCANZ 2000). - metals may cause fish population decline as a result of increased susceptibility to diseases or mortality or reduced fecundity (Kibria et al. 2010b). - metals pollution can cause reduce biodiversity, eliminate sensitive species or reduce species abundance (Kibria et al. 2010a). - cultivation of crops for human or animal consumption on contaminated soil can potentially lead to uptake and accumulation of trace metals (Cd, Pb) in edible plant parts with a resulting risk to human and animal health (Mills et al. 2004; Jamali et al. 2009; Peralata-Videa et al. 2009). -exposure of humans to heavy metals can cause damage to the kidney and nervous system. Lead and cadmium are considered as potential carcinogen (Zhuang et al. 2009; Peralta-Videa et al. 2009).	***Cadmium** (carcinogenic to humans; IARC class 1; EDCs). ***Copper** (not classifiable as to carcinogenicity in humans-IARC class 3). ***Lead** (probably carcinogenic to humans; IARC class 2B, EDCs) ***Mercury** (possibly carcinogenic to humans; biomagnify up the food chain; inorganic mercury IARC class 3, EDCs). ***Zinc (**Not classified by IARC) (PAN 2005; IARC 2006; Rose and Kibria 2006; Rose and Kibria 2007). -Organomercurials are readily absorbed into fish and can make its way up the food chain through fish. The major toxic effects of methyl mercury (MeHg) are on the nervous system. In addition, the surviving victims and their offspring displayed mental retardation, cerebral palsy, muteness, which was observed in children exposed while in the foetal stage (Bubb and Lester 1999; ANZECC & ARMCANZ 2000; Peralta-Videa et al. 2009).

Table 3: *Hazards identified (Endocrine disrupting chemicals) in G-MW catchment and their possible threats to environmental ecosystems, food security, water security, biodiversity, and human health* *[note: B= Bio-accumulative, EDC= endocrine disrupting chemicals; H= herbicides; I= insecticide; IARC= International Agency for Research on Cancer; F= fungicide; LOEC= Lowest tested concentration at which noted effect occurred; NA= not available T= Toxic; PNEC= predicted no effect concentration; NOEC= no observed effect concentration; pg=picogram (one trillionth of a gram)].*

Chemicals group and examples	Possible source(s) in the catchment	Physicochemical characteristics (Log K_{ow}, half life, bioconcentration) and toxicity guideline values	Listed hazards and their effect to environment, biodiversity, water security, food security (examples)	Specific effects to humans (hazardous or carcinogenic or EDCs) * == *detected in G-MW region*
Endocrine disrupting chemicals (EDCs) *(e.g. Hormones) 17β-Estradiol (E2), 17α-ethynylestradiol (EE2).*	Livestock farming; wastewater effluent (run-off and waste water discharge from intensive dairy, beef-cattle, poultry pigs and aquaculture farms); sewage treatment plants; contraceptive pills.	***Log K_{ow}:*** 17β-Estradiol (E2)- 3.94 to 4.01; 17α-ethynylestradiol (EE2)- 3.67 to 4.15 (Campbell et al. 2006; Williams et al. 2007; Nagpal and Meays 2009). ***Half-life:*** 17β-Estradiol (E2)~ 13 hours; 17α-ethynylestradiol (EE2)- 33±13 hours (Nagpal and Meays 2009; *http://en.wikipedia.org/wiki/Estradiol/ Ethinylestradiol*). ***Bioconecntration factors:*** EE2: 15849 (Lai et al. 2002; Nagpal and Meays 2009). ***Toxicity: LC_{50} (freshwater fish)**:*17β-Estradiol (E2) NA; 17α-ethynylestradiol (EE2)- 16 mg/L (Crane et al. 2006); EE2 (NOEC): range 0.2-261 ng/L (Nagpal and Meays 2009); EE2 (LOEC): range 1-500 ng/L (Nagpal and Meays 2009). ***Freshwater trigger value (PNEC):*** 17β-Estradiol (E2): 1 ng/L; 17α-ethynylestradiol (EE2): <0.1 ng/L (Williams et al. 2007; Goonan 2008). ***Freshwater aquatic life protection:*** EE2: <0.5 ng/L (Nagpal and Meays 2009). ***Australian water quality guidelines (recycled water):*** 17β-Estradiol (E2): 175 ng/L; 17α-ethynylestradiol (EE2): 1.5 ng/L (NWQMS 2008).	-Natural and synthetic estrogens have been detected in different environmental compartments (e.g. surface waters, sediments) from Australia, Belgium, Canada, China, France, Germany, Japan, Israel, Italy, Spain, the Netherlands, UK, and USA (Purdom et al. 1994; Manning 2005; Andrew et al. 2008; Matozzo et al. 2008; Jugan et al. 2009; Kawahara et al. 2009). -Estrogens such as EE2, and E2 are more potent EDCs and likely to pose greatest effect to the environment and wildlife. EE2 as low as 0.1 ng/l and E2 as low as 1.0 ng/l can cause increased level of vitellogenin (an egg yolk precursor protein) in fish (Sumpter and Jobling 1995; Hansen et al. 1998; Metcalfe et al. 2000). -17β-Estradiol (E2): 0.01-5000 ppb (LOEC) caused the following effects on fish Medaka: No egg production; high mortality; reduced egg production; decreased male sexual behaviour; all female fish; males with testis-ova; reduced male GSI, egg production and fertility; decreased egg hatch; more phenotypic females than males (Mills and Chichester 2005;Hecker et al. 2006; Hogan et al. 2008; Gyllehammar et al. 2009). -17α-Ethynyl estradiol (EE2): fish Medaka (0.01-0.488 ppb-LOEC). All males with testis ova; more females than males; high mortality with only females surviving; reduced egg production and high male mortality (Mills and Chichester 2005;Hecker et al. 2006; Hogan et al. 2008; Gyllehammar et al. 2009).	-sediments, periphyton and fish can accumulate natural and synthetic estrogens and thereby through diet (food chain) human can get accumulation of natural and synthetic estrogens (Viganó et al. 2008).

Table 4: ***Hazards identified (livestock pharmaceuticals) in G-MW catchment and their possible threats to environmental ecosystems, food security, water security, biodiversity, and human health*** *[note: B= Bio-accumulative, EDC= endocrine disrupting chemicals; H= herbicides; I= insecticide; IARC= International Agency for Research on Cancer; F= fungicide; LOEC= Lowest tested concentration at which noted effect occurred; NA= not available T= Toxic; PNEC= predicted no effect concentration; NOEC= no observed effect concentration; pg=picogram (one trillionth of a gram)].*

Chemicals group and examples	Possible source(s) in the catchment	Physicochemical characteristics (Log K_{ow}, half life, bioconcentration) and toxicity and guideline values	Listed hazards and their effect to environment, biodiversity, water security, food security (examples)	Specific effects to humans (hazardous or carcinogenic or EDCs) * == *detected in G-MW region*
Pharmaceuticals (livestock) *(e.g. Antibiotics-Amoxicillin, Erythromycin, Oxytetracycline, sulphonamides sulfadimethoxine, sulphadimidine, sulphapyridine), Tetracycline)*).	Livestock effluents, manures.	***Log K_{ow}:*** Amoxicillin- 0.97; Erythromycin- 3.06; Oxytetracycline-2.08; Tetracycline -1.33 (Daughton and Ternes 1999; Thiele-Bruhun 2003; Chenxi et al. 2008). ***Half-life:*** Amoxicillin- 61.3 minutes; Erythromycin- 1.5 hours; Oxytetracycline- 6-8 hours; Sulfonamides: 10 hours; Tetracycline- 6-11 hours (http://en.wikipedia.org/wiki/Amoxicillin/erythromycin/oxytetracycline/sulfonamides/tetracyclines). ***Bioconcentration factors:*** Erythromycin***:*** 4492 L/kg (Gao et al. 2012). ***LC_{50} (freshwater fish)****:* Amoxicillin- >182.7 mg/L; Erythromycin- 80 to 410 mg/L; Oxytetracycline- 62.5 mg/L; Tetracycline -182-220 mg/L (Enick and Moore 2007;Sanderson and Thomsen 2009). ***Freshwater trigger value (99% or 95% aquatic species protection):*** NA. ***Australian water quality guidelines (recycled water):*** Amoxicillin- 7000 µg/L; Erythromycin- 175 µg/L; Oxytetracycline- 105 µg/L; Tetracycline - 105µg/L (NWQMS 2008).	-pharmaceutical ingredients (including antibiotics) have been reported to be ubiquitously present in sewage treatment effluents, other wastewaters (hospital wastewaters), surface waters and groundwaters, sediments and drinking water reservoirs in the ng/l to µg/l range (Boxall 2004; Hernando et al. 2006; Mompelat et al. 2008; Kümmerer 2009; Watkinson et al. 2009). -The impact of pharmaceuticals on environment include negative effects on fish, crustaceans (daphnids), algae, bacteria, earthworms, plants and dung invertebrates, in particular, algae and bacteria were found to be in general more sensitive to pharmaceuticals than zooplankton and fish (Boxall et al. 2003; Boxal 2004). -The spread of antibiotics in the environment can contribute to bacterial resistance or transfer of drugs through food chain. For example, sulfonamides and tetracyclines have high persistence and adsorption capability, therefore repeated application of manure containing such residues to agricultural field can risk contamination of the food chain (Kümmerer 2004; Kümmerer 2009) .	-Pregnant women and their babies, as well as children, are at particular risk from consumption of drinking water contaminated with pharmaceuticals. Some of the drugs that are of high risk during pregnancy and breast feeding and are detected in drinking water are aspirin, atenolol, carbamazepine, clofibric acid, cyclophosphamide, diazepam, gemfibrozil, oxytetracycline, tetracycline and sulfamethoxazole (Collier 2007).

Table 5: *Hazards identified (Dioxins) in G-MW catchment and their possible threats to environmental ecosystems, food security, water security, biodiversity, and human health* *[note: B= Bio-accumulative, EDC= endocrine disrupting chemicals; H= herbicides; I= insecticide; IARC= International Agency for Research on Cancer; F= fungicide; LOEC= Lowest tested concentration at which noted effect occurred; NA= not available T= Toxic; PNEC= predicted no effect concentration; NOEC= no observed effect concentration; pg=picogram (one trillionth of a gram)].*

Chemicals group and examples	**Possible source(s) in the catchment**	**Physicochemical characteristics (Log K_{ow}, half life, bioconcentration) and toxicity and guideline values**	**Listed hazards and their effect to environment, biodiversity, water security, food security (examples)**	**Specific effects to humans (hazardous or carcinogenic or EDCs) * ==** ***detected in G-MW region***
Dioxins *(e.g. Polychlorinated dibenzo-p-dioxin or PCDDs, Polychlorinated dibenzofurans or furans or PCDFs & polychlorinated biphenyls or PCBs).*	Natural (bush fires); waste incineration (e.g. municipal, medical waste); compost burning, wood stoves, power generation, metal smelting, chlorine bleaching of pulp and paper mill and the manufacture of some agricultural chemicals (e.g. pesticides, herbicides) and cremation.	***Log K_{ow}:*** PCDDs: 6 to 9; PCBs: 6 to 9 (Gatehouse 2004; Srogi 2008). ***Half-life:*** PCDDs: 9-15 years; PDFs: 7 years (Gatehouse 2004; Srogi 2008). ***Bio-concentration factors:*** PCDD: 130,000; PCDF: 61,000; PCBs: 60,000-270,000 (Gatehouse 2004; Srogi 2008). ***LC_{50} (freshwater fish):*** PCDDs: 65 pg /g (Gatehouse 2004); PCBs (Aroclor 1242: 15-5430 µg/L; PCBs; Aroclor 1254: 0.3-42500 µg/L (ANZECC & ARMCANZ 2000). ***Freshwater trigger value (99% or 95% aquatic species protection):*** PCDDs: NA; PCBs (Aroclor 1242): 0.3 µg/L; PCBs (Aroclor 1254): 0.01 µg/L (ANZECC & ARMCANZ 2000). ***Ecological screening values:*** USEPA ecological screening values **(soil)** for total PCDDs and total PCBs are 0.199 and 38.6 pg/g bw respectively (USEPA 2003); USEPA ecological screening values **(freshwater)** for total PCDDs and total PCBs are 0.000000003.1 µg/L and 0.000074 µg/L respectively (USEPA 2003). ***Drinking water guideline values:*** 0.0013 pg/L (USEPA 1984).	-Dioxins have been detected in almost all environmental matrices such as air, soil, sediments, vegetation, biota (kangaroo, platypus, birds, fish, shellfish, marine mammals), food (dairy products, beef, pork, chicken, duck, eggs, vegetables, cereals, rice), human women milk, and human blood/serum (Rappe 1996; DEH 2004; Reiner et al. 2006; Birch et al. 2007; LaKind 2007; Tanabe and Kunisue 2007; Mai et al. 2007; Srogi 2008; Li et al. 2009; Zhao et al. 2009). -Dioxins are most potent toxicants at very low concentrations and can disrupt the endocrine, reproductive, immune and nervous system of the offspring of fish, birds and mammals (Gatehouse 2004; Srogi 2008). -Dioxins are highly toxic to fish, birds and mammals but significantly less toxic or non-toxic to amphibians, invertebrates and plants (Gatehouse 2004).	*PCDD/ TCDD* (carcinogenic- IARC class 1, EDC). *Furans* (carcinogenic , IARC class 2B; EDC). *PCBs* (carcinogenic, IARC class 2A; EDC) (Gatehouse 2004; IARC 2006). -Dioxin exposure has been linked to birth defects, inability to maintain pregnancy, decreased fertility, reduced sperm counts, endometriosis, diabetes, learning disabilities, lung problems; and lowered testosterone levels (Srogi 2008; http://www.ejnet.org/dioxin/).

Ecological screening values are concentrations of contaminants in soil or water that are protective of ecological receptors that commonly come into contact with soil or water ingest biota that live in or on soil and water.

Table 6: ***Hazards identified (algal toxins) in G-MW catchment and their possible threats to environmental ecosystems, food security, water security, biodiversity, and human health*** *[note: B= Bio-accumulative, EDC= endocrine disrupting chemicals; H= herbicides; I= insecticide; IARC= International Agency for Research on Cancer; F= fungicide; LOEC=*
Lowest tested concentration at which noted effect occurred; NA= not available T= Toxic; PNEC= predicted no effect concentration; NOEC= no observed effect concentration; pg=picogram (one trillionth of a gram)].

Chemicals group and examples	**Possible source(s) in the catchment**	**Physicochemical characteristics (persistent, half life, bioconcentration) and toxicity and guideline values**	**Listed hazards and their effects to environment, biodiversity, water security, food security (examples)**	**Specific effects to humans (hazardous or carcinogenic or EDCs) * ==** *detected in G-MW region*
6. Algal toxins *(e.g. blue-green algal toxins/cyanobacterial toxins-e.g. microcystins-LR or MC-LR)).*	Natural, agricultural fertilizers/ nutrients (N,P).	***Log K_{ow}:*** MC-LR: 2.18 (pH 1) to – 1.76 (pH 10) (pH dependent) (Gert-Jan De Maagd et al. 1999). ***Half-life* (water):** microcystins: 3 weeks to 10 weeks (WHO 2003). ****Bioconcentration factors:*** 0.6 to 1.7 (muscle of common carp & silver carp); 7.3 to 13.3 for (hepatopancreas of common carp & silver carp) (Adamovsky et al. 2007). ***LD_{50} (freshwater fish):*** 20 to 1500 µg microcystin LR/ kg (Malbrouck and Kestemont 2006). ***LD_{50} (i.p. mouse) of pure toxin*: (**µg/kg bw): MC-LR: 25-150 (Chorus and Bartram 1999). ***Drinking water guidelines***: Microcystin (MC-LR): 1.0-1.3 µg/l (Burch 2008). ***Seafood guidelines:*** 0.04 µg/kg per day of MC-LR (tolerable daily intake) (WHO 2006).	-The cyanotoxins such as microcystins can be taken up by plants (rape, rice and lettuce) and can induce various metabolic and morphological changes such as inhibition of photosynthesis, germination and growth inhibition, decrease in roots development and leaf necrosis (McElhiney et al. 2001; Babica et al. 2006). -Cyanobacterial toxins such as microcystins may be accumulated in organs of freshwater fish, mussels and shrimps. Therefore, the transfer of the microcystins to human through the food web is easily possible (Chorus and Bartram 1999; Ibelings and Chorus 2007; van Apeldoorn et al. 2007; Ibelings and Havens 2008). -Toxic blue-green algae can affect water quality by causing peculiar tastes and odours, discolouration and unsightly scums. Geosmin (E1, 10-dimethyl-E-9-decalol) and MIB (2-methyl isoborneol) accounts for the majority of off-flavour odour (Smith et al. 2008). -Animals that can be killed due to cyanobacterial toxins are birds, cats, cattle, chicken, dogs, ducks, fish, horses, human, lambs, monkeys, sheep, squirrels, pigs, rhinoceros, rodents and invertebrates (de Figueiredo et al. 2004; van Apeldoorn et al. 2007; Stewart et al. 2008).	Microcystin LR is a liver toxin and can cause liver damage. Symptoms of acute microcystin exposure in humans include gastroenteritis's (vomiting, diarrhea, abdominal cramping) and blistering around the mouth (Dyble et al. 2011).

*IARC classifications: Group 1= carcinogenic to humans; Group 2A= probably carcinogenic to humans; Group 2B= possibly carcinogenic to humans; Group 3= not classifiable as to its carcinogenicity to humans; Group 4= probably not carcinogenic to humans; microcystin-LR (common toxins) contains the amino acids Leucine (L) and Arginine (R). *Bioconcentration factors: ratio between the mean/maximum tissue concentration and the average water concentration of 17 µg/L (Adamovsky et al. 2007).*

2. Rationale for G-MWs ERA

G-MW is Australia's largest rural water corporation managing around 70% of Victoria's stored water resources; around 50% of Victoria's underground water supplies. G-MW is responsible for the management of seven river basins (upper Murray, Kiewa, Ovens, Broken, Goulburn, Campaspe and Loddon; see Figure 1) and their associated water supply systems, north of the Great Dividing Range covering approximately 68,000 square kilometres (Figure 1). Each major river basin is composed of the catchment for one or more lesser ***Rivers*** (e.g. Broken, Buffalo, Campaspe, Coliban, Goulburn, Howqua, Jamieson, Kiewa, King, Loddon, Murray, Mitta Mitta, Oven), ***Creeks*** (e.g. Axe, Barr, Bendigo, Broken, Boosey, Fifteen, Ford, Gunbower, Little Snowy, Livingstones, Hollands, Mc Ivor, Merton, Middle, Pyramid, Reedy, Snowy, Sheep wash, Yackandandah), ***Lakes*** (e.g. Dartmouth, Hume, Eildon, Eppalock, Mulwala, Nillacootie) and their tributaries (see Table 7). Waters (Rivers, lakes, creeks, lakes, groundwater and reclaimed water) from seven G-MW catchment region (see Figure 1) are used for a variety of purposes as listed below: (see also Table 7)

Water usages (major)

- Irrigation, mainly pasture, around 95% of the water managed by G-MW is used for irrigation (comprising *dairy-36%, grazing- 33%, cropping & grazing (mixed farming)- 18%, horticulture- 13%) (source: G-MW 1999 fact sheet).*
- environmental flows (the environment uses around 3% of water of G-MW, environmental flows support rivers and sensitive wetlands such as RAMSAR sites including Barmah forest (28,515 hectares), Gunbower forest (19,931 hectares), Kerang wetlands (9419 hectares).
- raw urban water supply/raw town supply (untreated water) (around 2% water of G-MW)

Water usages (minor)

- domestic purpose (showering, bathing, washing).
- industrial (food processing).
- aquaculture/fish farming (trout farms near Snobs Creek, Eildon and some yabby farms across the region).
- recreation (boating, swimming, canoeing, fishing, house boats and caravan parks in lakes and storages).
- reclaimed water/recycled water (used in parks and gardens).

G-MW water customers (G-MW customers are classified by customer groups based on their access to water).

- *Unregulated Rivers and Creeks***:** private diverters (pumpers) whose properties adjoin unregulated rivers and creeks where water flows without control or regulation.
- *Storage Diversions:* private diverters (pumpers) whose properties back directly onto storage.
- *Regulated Rivers:* private diverters (pumpers) who order and access water in regulated river reaches downstream of a storage where flows can be regulated.
- *Diversion Channels in Irrigation Areas:* gravity fed diversion of water from G-MW diversion channels on to a private property channel network via a water wheel or Total Channel Control (TTC) software automated door.

Groundwater bores: customers with a license to extract from a groundwater bore located on their property.

Farm Dams: customers with a license to fill and extract water from a farm dam that fills naturally on their property

Source: http://www.g-mwater.com.au.

G-MWs region including seven River basins (Figure 1) could be a source of a number of harmful chemicals from activities such as **agriculture** (orchards, vines, olives, vegetables, crops (wheat, barley and rice)), **livestock** (beef cattle, dairy, sheep, pig, poultry), and **aquaculture** (trout, yabby). For example, a survey conducted as part of ERA found that 76 pesticides were used to control pest plants and animals across the G-MW region (see Krake et al. 2001, Appendix 1). Moreover fertilizers and pesticides used to grow vegetables, and crops and orchards could be a source of toxic heavy metals/trace metals such as cadmium, chromium copper, lead, manganese mercury, nickel and zinc (Marcotullio 2007; Table 2). New and old mines may also be an additional source of heavy metals (mercury) input into waterways (e.g. AI gold mine in upper Eildon river, Woods Point, Mansfield; Old mines (1800s)- upstream of the Howqua River at Sheep Yard flat, Little Nell, Mountain Chief and Great Rand; Old mines (1800s)- upstream of the Buffalo River at Buckland Valley)) (DH 2011; personal communications- John Herridge (G-MWs, Eildon Office) and Cameron McGregor (Buffalo office), August 2012).

Figure 1: Goulburn Murray region showing six irrigation areas and major Rivers, Creeks, Lakes and Storages.

Table 7: ***Description of seven river basins within G-MWs 68,000 square kilometres catchment and land and water use and important aquatic ecosystems in each basin*** *[http://www.g-mwater.com.au/; http://www.g-mwater.com.au/water-resources/catchments] [note: ML= mega litres; 1 ML= one million litres).*

Basins	Location	Important aquatic ecosystems	Land and water use
Upper Murray Basin- 10,150 km^2 **Irrigation intensity:** water use/total area (4,830 ML/10,150 km^2) = 0.5 ML//km^2	Catchment of Hume reservoirs	*Rivers:* Big, Bundara, and Cobungra, Dart, Gibbo and Mitta Mitta. *Creeks:* Hollands, Larsen, Little Snowy, Little Scrubby, Livingstone, Morass, Snowy, Tallangatta Watchingorra. *Lakes:* Dartmouth Dam (3,906,000 ML capacity), Lake Hume (3, 038,00 ML capacity).	**Water use:** 4,830 ML (Victorian section of the Basin) of which 75% for irrigation mainly for pasture. **Water Storages:** Dartmouth Dam, Kow Swamp, Lake Hume, Lake Boga, Mildura Weir, Torrumbarry Weir (117,500 ML capacity), and Yarrawonga Weir (117,500 ML capacity). **Land use:** Water conservation, forestry, grazing and agriculture. Major (dairying, grazing of sheep for wool and meat, and beef cattle fattening).
Kiewa Basin- 2000 km^2 **Irrigation intensity:** water use/total area (13,160 ML/2000 km^2) = 6.6 ML//km^2	A narrow strip in the north-east of the state	*Rivers:* Kiewa *Creeks:* Middle, Mountain, Yackandandah	**Water use:** 13,160 ML of water are used per year (average year) of which urban and industrial and domestic use accounts for about half the total use, and the other half are used for irrigation (mainly for pasture) and other crops and horticulture. **Water resource:** Surface water (657,000 ML), groundwater (7,000 ML) and recycled water (230 ML). **Water Storages:** Lake Guy (Bogong Village), Mt Beauty Pondage, Pretty Valley Pondage (Bogong High Plains), and Rocky Valley Reservoir. **Land use:** no information is available.
Ovens Basin-7,985 km^2 **Irrigation intensity:** water use/total area (29,580 ML/7985 km^2) = 3.7 ML//km^2	North-east Victoria and the area extends from the Murray River in the north, to the Great Dividing Range in the south and is bordered by the Broken River Basin in the west and the Kiewa River Basin in the east	*Rivers:* Buckland, Buffalo, Catherine, Dandongadale, King, Murray, Oven, Reedy and Rose *Creeks:* Fifteen *Lakes:* Lake Mulwala, Lake Buffalo (23,340 ML), Lake William Hovell	**Water use:** 29,580 ML water are used in the Basin, of which approx. 55% used by private diverters for irrigation and the vast majority of water for urban and industrial use. A small quantity of water is extracted from the groundwater resource for commercial use, and reclaimed water is used for parks and gardens. Water for rural use is all self-extracted from the groundwater resource; approximately half is withdrawn from divertible resources and half from minor sources. **Water resource:** Surface water (1,425,800 ML), groundwater (18,800 ML) and recycled water (2,860 ML). **Water Storages:** Lake Buffalo (23,340 ML), and Lake William Hovell (13,500 ML). **Land use:** *Ovens/King region-* Previously used to grow tobacco (three-quarters of the tobacco grown in Victoria). Others include livestock production, sheep for meat and wool, beef cattle and some *dairying. Central and south-eastern regions-* hardwood logging and forest grazing and agriculture (central region), North-east (forest grazing, beef, wool and fat lamb).
Broken Basin- 7,723 km^2 **Irrigation intensity:** water use/total area (43630 ML/7723 km^2) = 5.7 ML//km^2	The Broken River is one of the tributaries of the Goulburn River in north-eastern Victoria. The River Basin named after it also includes the	*Rivers:* Broken, Goulburn, Murray *Creeks:* Blind, Broken, Boosey, Holland Moonee, Ryans *Lakes:* Lake Nillahcootie (40, 400 ML)	**Water use:** 43630 ML **Water resource:** Surface water (257,500 ML), groundwater (NA) and recycled water (630 ML). **Water Storages:** Lake Nillahcootie (40, 400 ML). **Land use:** Most of the Basin has been cleared for agriculture and are used for grazing, mixed cereal fruit

	catchment of Broken Creek which diverges from the Broken River and flows in a north-westerly direction to the Murray River.		growing, dairying and livestock production.
Goulburn Basin-16191 km^2 **Irrigation intensity:** water use/total area (1547160 ML/ 16191 km^2) = 96 ML//km^2	Central Victoria and extends from the Great Dividing Range near Woods Point, to the Murray River in the north-west near Echuca	*Rivers:* Acheron, Big, Delatite, Goulburn, Howqua, Jamieson, Rubicon and Yea *Creeks:* Ford and Merton *Lakes:* Lake Eildon (3,334, 160 ML)	**Water use:** 1547160 ML **Water resource:** Surface water (1,958,600 ML), groundwater (NA) and recycled water (9,390 ML). **Water Storages:** Goulburn Weir (25,500 ML), Greens Lake (32, 500 ML), Lake Eildon (3,334, 160 ML), and Waranga Basin (432, 360 ML). **Land use:** Hardwood timber production, dairying (Tongala, Tatura and Shepparton) and fruit production (pome and stone fruit) in the north. The Lake Eildon (sheep for wool, beef and dairy cattle), Goulburn Valley (sheep and cropping). Aquaculture (trout and yabby).
Campaspe Basin- 4179 km^2 **Irrigation intensity:** water use/total area (68080 ML/ 4179 km^2) = 16 ML//km^2	North central Victoria. It extends 150 km south from the Murray River to the Great Dividing Range and is 45 km wide at the widest point.	*Rivers:* Coliban and Campaspe *Creeks:* Axe, McIvor, Mt Pleasant and Sheepwash *Lakes:* Lake Eppalock (304,650 ML)	**Water Use**: 68,080 ML; 92% of the water used for irrigation with the rest going to rural use, and urban, domestic and industrial consumption. Much of the water is imported from outside of the Basin, largely from the Goulburn system. **Water resource:** surface water (85,700 ML), groundwater (NA) and recycled water (1,310 ML). **Water Storages:** Lake Eppalock (340, 650 ML), Lauriston, Malmsbury, Upper Coliban. **Land Use:** Most of the Basin has been cleared for agriculture. Agriculture include irrigated agriculture (dairying and fruit) and dry land farming (cereal crops, beef cattle, lambs and wool).
Loddon Basin: 15319 km^2 **Irrigation intensity:** water use/total area (87,720 ML/ 15319 km^2) = 5.7 ML//km^2	Between Daylesford and Creswick, to Swan Hill on the Murray River	*Rivers:* Loddon River. *Creeks:* Barr, Bet Bet, Bullock, Bendigo, Gunbower, Mt Hope, Piccaninny, Tullaroop, Reedy, Pyramid *Swamp:* Kow Swamp	**Water use:** Average annual water use is 87,720 ML, of (95% is used for irrigation) and 5% for urban, industrial and rural use. **Water resource:** Surface water (121,000 ML), groundwater (NA) and recycled water (8,720ML). **Water Storages:** Cairn Curran Reservoir (147,130 ML), Hepburns Lagoon, Laanecoorie Reservoir (8,000 ML), Newlyn Reservoir, Tullaroop Reservoir (72,950 ML). **Land Use:** Mixed grazing of sheep and cattle, crop production, fruit, vegetable and forest industries. Crops (wheat, barley, oats and hay) are grown under irrigation. Pig and poultry farming are also significant.

Livestock effluents and manures could be a source of hormones (endocrine disrupting chemicals or EDCs such as potent 17β-Estradiol or E2, 17α-ethynylestradiol EE2 (Ying and Kookana 2002; Williams et al. 2007; Table 3)) and pharmaceuticals (antibiotics) (Table 4) in the areas (via drainage discharge of farm effluents or from livestock access to G-MWs open channels and drains) (Mompelat et al. 2008). Natural cause or climate change related bush fires/forest fires could be a significant source of dioxins inputs into waterways (Table 5) via aerial transport (http://www.dioxinfacts.org/dioxin_health/dioxin_tissues/threshold.html). Blue green algal blooms/cyanobacterial blooms are common phenomena in the region (lakes) due to damming of rivers, and nutrient inputs (N,P) into waterways (resulting from agricultural activities in the region) (Table 6). Moreover projected climate change related increases of temperature and carbon dioxide (CO_2) may enhance blue-green algal blooms such as proliferation of *Microcystis* spp. which produce toxin microcystins (Håkanson et al. 2007; Moore et al. 2008; Paerl and Paul 2012) and thereby may cause contamination of water and food by microcystins (See Table 6).

It is therefore necessary to ascertain the levels of chemical contaminants in G-MWs supply channels, drains (e.g. 6,300 km channels, 3,000 km drains and 900 km pipes delivering water to domestic and stock and irrigation customers) to establish risk levels and ensure that appropriate measures can be taken to reduce risks from such chemicals. Furthermore, G-MW has a duty of care to ensure that the water it supplies to customers via network of irrigation channels and drains is fit for purpose. As a sustainable water authority, it is also obliged to adapt risk mitigation measures to reduce or minimize any impacts of pollutants (such as pesticides, herbicides, heavy metals) on biodiversity, irrigation water quality, and drinking and recreation water quality and human health and natural water course downstream of channels and drain outfalls.

3. G-MWs ERA mode

G-MWs ERA model was developed (*in collaboration with federal, state and regional government departments and universities as mentioned in section 1*) with the aim to assess risks to all beneficial water usage (= receptors) including irrigation, stock consumption, domestic use (bathing, showering), food processing, raw town water supply, drinking water, flora and fauna, biodiversity (fish), aquaculture, aquatic ecosystems protection, recreation, and humans from possible effects of toxicants such as pesticides, herbicides and trace metals. Though the ERA model developed principally for pesticides, herbicides and trace metals (Tables 1 and 2) but can also be used for assessing risks to other harmful chemicals group such as endocrine disrupting chemicals (EDCs), pharmaceuticals, dioxins, and algal toxins. Preliminary hazards information related to these chemicals group are provided in Tables 3 to 6. Furthermore the risk assessment covers the whole catchment (68,000 square kilometres and including the six irrigation areas-Murray Valley, Shepparton, Central Goulburn, Rochester-Campaspe, Pyramid Hill-Boort and Torrumbarry and seven basins (Figures 1and 2). The ERA model includes a number of steps (8 steps), summarized below (for details see Table 8):

Hazard identification	**Step 1:** An inventory of pesticides and trace metals usage and sources in the region (see Table 8 for details).
	Step 2: A preliminary hazard attribution of pesticides and trace metals using toxicity values (LC_{50}, LD_{50}) to different receptors (see Table 7 for details).
Risk assessment *(risk sites ID and use of novel technology)*	**Step 3:**A survey to identify the potential and possible risk sites (high, medium and low and least risk sites) for assessing risks level in the whole catchment (see also Table 8).
	Step 4. An innovation or development or use of novel technology to accurately measure and assess risks of micro-pollutants (pesticides and trace metals) at µg/l to ng/L (see Table 8 for details).
	Step 5: Use of multiple sampling strategies (novel technology, and use of native biota (fish, mussels) and spot sampling) (see Table 8 for details).
Risk assessment *(monitoring & exposure assessment)*	**Step 6.** A pilot trial to evaluate the effectiveness of the novel technology in risk assessment (see Table 8 for details).
	Step 7: A two years continuous monitoring using novel technology, native biota and spot sampling (see Table 8 for details).
Toxicity assessment (*dose response- effects assessment*)	**Step 8:** An assessment of the effects of most frequently detected pollutants (pesticides and metals) on native biota (see Table 8 for details).

Table 8: ***Steps in G-MWs ERA model for pesticides, herbicides and trace metals***
[CG= Central Goulburn Irrigation area; H=herbicides; I=insecticides; F=Fungicides; MV= Murray valley Irrigation area; PH-B= Pyramid Hill and Boort Irrigation area; R-C- Rochester Campaspe Irrigation area; S= Shepparton irrigation area; T= Torrumbarry irrigation area].

Name	Steps	ERA methodology	Results/Outcome ***Bold=** detected in G-MW waterways in steps 6 and 7
Hazard identification	**Step 1**	A survey was conducted to obtain information on pesticides usage in the whole G-MW catchment including the six irrigation areas (Krake et al. 2001).	-The survey found that 76 pesticides were used in the G-MW catchment areas including 23 insecticides, 36 herbicides and 17 fungicides (see appendix 1; see Krake et al 2001).
	Step 2	Data collected (in step 1) were used to assess a preliminary (tier 1) hazard attribution of pesticides (high, medium and low risks) taking into account of (a) the hazard (toxicity values) of different receptors such as fish (LC_{50}), aquatic ecosystems (invertebrates such as daphnia (LC_{50}), pastures (phytotoxicity for crops- EC_{50} for algae), mammals-rats (LD_{50}); (b) amount of pesticide used; (c) the different pathways through which the receptor organisms is likely to be exposed (e.g. drift, drainage discharge, accidental spills and unlawful acts); and (d) Pesticides Impact Ranking Index (PIRI) (see Kookana et al. 2003). For heavy metals/trace metals, the standard toxicity values (e.g. LC_{50} for fish) and bioconcentration factors and half-life (as shown in Table 2) for various metals were used for risk ranking.	-The preliminary hazard assessment (tier 1) found 10 pesticides were of very high risk (see below) and 7 pesticides were of high to moderate overall risk (see below) to all receptors (aquaculture, and aquatic ecosystems animals and humans) (see Kookana et al. 2003). -*Very high risk pesticides were* ***azinphos methyl** (I), ***copper** hydroxide (F), ***parathion methyl** (I), ***chlorpyrifos** (I), omethoate (I), esfenvalerate (I), methomyl (I), thiram (F), bifenthrin (I), mancozeb (F) (see Kookana et al. 2003). -*High to moderate risk pesticides were:* ***metriram** (F), chlorothalonil (F), fenthion (I), carbaryl (I), tau-fluvalinate (I), ***atrazine** (H), diquat (H), ***endosulfan** (I) (see Kookana et al. 2003). -Some 83% of pesticides that were rated to be of high risks were found to be those that are used in the fruit and vegetables production areas (see Kookana et al. 2003). -Based on toxicity values and chemical properties (Table 1), ***copper**, ***cadmium**, * **lead,** ***mercury** and ***zinc** were identified as of highest overall risks to all receptors (see Kibria et al. 2010a and Kibria et al. 2010b).
Risk assessment (Risk sites identification)	**Step 3**	The whole G-MW catchment was surveyed to identify some potential risk sites in relation to pesticides and trace metals usage and sources in each of the six irrigation areas. Risk sites selected were based on the intensity of farming (e.g. orchards- pome & stone fruit, vine yards olive culture; tomatoes, crops), livestock (dairy, pigs, poultry, aquaculture) and the proximity of farms in relation to irrigation channels, drains, rivers and creeks; town supply off take points; channel and drain outfalls to natural rivers (Goulburn and Murray, ecologically sensitive areas (RMASR sites). In addition to the above, 1-2 reference/control sites (e.g. first channel offtake point of main irrigation channels or upstream of Rivers in forested areas without farming or human habitation were also selected for comparison of data obtained at risk sites.	-15 sites were selected for pesticides monitoring across the catchment. These sites were Torgannah lagoon (MV), Burramine (Reference/control), Katamatite (MV), Shepparton (S), Mooroopna (CG), Ardmons (CG), Kyabram (CG), Tatura (CG), Nagambie (Reference/control), Corop/Rochester (R-C), West Boort (PH-B), Appin (PH-B), Kerang (T), Kangaroo lake (T), and Gunbower (Reference) (see Rose and Kibria 2006; Rose and Kibria 2007). -10 sites were selected for trace metals monitoring. These sites were Buffalo (Reference/control), Howqua (Reference/control), Cobram (MV), Shepparton (S), Mooroopna (CG), Tatura (CG), Corop/Rochester (R-C), West Boort (PH-B), Kerang (T) and Kangaroo Lake (T) (see Kibria et al. 2010b).

Steps	Name	ERA methodology	Results/Outcome ***Bold=** detected in G-MW waterways in steps 6 and 7
Risk assessment (Innovation/ development/use of novel technology)	**Step 4**	In order to determine most accurate level of pollutants in waterways (pesticides and metal type and concentrations at µg/l to ng/L), an efficient risk assessment tool called "cutting edge passive sampling technology" were innovated/developed/used (as part of R&D collaboration with G-MW). The technology provided time-weighted average concentrations (pesticides, herbicides and metals) of pollutants. The novel technologies used were passive samplers with TRIMPS for pesticides (Rose and Kibria 2007) and Artificial mussels for trace metals (Kibria et al. 2010b).	-TRIMPS and Artificial mussels technology were successfully applied to monitor and assess risks of pesticides and trace metals (see steps 6 and 7). -The passive samplers allowed to measure concentrations of freely dissolved analytes (both bio-available and toxic fractions) and provided useful data on the variability of contaminant concentrations (spatial and temporal variations) or temporal changes in toxicity.
Risk assessment (Sampling strategies)	**Step 5**	Three ways monitoring strategies are suggested for monitoring and assessing risks of pesticides and trace metals and other harmful chemicals listed in Table 1 (where possible and feasible). These include (a) use of novel technology (as described in step 4), the technology of which will provide the most accurate spatial and temporal estimations of pollutants and helps to identify pollutants "hot spots" (b) use of live native animals such as mussels or native fish will provide both spatial and temporal bioaccumulation of pollutants in native biota (seafood) and (c) use of spot water samples (see Kibria et al. 2012 section 17 for further details).	Three ways monitoring strategies comprising use of novel technology, native biota and spot sampling were successfully tested.
Risk assessment (Monitoring- pilot trial study)	**Step 6**	To assess the suitability of the novel technology for monitoring and risk assessment (as discussed in step 4), pilot trials were conducted (see Rose and Kibria 2004; Kibria et al. 2010a). The trial includes the preparation of passive samplers (2,2,4-trimethylpentane containing passive samplers or TRIMPS and Artificial mussels (AM)), their deployment and retrieval process, monitoring in few selected risk sites within one irrigation area (out of six irrigation areas), development of occupational health and safety requirements procedure for field and lab works, setup of monitoring sites and development of analytical protocol. The pilot trials helped to improve passive sampling regimes for example for endosulfan and chlorpyrifos (most commonly detected pesticides) and trace metals etc (see Rose and Kibria 2004; Rose and Kibria 2006; Kibria et al. 2010a; Kibria et al. 2012).	Pilot trials carried out found that the passive sampling techniques (TRIMPS, AM) are viable and effective techniques for monitoring of targeted pesticides (e.g. ***azinphos methyl**, ***chlorpyrifos**, ***endosulfan**) and targeted trace metals (e.g. ***cadmium**, ***copper**, ***lead**, ***mercury** and ***zinc**) since all of these chemicals were accumulated in the novel passive samplers deployed at waterways including rivers, creeks, irrigation channels and drains (see Rose and Kibria 2004; Kibria et al. 2010a). Because of the success with the pilot trial, the pilot study model extended for continuous two years monitoring (see step 7). The "passive samplers accumulated both isomers of endosulfan (α endoculfan, β endosulfan) and the metabolite endosulfan sulphate" .

Steps	Name	ERA methodology	Results/Outcome ***Bold=** detected in G-MW waterways
Risk assessment (monitoring-extended study)	**Step 7**	The pilot study model was extended for a continuous 2 years to assess the long-term environmental conditions with respect to pesticides and trace metals concentrations (spatial and temporal variations of pollutants inputs and transport with respect to climate variability impacts such as dry vs. wet years).	-The study found three agricultural pesticides on a regular basis across the six irrigation areas including ***endosulfan** (an organochlorine insecticide), ***atrazine** (herbicide) and ***copper** (fungicide). The three other pesticides that were found on a less regular basis were ***chlorpyrifos** (an organophosphorous insecticide), ***parathion methyl** (an organophosphorous insecticide) and ***azinphos methyl** (an organophosphorous insecticide). The monitoring found that water at some channel sites exceeded the ANZECC and ARMCANZ (2000) guideline values of both ***endosulfan** (<0.003 µg/L) and ***chlorpyrifos** (<0.001 µg/L) for aquaculture or fish farming (see Rose and Kibria 2006; Rose and Kibria 2007). -The artificial mussel technology deployed within GMW catchment had accumulated all the targeted (***Cd**, ***Cu**, ***Hg**, ***Pb**, and ***Zn**) and non-targeted metals (***Cr**, ***CO**, ***Fe**, and ***Ni**) (Kibria et al. 2010a). The study found that Melbourne-Yarra catchment was most polluted (Cu and Zn) compared to upper Loddon River catchment of North Central CMA (NCCMA), and Goulburn Murray Water catchments (GMW) (see Kibria et al. 2010b). Further studies within G-MW catchment showed that climate variability (dry vs. wet years) can influence inputs, transport and bioavailability of pollutants in waterways, for example during the dry year elevated levels of copper were detected, while elevated levels of zinc were found during the wet year (see Kibria et al. 2011).
Toxicity assessment (dose-response effects assessment on native biota)	**Step 8**	High risk pesticides and trace metals detected in waterways (step 7) (e.g. ***endosulfan**, ***copper**) were further evaluated to assess the risks to native biota (fish). This was designed to observe and record the effects (lethal and sub-lethal effects) of these toxicants on the early life stages of iconic native fish (endangered and threatened native fish such as Murray cod, *Maccullochella peeli peeli* and Murray River rainbow fish, *Melanotaenia fluviatilis*) found in Goulburn and Murray Rivers) (see Raymond et al. 2006).	Murray cod larvae (< 2 days old) exposed to ***copper** and ***endosulfan** (1 to 100 µg/L) did not result in any deaths indicating that Murray cod are less sensitive to these two toxicants. However, Rainbow fish were found very sensitive to ***endosulfan** as mortality was recorded as low as 1 µg/L (see Raymond et al. 2006).

4. Results and discussion

The ERA model that has been developed in collaboration with federal, state and regional government departments and Universities (Table 8) helped G-MW in assessing risks posed from harmful chemicals/toxicants (pesticides, herbicides and trace metals) to various receptors (drinking water, raw town supply, biodiversity (fish), flora and fauna, stock and domestic supply, food security, water security, recreation, aquatic ecosystems and humans.

The collaborative arrangement has developed two new risk assessment tools, one for hydrophobic pesticides and the other for trace metals that has given G-MW an accurate picture of the high-risk pesticides, herbicides and metals present across its entire region. For example, use of novel risk assessment tool such as TRIMPS and AM facilitated accurate and continuous determination of the type of pesticides and metals and their concentrations (at µg/L to ng/L) at various waterways (Rivers, creeks, irrigation channels and irrigation drains) during the two irrigation seasons. The passive samplers used also showed that there were spatial and temporal variations in accumulation of pesticides and metals (Rose and Kibria 2007; Kibria et al 2011). The novel tools further assisted in identifying pollutant “hot spots” in the catchment (e.g. pesticides “hot spots” were Mooroopna, Shepparton, Ardmona, and Kyabram (Rose and Kibria 2007) and trace metals “hot spots” were Shepparton, Tatura, Rochester, West Boort, Kerang, Kangaroo Lake (Kibria et al. 2011). These “hot spots” were close to orchards, vineyards, mixed farming, olive culture and vegetable growing areas- located in channel irrigation areas. The ERA results showed that high risk sites (‘hot spots’) are located within one irrigation area (Central Goulburn, out of six irrigation areas) which would be indicative of intensive pesticide and agricultural fertilizer usage in the Central Goulburn area. For example, as shown in Table 7, this level of risk can be correlated with the significantly higher irrigation intensity for Central Goulburn (96 ML/km^2) when compared to all other irrigation areas and thus contributes to attribution of the highest level of risk for agrochemicals (pesticides) and trace metals (copper).

5. Conclusion

The model ranked risks of toxicants (pesticides, herbicides and traces metals) into high, medium and low categories (Kookana et al. 2003; Rose and Kibria 2006; Rose and Kibria 2007; Kibria et al. 2000a and Kibria et al. 2011). It showed that climate variability (dry vs. wet years) can influence the inputs, transport and bioavailability of pollutants in waterways (Kibria et al. 2011). Comparing the ANZECC and ARMCANZ (2000) water quality guideline trigger values for most detected toxicants such as pesticides (e.g. endosulfan) and metals (e.g. copper), it appears that irrigation water may not be suitable for fish farming or aquaculture, though it needs further investigation to confirm such findings. However, the ERA found that water quality of Rivers, creeks, channels and drains was safe or within guideline values for most beneficial usages including irrigation, stock and domestic supply, raw town supplies, recreational activities and aquatic ecosystems protection (see Rose and Kibria 2006; Rose and Kibria 2007; Kibria et al. 2010a and Kibria et al 2010b; Kibria et al. 2011).

6. Recommendations

It is recommended that G-MW should undertake a similar risk assessment for other harmful chemicals/toxicants such as endocrine disrupting chemicals and livestock pharmaceuticals (Tables 3 to 6) since the G-MW region is the home of intensive livestock industries (dairy, beef cattle, sheep, poultry, piggery, and aquaculture) and livestock effluents and manures could be a source of these chemicals in waterways (Boxall 2004; Kümmerer 2004; Campbell et al. 2006; Kümmerer 2009; Williams et al. 2007). It is also suggested to assess further impacts of pesticides and trace metals within the environment (Natural Rivers such as Goulburn and Murray or RMASR wetlands) and threatened native biota (fish) as a consequence of G-MWs channels and drain outfalls.

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8. Appendix

Appendix 1. Pesticides used in 6 Irrigation Areas within Goulburn-Murray Water catchment (G-MW) during 2001.
Note: Pesticide usage information of Central Goulburn, Shepparton and Murray Valley Irrigation Areas were combined and reported as Goulburn-Murray Valley or GMV; Krake et al 2001). *Half-life and log K_{ow} values are based on Tomlin (2006).*

Appendix 1A: HERBICIDES

	Herbicides	Herbicide group	Sold as L=Liquid; G=Granular; P=Powder C=Crystals	Half life ($t_{1/2}$) D=days	K_{ow} logP	Quantity used per annum (total of all G-MW areas) (2001).	Usage in farming sectors	Application method	Areas where used : GMV=Goulburn Murray Valley includes Central Goulburn, Shepparton, Murray Valley; R=Rochester-Campaspe; P-B=Pyramid-Boort and T=Torrumbarry
1	**2,4-D**	Aryloxyalkanoic acid/phenoxy compound	L	<7d	2.58-2.83	14853L	Irrigated pasture, Irrigated pasture (fat lamb, cattle, dairy)	Boom spray	GMV, P-B (Pyramid Hill), T (Swan Hill)
2	**Amitrole**	Triazole	L	<5-56d	-0.97	35000L	Irrigated pasture	Misting machine	GMV
3	**Glufosiante-ammonium salt**	Phosphinic acid	L		<0.1	30000L	Stone fruit, pome fruit,	Boom spray, Knapsack, Control droplet application (CDA)	GMV
4	**Atrazine**	1,3,5 triazine	L,G	16-77d	2.5	3000L	Irrigated pasture	Low volume boom spray	P-B (Boort)
5	**Bensulfuron-methyl**	Sulfonylurea	G	4- 6d	2.45	2,860 kg	Rice, irrigated cropping (rice & millet)	??	GMV, T (Kerang)
6	**Bromoxynil**	Hydroxybenzonitrile	L	< 1d	2.8	5162L	Lucerne, irrigated cereals (wheats, oats, canola, faba beans), irrigated pasture	Boom spray	T (Kerang), P-B (Pyramid Hill)
7	**Butroxydim**	cyclohexanedione oxime	G	9d	1.9	1343L	Irrigated pasture, irrigated cereals (wheat, oats, canola, faba beans)	Boom spray	P-B (Boort), T(Kerang)
8	**Clomazone**	isoxazolidinone	L	30-135d	2.5	143L	Irrigated cropping (rice & millet)		T (Kerang)
9	**Chlorosulfuron**	Sulfonylurea	G	4-6 weeks	-0.99	52kg	Irrigated pasture, irrigated cereals (wheat, oats, canola, faba beans)	Boom spray	P-B (Boort), T (Kerang)
10	**Dalapon**	2,2-dichloro-proprionic acid	L	Rapid degradation	0.778	9000L	Stone fruit, pome fruit	Dip	G-MV
11	**Diclofop-**	Aryloxypheoxypropionat	L		4.58	1600L	Irrigated pasture	Boom spray	P-B (Boort)

Appendix 1A: HERBICIDES

	Herbicides	Herbicide group	Sold as L=Liquid; G=Granular; P=Powder C=Crystals	Half life ($t_{1/2}$) D=days	K_{ow} logP	Quantity used per annum (total of all G-MW areas) (2001).	Usage in farming sectors	Application method	Areas where used : GMV=Goulburn Murray Valley includes Central Goulburn, Shepparton, Murray Valley; R=Rochester-Campaspe; P-B=Pyramid-Boort and T=Torrumbarry
	methyl	e							
12	**2,4-DB**	Aryloxyalkanoic acid/phenoxy compound	L	< 7d	440	1280L	Irrigated pasture	Boom spray	P-B, T
13	**Diflufenican**	pyridinecarboxamide	L, G	85.6-282d	4.9	3015kg	Irrigated pasture, irrigated pasture (fat lambs, cattle, dairy),	Boom spray	P-B (Boort), P-B (Pyramid Hill), T (Kerang)
14	**Diquat or diquat dibromide**	bipyridylium	L	<1 week	-4.60	16430L	Irrigated pasture, viticulture, Lucerne	Boom Spray	P-B (Boort), GMV, T (Kerang), R
15	**Diuron**	urea	L, G	90-180d	2.85	5515L	Lucerne, irrigated pasture	Boom spray	T (Kerang, Swan Hill), R,
16	**Fenoxaprop-p-ethyl**	2-(4-aryloxypheoxypropionate	L	1-10d	4.58	1600L	Irrigated pasture	Boom spray	P-B (Boort)
17	**Fluazifop-P butyl**	aryloxypheoxypropionate	L	<24 hours	3.1	2,500L	Vegetables (tomatoes), irrigated pasture, vegetables	?, Boom spray, Knapsack	GMV, T
18	**Fluroxypyr**	pyridinecarboxylic acid	L	5-9d	4.53	500L	Rice		GMV
19	**Glyphosate**	glycine derivative	L, G	1-130d	<-3.2	121,110L	Irrigated pasture, stone fruit, pome fruit, viticulture, irrigated cereals (wheat, oats, canola, faba beans)	Boom spray, Wiper equipment, Hand gun, Knapsack, CDA	P-B (Boort), GMV, T (Kerang, Swan Hill), R,
20	**Imazethapyr**	imidazolinone	G	90d	1.04	72kg	Lucerne	Boom spray	T (Kerang)
21	**MCPA**	Phenoxyacetic acid/Aryloxyalkanoic acid	L	<7d	2.75	29,784L	Irrigated pasture, irrigated pasture (fat lamb, cattle, dairy), Irrigated cropping (rice & millet),	Boom spray	P-B, GMV, T (Kerang),
22	**Metribuzin**	1,2,4 triazione	L	1-2months	1.6	4000 L	Vegetables (tomatoes), other vegetables	Boom spray	GMV
23	**Metsulfuron -methyl**	sulfonylurea	G	52d	-1.74	126kg	Irrigated pasture, Irrigated cereals (wheat, oats, canola, Faba beans),	Boom spray	P-B (Boort), T (Kerang)
24	**Molinate**	thiocarbamate	L	8-25d	2.88	?	Rice	Boom spray	GMV

Appendix 1A: HERBICIDES

	Herbicides	Herbicide group	Sold as L=Liquid; G=Granular; P=Powder C=Crystals	Half life ($t_{1/2}$) D=days	K_{ow} logP	Quantity used per annum (total of all G-MW areas) (2001).	Usage in farming sectors	Application method	Areas where used : GMV=Goulburn Murray Valley includes Central Goulburn, Shepparton, Murray Valley; R=Rochester-Campaspe; P-B=Pyramid-Boort and T=Torrumbarry
25	**Oryzalin**	dinitroaniline	G	1.2 months	3.73	600kg	Viticulture	Low pressure sprayer	GMV
26	**Oxyfluorfen**	diphenyl ether	L	5-55d	4.47	1,143L	Irrigated cereals (wheat, oats, canola, faba beans), Stone fruits, pome fruits	Boom spray	T (Kerang), GMV
27	**Paraquat dichloride**	bipyridylium	L	>1000 d	-4.5	1500L	Stone fruits, pome fruits	Boom spray	T (Swan Hill)
28	**Pendimethalin**	dinitroaniline	L	3-4 months	5.18	20,500L	Irrigated pasture, stone fruits, viticulture,	Boom spray	P-B (Boort), GMV, R, T (Swan Hill)
29	**Propaquizafop**	aryloxypheoxypropionate	L	15	4.78	500L	Irrigated pasture	Boom spray	R
30	**Quizalofpo**	aryloxypheoxypropionate	L	<1d	4.28	500L	Irrigated pasture	Boom spray	P-B
31	**Rimsulfuron**	sulfonylurea	G	10-20d	0.288	80kg	Vegetables	Boom spray	R
32	**Simazine**	1,3,5-triazine	L, G	27-102d	2.1	4,500L	Irrigated pasture, viticulture	Boom spray, Knapsack sprayer	P-B (Boort), R
33	**Thiobencarb**	thiocarbamate	L	2-3 weeks	3.42	429L	Rice, irrigated cropping (rice & millet)	SCWIRT (soluble chemical water injection in rice technique)	GMV, T (Kerang)
34	**Tralkoxydim**	Cyclohexanedione oxime	L	2-5d	2.1	1629L	Irrigated pasture, Irrigated cereals (wheat, oats, canola, Faba beans)	Boom spray	P-B (Boort), T (Kerang)
35	**Triasulfuron**	sulfonylurea	G	3d	1.1	29 kg	Irrigated cereals (wheat, oats, canola, faba beans)	Boom spray	T (Kerang)
36	**Trifluralin**	dinitroaniline	L	25-201d	4.83	14,430L	Irrigated pasture, irrigated cereals (wheat, oats, canola, faba beans)	Soil incorporation	P-B (Boort), T (Kerang)

Appendix 1B: INSECTICIDES

	Insecticides	Insecticide group	Sold as L=Liquid; G=Granular; P=Powder C=Crystals	Half-life	K_{ow} logP	Quantity used per annum	Usage in farming sectors	Application method	Areas where used : GMV=Goulburn Murray Valley includes Central Goulburn, Murray Valley an Shepparton ; R-C=Rochester-Campaspe; P-B=Pyramid-Boort and T=Torrumbarry
1	**Alpha-Cypermethrin**	pyrethroid	L	6.6	6.94	6,000L	Irrigated pasture, vegetables,	Boom Spray	GMV, P-B (Pyramid Hill)
2	**Azinphos methyl**	organophosphorous	L	Several weeks	2.96	80,000L	Stone fruit, pome fruit	Air blast	GMV
3	**Bacillus thuringiensis delta endotoxins**	bacterium	G	14d	-	250kg	Viticulture	Air blast	T (Swan Hill)
4	**Beta-Cypermethrin**	pyrethroid	L	1-10d	>4.7	4000L	Vegetables	Air blast	R
5	**Bifenthrin**	pyrethroid	L	65-125d	>6	2943L	Irrigated cereals (wheat, oats, canola, faba beans), irrigated cropping (canola, wheat, lucerne, barley, clover), vegetables, irrigated pasture	Boom spray, Misting machine	T, R,
6	**Carbaryl**	carbamate	L,P	7-28d	1.59	3000kg	Stone fruit, pome fruit	Air blast	GMV
7	**Chlorpyrifos**	organophosphorous	L,G	33-56d	4.7	20,943kg	Stone fruit, pome fruit, viticulture, Irrigated cropping (rice & millet), irrigated cropping (canola, wheat, lucerine, barley, clover), vegetables, viticulture, irrigated pasture	Air blast, Boom spray	GMV, T, P-B (Pyramid Hill),R,
9	**Dimethoate**	organophosphorous	L	2-4.1d	0.704	21,340L	Irrigated pastures, stone fruit, pome fruit	Boom spray	P-B (Boort), GMV, T
10	**Endosulfan**	organochlorine	Lk	30-70d	4.74	2229L	Irrigated pasture, vegetables, irrigated cropping (canola, wheat, lucerne, barley, clover), irrigated cereals (wheat, oats, canola, faba beans)	Boom spray	P-B (Boort), P-B (Pyramid Hill), R, T
11	**Esfenvalerate**	pyrethroid	L	287d	6.22	1000L	Vegetables	Air blast	R
12	**Fenthion**	organophosphorous	L	1.5d	4.84	2000L	Vegetables (tomatoes)	Air blast	GMV
13	**Fipronil**	phenyl pyrazole	L	Readily degraded	4	29L	Irrigated pasture (fat lambs, cattle, dairy)	?	T (Kerang)
14	**Imidacloprid**	neonicotinoid	L	-	0.57	1000L	Stone fruit, pome fruit,	Air blast	GMV, T (Swan Hill)
15	**Methomyl**	Oxime carbamate	L	4-8d	0.093	6350L	Tomatoes, vegetables, viticulture	Air blast, Boom	GMV, T (Swan Hill)

Appendix 1B: INSECTICIDES									
	Insecticides	**Insecticide group**	**Sold as** L=Liquid; G=Granular; P=Powder C=Crystals	**Half-life**	**K_{ow} logP**	**Quantity used per annum**	**Usage in farming sectors**	**Application method**	**Areas where used :** GMV=Goulburn Murray Valley includes Central Goulburn, Murray Valley an Shepparton ; R-C=Rochester-Campaspe; P-B=Pyramid-Boort and T=Torrumbarry
								spray	
16	**Omethoate**	organophosphorous	L	7d	-0.74	24,286L	Irrigated pasture, irrigated pasture (fat lambs, cattle, dairy), Lucerne	Boom spray, Air Blast	P-B (Boort), GMV, T, R,
17	**Parathion Methyl**	organophosphorous	L	-	3.0	17,000L	Stone fruit, pome fruit	Air blast	GMV
18	**Phorate**	organophosphorous	G	7-10d	3.92	8,000kg	Vegetables	Soil applied granular form	R
19	**Phosmet**	organophosphorous	G	Rapid degradat ion	2.95	1773kg	Irrigated pasture (fat lambs, cattle, dairy), irrigated cereals (wheat, oats, canola, faba beans)	Boom spray, Misting machine	T (Kerang),
20	**Pirimicarb**	carbamate	G	7-234d	1.7	1000kg	Stone fruit, pome fruit	Air blast	GMV
21	**Sodium sulfate**		C			40,000Kg	Stone fruit, pome fruit	Dip	GMV
22	**Tau Fluvalinate**	Pyrethroid	L	12-92d	4.26	?	Stone fruit, pome fruit	Air blast	T (Swan Hill)
23	**Tebufenozide**	diacylhydrazine	G	7-66d	4.25	1400kg	Stone fruit, pome fruit	Air blast	GMV
24	**Thiodicarb**	Oxime carbamate	L,G	3-8d	-	4000L	Vegetables (tomatoes), vegetables	Air blast	GMV, R

Appendix 1C: FUNGICIDES									
	Fungicides	**Fungicides group**	**Form as sold**	**Half-life**	**K_{ow} logP**	**Quantity**	**Usage in farming sectors**	**Application method**	**Area used**
1	**Azoxystrobin**	strobilurin	G	14d	2.5	?	Viticulture	Boom spray	
2	**Carbendazim**	benzimidazole	L	8-32d	1.38	2000L	Stone & pome fruit	Spray & dip	GMV
3	**Chlorothalonil**	chloronitrile	L,G	0.3-28d	2.92	30.86T	Irrigated cereals (wheat, oats, canola, faba beans), vegetables	Misting machine, Boom Sprayer	R, T (Kerang)
4	**Copper hydroxides**	inorganic	G	-	0.44	55,000kg	Tomatoes; Stone fruit, pome fruit, viticulture	Boom Spray, Knapsack, Air Blast	GMV,R
5	**Copper sulphate**	Inorganic	C	-	-	32kg	Irrigated cropping (rice & Millet)		T (Kerang)
6	**Imazalil**	imidazole	L,G	100d	3.82	800kg	Stone fruit, pome fruit	?	GMV
7.	**Iprodione**	Dicarboximides		20-80d	3.0	12000L	Pome fruit, stone fruit, viticulture	dips	GMV
8	**Mancozeb**	Alkylenebis	L,G	<1d	0.26	20,330L	Stone fruit, pome fruit, viticulture,	Low volume Air	T, R, P-B (Boort

Appendix 1C: FUNGICIDES									
	Fungicides	**Fungicides group**	**Form as sold**	**Half-life**	**K_{ow} logP**	**Quantity**	**Usage in farming sectors**	**Application method**	**Area used**
		(dithiocarbamate)					irrigated cereals (wheat, oats, canola, faba beans), vegetables, irrigated pasture	blast, Boom sprayer, Knapsack	
9	**Metalaxyl-M**	Phenylamide-Acylalanine	L,G	21d	1.75	5000L	Viticulture	Soil applied granular herbicide	GMV
10	**Metiram**	Alkylenebis (dithiocarbamate)	G	2.7d	0.30	40,000Kg	Stone fruit, pome fruit	Air blast	GMV
11	**Penconazole**	DMI : Triazole	L	133-343d	3.72	300L	Viticulture	Air blast	T (Swan Hill)
12	**Propiconazole**	DMI : Triazole	L	29-70d	3.72	5000L	Stone fruit, pome fruit	Air blast	GMV
13	**Procymidone**	Dicarboximides	L	4-12 weeks	3.14	12000L	Pome fruit, stone fruit, viticulture	dips	GMV
14	**Sulfur or wettable sulfur**	inorganic	L,G	-	-	30.50T	Vegetables, viticulture	Air blast	T (Swan Hill), R, GMV
15	**Thiram**	dimethyldithiocarbamate	L,G	0.5d	1.73	14T	Stone fruit, pome fruit	Air blast	GMV
16	**Vinclozolin**	Dicarboximides	L	-	3			Immersion	GMV
17	**Ziram**	dimethyldithiocarbamate	G	4 2 hours	1.23	50T	Stone fruit, pome fruit	Air blast	GMV