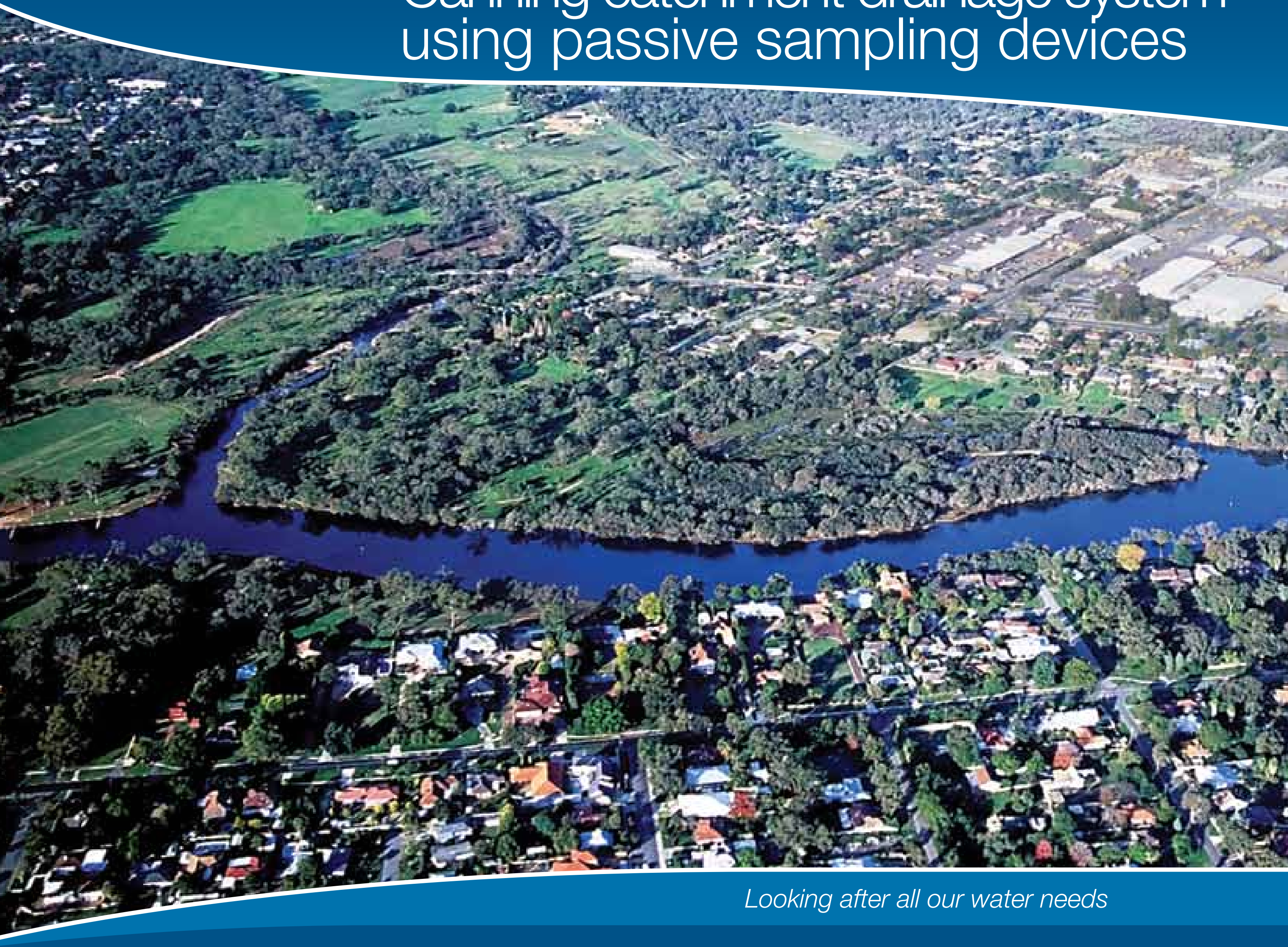
Government of **Western Australia**
Department of **Water**

A baseline study of organic contaminants in the Swan and Canning catchment drainage system using passive sampling devices



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A baseline study of organic contaminants in the Swan and Canning catchment drainage system using passive sampling devices

Department of Water

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Executive Summary

Ten Swan and Canning catchment drainage systems were sampled four times over a one year period using three types of passive sampling devices to monitor concentrations of herbicides, insecticides and polycyclic aromatic hydrocarbons (PAHs) in water. Passive samplers are a developing technology and this study was the first comprehensive trial of their use in the Swan Canning system. Contaminants were detected in surface water in all of the sub-catchments; with the concentrations present representing the fraction that is most bioavailable to fish and other aquatic organisms. The passive samplers adsorb contaminants dissolved in water but not contaminants bound to suspended solids. Contaminants varied in type between and within the drainage systems and concentrations of contaminants varied temporally. Broadly, the highest and most widespread organic contaminant levels were detected in the Bayswater, Southern River, Belmont South and Perth Airport South sub-catchments.

In introducing this technology to monitoring programs, attention will need to be given to the use of guideline comparisons. In this study concentrations of organic compounds have been compared to ANZECC and ARMCANZ guidelines (ANZECC & ARMCANZ 2000), although it should be noted that these guidelines were not developed to take into account time averaged samples as generated by passive sampling devices. Exceedance of the guideline in the time averaged sample does indicate that at some time(s) during the sampler deployment the water concentrations were in excess of the guideline. In our view passive sampling devices provide relevant data from which to assess exposure of aquatic organisms to contaminants, especially in the context of environmental risk assessment.

Twenty five pesticides (including insectides and herbicides) were detected in total, of which simazine, diuron and atrazine were the most prevalent, being detected in every drain during almost every sampling event. Diazinon, trifluralin and metachlor were also detected in several drains. The herbicides simazine, diuron and metolachlor were measured above freshwater ecosystem trigger values (ANZECC & ARMCANZ 2000), as were the insecticides diazinon, chlorpyrifos and dieldrin. Two metabolites of atrazine were also detected. Atrazine has been linked to hermaphroditism in male frogs, mutagenicity and carcinogenicity (Hayes et al. 2002; Cox 2002). Simazine is a suspected endocrine disrupting chemical (Cox 2002). The highest herbicide concentrations were detected in Southern River, Belmont South and Bennett Brook during the wetter April and July months. Concentrations of herbicides were notably lower in January.

Pesticides that are highly water soluble, relatively persistent, and not readily adsorbed to soil particles have the greatest potential for mobilisation in the aquatic environment (Australian Academy of Technological Sciences 2002). Of note is the regular detection of banned organochlorine pesticides chlordane, dieldrin and heptachlor, or the metabolites of these compounds in this study. A number of these are suspected endocrine disrupting compounds, having oestrogenic properties that are able to interfere with reproductive system function, inducing reproductive organ abnormalities and fertility problems (Ulrich et al. 2000). These compounds are also carcinogenic, mutagenic and teratogenic (Fox 1995). They are also environmentally persistent and most likely to be a legacy of historic use as they have been banned for many years (Department of the Environment, Water, Heritage and the Arts 1997).

A wide variety of PAHs were detected in all sub-catchments. None of the PAHs exceeded freshwater ecosystem trigger values (ANZECC & ARMCANZ 2000). Phenanthrene, fluoranthene, pyrene and chrysene were the most commonly detected PAHs. Due to their hydrophobic nature most PAHs, particularly the high molecular weight (HMW) PAHs, are likely to be bound to sediment. The lower molecular weight (LMW) PAHs are more volatile, and degrade more quickly than HMW PAHs, so may not be present in samples (Neff 1979). PAH profiling using the phenanthrene and anthracene ratio showed that the provenance of the majority of PAHs is likely to be from pyrogenic (combustion) sources (Wilson et al. 2003). Bennett Brook, Southern River, Bayswater and Ellen Brook are possible exceptions that may have encountered significant inputs of petroleum-derived PAHs.

While there are numerous contaminants present within the surface waters of the study sites, the impact of these contaminants on downstream environments is unknown. This can be specifically addressed by ecological and ecotoxicological investigations and in situ bioaccumulation studies of organisms in the receiving waterbodies. This approach should be accompanied by comprehensive land use assessments in the sub-catchments to help identify sources of the contaminants. The promotion of best management practices in the use of herbicides and insecticides and improved stormwater management are recommended steps to reducing the concentrations of contaminants in the receiving environment.

1 Introduction

1.1 Background to the Non-Nutrient Contaminants Program (NNCP)

The Non-Nutrient Contaminants Program (NNCP) was a three year project to determine the nature of contaminants (other than nutrients) delivered to and present in the Swan Canning system. The Swan Canning system comprises the Swan and Canning rivers and estuaries. Non-nutrient contaminants assessed as part of this program included pathogens, heavy metals, low-level persistent organic compounds such as pesticides and herbicides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and anionic surfactants.

The need to conduct a 'non-nutrient' assessment of contaminants within the system was identified by earlier Swan River Trust programs and investigations conducted by the Water and Rivers Commission operating within the Department of Environment during the period 1990 - 1999. In 1999 the Swan River Trust established the Swan Canning Cleanup Program (SCCP) to reduce nutrient loads entering the Swan Canning system. The aim was to reduce the extent and frequency of algal blooms. Contaminants other than nutrients were not a focus of this program.

The SCCP Action Plan (Swan River Trust 1999a) and the SCCP review of contaminants in the Swan Canning system (Swan River Trust 1999b) recommended an assessment of non-nutrient contaminants within the Swan Canning system itself (the receiving environment), within existing drainage networks that discharge directly to the Swan Canning system; and in groundwater from disused waste disposal sites adjacent to the Swan Canning system's waterways and drains.

Major findings from the 1999 SCCP review of contaminants in the Swan Canning system (Swan River Trust 1999b) were that metal data in water, sediment and biota were spatially and temporally irregular. Data were also found to be compromised by inconsistent sampling and analysis methods and unsuitable limits of reporting. In addition, there was a paucity of data for persistent organic compounds such as pesticides, herbicides, PAHs and PCBs within the Swan Canning system.

The need for a more comprehensive understanding of the non-nutrient component of contaminants both within and entering the Swan Canning system was also highlighted by subsequent drainage impact studies conducted by the Water and Rivers Commission (operating as the Department of Environment) in relation to fish kills in the vicinity of drain outfalls to the Swan Canning system (Department of Environment 2003a; Department of Environment 2003b). As such, the NNCP was developed to measure contaminants other than nutrients in the estuaries, rivers and drains of the Swan Canning system to complement existing nutrient-focused monitoring.

1.2 Scope of the overall NNCP

The Non-Nutrient Contaminants Program (NNCP) was a three year program that commenced in January 2006. The objective of the overall program was:

To determine the nature (types, concentrations and spatial variability) of non-nutrient contaminants delivered to and present in the Swan Canning system.

The NNCP comprised a series of studies:

- A baseline study of contaminants in the Swan and Canning catchment drainage system (Nice et al. 2009)
- A baseline study of contaminants in groundwater at disused waste disposal sites in the Swan Canning catchment (Evans 2009)
- A baseline study of organic contaminants in the Swan and Canning catchment drainage system using passive sampling devices (this study)
- A baseline study of contaminants in the sediments of the Swan and Canning estuaries (Nice 2009)

1.3 Objectives of this project

The objectives of the study are:

- to determine concentrations of a range of organic contaminants comprising insecticides, herbicides and PAHs in selected Swan Canning drains
- to conduct time-integrated measurements of organic contaminants in order to capture 'one-off' or 'flash' pollution events on addition to base concentrations
- to suggest possible sources and potential environmental impacts of any detected organic contaminants

1.4 Background to this project

Passive sampling devices can be used to accumulate various types of organic pollutants including pesticides, PCBs and PAHs in surface waters. These devices typically consist of a membrane, sorbent and an outer housing (Kapernick et al. 2006). The devices are deployed in waterways, allowing the organic pollutants to partition between the water and the sorbent phase over time. Extraction and analysis of the passive sampling devices allows the concentrations of contaminants to be calculated. There are a range of passive samplers that accumulate chemicals according to their polarity. Three types were used in this study. Empore Disks (EDs) were selected to target the polar compounds, particularly the herbicides; whereas the less polar pesticides are absorbed into the sorbent of the Polydimethylsiloxane samplers (PDMSs); and the non-polar PAHs are absorbed into the sorbent of the Semi Permeable Membrane Devices (SPMDs).

To our knowledge, this study is the first reported instance where passive samplers have been used to systematically monitor a range of persistent organic pollutants in the Swan Canning catchment. There are two main advantages that passive sampling devices hold over conventional surface water monitoring techniques, both related to their ability to accumulate organic contaminants over an extended period (time-integrated sampling):

1. One-off, ephemeral or other time-dependent contamination events which result in fluctuating concentrations of contaminants may be sampled and concentrations averaged over time and reported.
2. Where present, abundances of organic contaminants are higher in the passive samplers than in the water in which they are deployed. The solvent extracts from the samplers are amenable to analysis using liquid chromatography – mass spectrometry (LC-MS) or gas chromatography – mass spectrometry (GC-MS) techniques, resulting in very low detection levels (e.g. ng/L) of contaminants.

The non-polar passive samplers also provide some measure of the bioaccumulation potential of contaminants in fish. The sorbent materials used in the passive samplers are lipophilic, similar to fish lipids and will retain contaminants from water in a similar way to fish in the environment (Chapman 2005). Advantages of using passive samplers rather than fish include:

- lower limits of reporting for contaminants due to the absence of interference from the fish lipids,
- it is easier to assess the variability due to the stationary nature of the passive samplers,
- fish may depurate contaminants from their tissues.

The initial field trial of these types of passive sampler in WA was conducted by the Water Corporation in Piesse Brook at a location downstream from a number of orchards in the Middle Helena Catchment. The trials were performed on five occasions between June and October 2003 and revealed that the concentration of the herbicide simazine on one occasion was approximately half the Australian Drinking Water Guideline (Kapernick et al. 2003). Prior to this, conventional grab sampling had not indicated the presence of herbicides in water from this site.

Following these Water Corporation trials, in June 2005 the Department of Water through funding from the Swan River Trust and in collaboration with EnTox undertook further field trials. These occurred in September and October 2005 using EDs, PDMSs and SPMDs (two of each) at three different sites. Various organic contaminants were identified in the drains including simazine and dieldrin (Kapernick et al. 2006). The trials demonstrated that these passive sampling devices were practicable and effective in the measurement of low concentrations of organic contaminants in waterways. Following the successful trials, the current study was commenced to assess organic contaminants entering the Swan and Canning rivers from ten sub-catchments between September 2006 and August 2007.

1.5 Sources and application of pesticides (herbicides and insecticides) and PAHs

Pesticides

A pesticide is a substance or a mixture of substances used to kill a pest, either plant or animal. Pesticides used in agricultural areas include insecticides, herbicides, and fungicides applied in the broadacre cropping, horticulture and livestock industries. In urban areas, pesticides are used primarily for weed control along roadsides, in parks, on golf courses and on private lawns, as well as for killing pests in and around residences. The pesticide loading in runoff water has been correlated to the amount of impervious cover and to the distance the runoff will travel prior to infiltration or decomposition (Pitt et al. 1996).

Herbicides are produced in the largest quantities of any of the pesticide products and their use has increased with the adoption of minimum tillage farming (Australian Academy of Technological Sciences 2002). Herbicides have a variety of properties and modes of action: pre-emergent herbicides are applied to the soil to prevent germination or early growth of weed seeds, while post-emergent herbicides will kill weeds in different stages of growth (United States Geological Survey 2006). Herbicides used to clear waste ground are nonselective and kill all plant material. However, selective herbicides kill specific targets while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed by disrupting plant hormones. Contact herbicides are fast acting and destroy only the plant tissue in contact with the chemical. Therefore they are less effective on perennial plants, which are able to regrow from roots or tubers. Systemic herbicides are translocated through the plant, either from foliar or soil application. They can destroy a greater amount of plant tissue than contact herbicides (Kerle et al. 2007).

The most extensively used herbicide in Australia today is glyphosate, a broad spectrum, non-selective post emergence herbicide with high activity on virtually all annual and perennial plants (Australian Academy of Technological Sciences 2002). Glyphosate shows no pre-emergence or residual activity because it binds strongly to soil particles and is readily metabolised by soil micro-organisms (ANZECC & ARMCANZ 2000). According to a publication in 2002 by The Australian Academy of Technological sciences (Australian Academy of Technological Sciences) the next most widely used herbicides are atrazine and simazine. These are selective systemic herbicides which provide knockdown and residual action for control of many broad-leafed weeds and some grasses in forestry and agricultural crops. The herbicides paraquat, diquat and 2,4-D and other phenoxy herbicides (e.g. MCPA), are other commonly used herbicides.

Insecticides also have different modes of action and can be applied as sprays, powders, pellets and baits (Australian Academy of Technological Sciences 2002). Insecticides may enter insects as stomach poisons, contact poisons or fumigants. Most insecticides affect one of five biological systems in insects (Australian Academy of Technological Sciences 2002), namely the nervous system, the production of energy, the production of the cuticle, the endocrine system and water balance.

In 2002, a report showed that the most widely used insecticides in years recent to that time were reported to be of the organophosphate type, with approximately 5000 t used annually (Australian Academy of Technological Sciences 2002). However these (including parathion methyl, chlorpyriphos, dimethoate, profensos and diazinon) were considered to be less environmentally persistent than the organochlorine pesticides. The next most significant group were the carbamates (3000 t used annually), of which metham sodium (500 t) was is the most widely used. At that time, pyrethroids and pyrethrins were also commonly used insecticides in Australia.

At present there is no detailed and publicly available information on the net usage of individual pesticides in Australia expressed either in terms of the active ingredient, or the formulated products. Therefore determining specific data about recent and current trends in the use of pesticides in Australia is difficult.

The toxic properties of pesticides vary greatly between species and the effects are influenced by a variety of environmental factors. Estimates of pesticide mobility can be made based on four mechanisms affecting the fate of organic compounds: degradation, volatilisation, sorption and solubility (Kerle et al. 2007). Application methods and formulation state can also play a significant role in pesticide mobility (Pitt et al. 1996). Pesticides decompose in soil and water but the total decomposition time can range from days to years (Kerle et al. 2007). Decomposition and dispersion rates in the soil depend upon many factors including pH, temperature, light, humidity, air movement, compound volatility, soil type and microbiological activity (Pitt et al. 1996).

PAHs

PAHs may be formed during incomplete combustion of organic material. The principle sources of PAHs in the environment are the incomplete combustion of fossil fuels, wood or other organic matter (pyrogenic sources) and inadvertent releases of oil or petroleum products (petrogenic sources) (Eisler 1987). PAHs are also used in the manufacture of dyes, plastics and pesticides. In general, they degrade slowly under microbial action and are considered to be moderately persistent chemicals, particularly in sediment with high organic carbon content and in the absence of oxygen (Vo et al. 2004). They do not dissolve easily in water and tend to adsorb to particulate matter and settle to the bottom of waterways (Vo et al. 2004). PAHs have moderate to high acute and chronic toxicity to aquatic life (Eisler 1987). Low molecular weight (LMW) PAHs (e.g. phenanthrene) have been shown to be acutely toxic and many high molecular weight (HMW) PAHs (e.g. benzo(a)pyrene) are mutagenic and carcinogenic (Boonchan et al. 2000).

The ratio of abundances of PAHs can provide evidence as to the likely source of contamination. Petrogenic aromatic hydrocarbon distributions are dominated by LMW PAHs and are therefore characterised by LMW:HMW PAH ratios greater than one (Vo et al. 2004). However, the chemical composition of petroleum may alter upon release into the environment with evaporation, dissolution and biodegradation processes (ie. weathering) depleting the petroleum of LMW compounds over time (Vo et al. 2004). Pyrogenic hydrocarbon mixtures contain a lower abundance of LMW PAHs and are enriched in HMW PAHs relative to petrogenic hydrocarbons, leading to LMW:HMW ratios of less than one.

The source of hydrocarbon contamination may also be inferred from the abundances of individual PAHs. For example, although anthracene and phenanthrene are structural isomers, anthracene is not usually found in petroleum but is rather an indicator of pyrogenic sources. Phenanthrene commonly occurs in both petrogenic and pyrogenic sources. So, if anthracene is present, then there is likely to be some contribution from pyrogenic sources. A phenanthrene:anthracene ratio of less than ten is used as a guide that pyrogenic sources predominate (Wilson et al. 2003). So if of these two PAHs only anthracene is present, the PAHs are most likely to have a pyrogenic source. If only phenanthrene is present, the source is most likely petrogenic and if both are present, the source of PAHs is most likely mixed. In the latter case, a phenanthrene to anthracene ratio of less than 10 may be used as a guide that pyrogenic sources predominate (Wilson et al. 2003).

1.6 Management and monitoring of pesticides (herbicides and insecticides) and PAHs in the Swan Canning catchment

Pesticides

The Australian Pesticide and Veterinary Medicines Authority is the Federal Government agency responsible for the registration of pesticides in Australia. Before a pesticide can be registered in Australia, it must be thoroughly assessed to ensure the safety of the user, the public and the environment, when used as directed by the manufacturer (Australian Pesticide and Veterinary Medicines Authority 2006). Pesticides banned in Australia and listed by the Stockholm Convention in an internationally legally binding agreement on persistent organic pollutants are the organochlorines aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, and toxaphene (Australian Pesticide and Veterinary Medicines Authority 2006).

The Health Department of WA is responsible for the control of use of registered pesticides in WA, to ensure that use is appropriate, in accordance with the manufactuter's specifications and has no untoward effects on humans, animals, agriculture or the environment. The Health Department authorises the use of only 2,4-D, amitrole, fluazifop-p-butyl, glyphosate, hexazinone, triclopyr and metsulfuron in drinking water sub-catchments (Department of Health 2006) and only when no other means are suitable for the control of weeds. Local government Environmental Health Officers are instrumental in the investigation of pesticide misuse affecting Public Health under the Health Act 1911.

Pesticides are freely available and widely used throughout WA by land owners and managers such as farmers, industry, home owners and state and local governments. For example, local governments carry out annual weed control programs around the rivers to maintain ovals, control mosquitoes and midges, keep infrastructure such as pathways and fencing clear and protect native vegetation. The City of Belmont, for instance, has a program for the use of Razor (active ingredient glyphosate) and Fusilade (active ingredient fluazifop-p-butyl) for general weed and grass control, Spearhead (active ingredients MCPA, clopyralid and diflufenican) to control broadleaf weeds and Dimension (active ingredient dithiopyr) for the control of crab grass (City of Belmont 2007).

Swan River Trust (1999b) reported the extensive use of pesticides in orchards, vineyards, market gardens, nurseries and turf farms. The report noted that the use of organochlorine pesticides had declined and there was an increased use of organophosphate pesticides. It found that historically, pesticide levels were generally below freshwater ecosystem guidelines but there were some instances where these were exceeded, usually in winter (ANZECC & ARMCANZ 2000). For instance, a survey in waters around Bayswater Main Drain in 1990 found levels of dieldrin that exceeded freshwater ecosystem guidelines (ANZECC & ARMCANZ 2000) and data collected in the 1980s showed some localised areas of DDT contamination near drain outlets and boat slipping facilities (Swan River Trust 1999b).

One notable example of the impacts of pesticides on the Swan River was a fish kill in 1997 near the Belmont Race Course, caused by runoff from rainfall containing the organophosphate insecticides azinphos-ethyl and fenamiphos (Linderfelt and Turner 2001).

In 2007, the Chemistry Centre of WA performed a snapshot study of pesticides in the Swan Canning Estuary using analytical chemistry techniques with low limits of detection (Chemistry Centre of WA 2007). The middle estuary was sampled at six sites with 12 of the 114 target pesticides reported. These pesticides included insecticides and fungicides used in gardens, parks and in horticultural activities; synergists used with insecticides in the control of mosquitoes and herbicides commonly used in the metropolitan area. Chemicals detected included heptachlor (and the degradation product heptachlor epoxide), dichlofop-methyl, piperonyl butoxide, metsulfuron-methyl, diuron, carbendazim, hexazinone, terbutryn, simazine, cararyl, methomyl and metolachlor.

The Chemistry Centre of WA also performed a snapshot survey of groundwater from 11 Perth bores in 2007, several of which border the Swan and Canning rivers. Where possible, surface water was collected at an adjacent point in the river at the same time as the groundwater collection. Atrazine, diuron and simazine were detected in the groundwater and the surface water samples. In addition, ametryn, hexazinone and terbutryn were detected in the surface water samples (Courtney and Foulsham 2007).

The Department of Water performed a comprehensive survey of Swan and Canning stormwater drains in 2006 (Nice et al. 2009). No organophosphate pesticides were reported which may be explained by the relatively high limit of reporting (0.1 ug/L). Of the organochlorine pesticides, dieldrin was detected in surface waters at Upper Swan and Helena River. In sediment, organochlorine pesticides were detected including heptachlor (and heptachlor epoxide), chlordane, dieldrin, endrin, DDT (and the DDD and DDE congeners) and aldrin were detected in 17% of samples.

Further work by the Department of Water investigated Swan Canning estuary sediments (within the estuarine receiving environment rather than in drains themselves) at 20 sites

(Nice 2009). Of the 16 organochlorine pesticides determined in this study, the DDT congeners, dieldrin, chlordane and aldrin were detected, with the DDT congeners and dieldrin present in concentrations that exceeded interim sediment quality guidelines (ANZECC & ARMCANZ 2000).

PAHs

Limited monitoring data for PAHs has been collected for the Swan and Canning rivers. Swan River Trust water sampling adjacent to the East Perth gasworks site (Swan River Trust 1999b) revealed PAH concentrations were below freshwater ecosystem trigger values (ANZECC & ARMCANZ 2000). Additionally, a Department of Water survey of stormwater drains in 2006 detected PAHs in 44% of sediment samples and 7% of surface water samples (Nice et al. 2009). All 15 PAHs targeted for determination in sediment were present and interim sediment quality guidelines (ANZECC & ARMCANZ 2000), where they exist for PAHs, were exceeded at Helena River, Perth Airport South and the Central Business District drains.

Further work by the Department of Water (Nice 2009) investigated Swan Canning estuary sediment (within the estuarine receiving environment) at 20 sites and found that each of the individual PAH compounds determined were reported at one or more sites. The concentrations of PAHs in the sediments were highly variable: Claisebrook, Maylands, Burswood, Central Business District and Blackwall Reach all had comparatively high concentrations of most PAHs but the interim sediment quality guidelines (ANZECC & ARMCANZ 2000) were not exceeded.

Additionally, the Department of Water sampled groundwater in three disused landfill sites adjacent to the Swan and Canning rivers (Evans 2009). There were numerous detections of PAHs, most commonly within the bores of Woodbridge Riverside Park, with naphthalene present in concentrations that exceeded freshwater ecosystem trigger values (ANZECC & ARMCANZ 2000).

2 Methodology

2.1 Contaminant selection

Herbicides, insecticides and PAHs were selected for determination in this study. These persistent organic compounds were identified as contaminants of concern in the Department of Water baseline study of the Swan Canning catchment drainage system (Nice et al. 2009). Individual herbicides, insecticides and PAHs were determined according to the characteristics of the passive sampling devices that were used. The ED, PDMS and SPMD were selected from a range of available passive sampling devices based on advice from EnTox chemists. It should be noted that some pesticides such as glyphosate and 2,4-D are not accumulated by these devices since they occur in ionic form in the environment and are therefore not retained by the sorbent material. Sixteen herbicides were determined in the ED extracts using LC-MS, 26 pesticides were determined in PDMS extracts using GC-MS and 17 PAHs were determined in SPMD extracts using GC-MS. A more extensive suite of herbicides, insecticides and PAHs was monitored during analysis, but because calibration data is not available yet for many of these compounds they were not quantified and are not included in this report.

2.2 Frequency of sampling

Sampling occurred on four occasions with passive samplers deployed for a four week period. Sampling dates were as follows:

- 27 September to 24 October 2007
- 12 January to 12 February 2007
- 13 April to 9 May 2007
- 20 July to 14 August 2007

2.3 Sampling sites

A total of 10 drains were sampled as part of this monitoring program as shown in Figure 1. Summaries of land uses in the sub-catchments and photos of the drains are shown in Appendix A and B. Eight sites were sampled at any one time. Ellen Brook was only sampled on one occasion as the water levels were too variable across sampling events, so subsequent sampling took place in the Helena River instead, which had a more constant water level. Similar problems were experienced at Southern River, so Mills St Compensating Basin was sampled instead on one occasion. Sites were selected based on the following characteristics:

- a history of contaminants in the catchment from previous water quality monitoring
- a broad range of land uses within the catchment
- year round water flows with suitable water depths at the site
- accessibility of sampling site
- unobtrusive sampling site to minimise potential vandalism

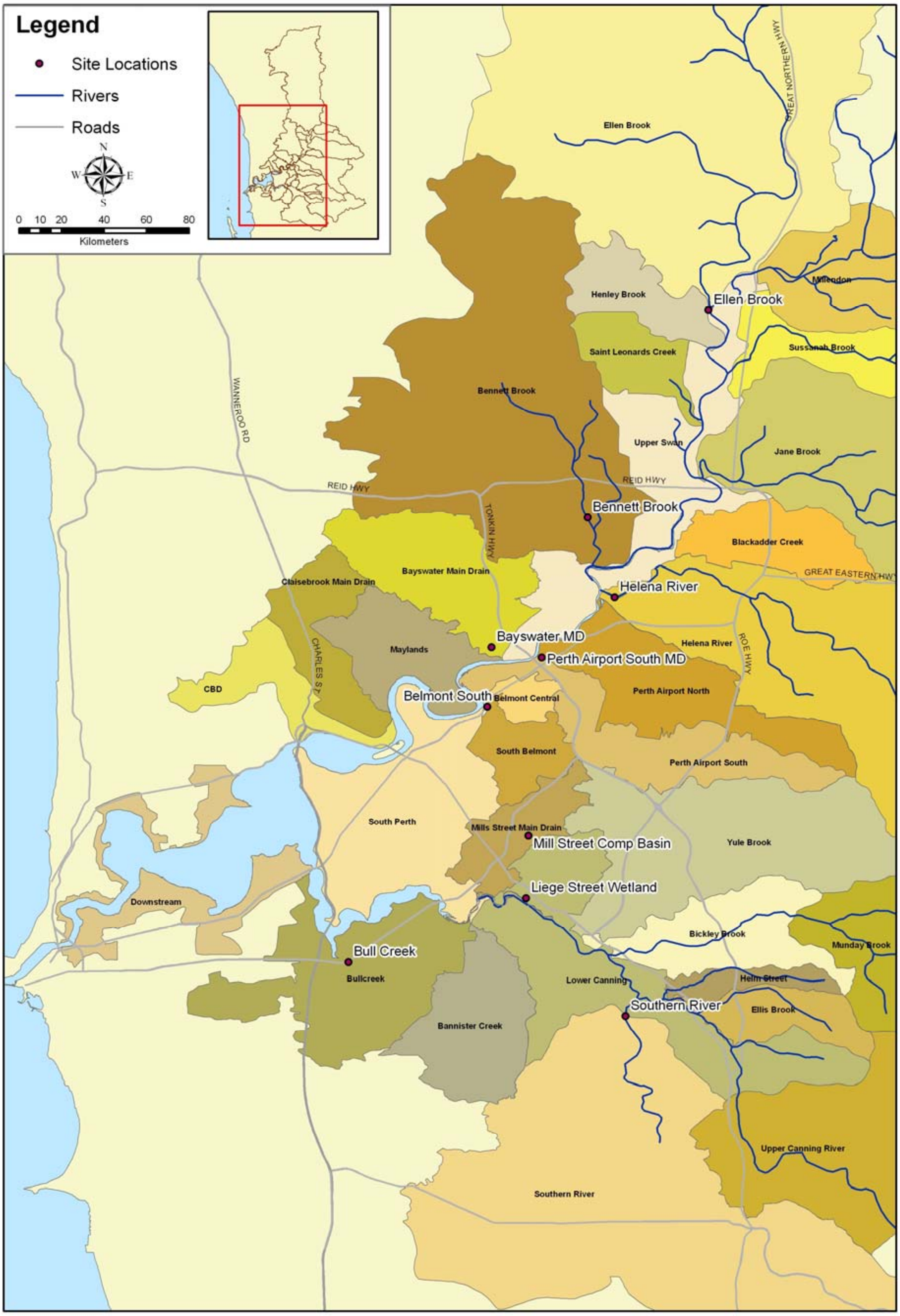


Figure 1. *Map of the Swan and Canning rivers showing the passive sampling sites and the sub-catchments.*

2.4 Site descriptions

Sites were selected at the bottom of sub-catchments where practicable to capture as broad a range of land uses as possible. Detailed site descriptions follow and maps and photographs of each site can be found in Appendix B.

Bayswater

Bayswater sub-catchment has an area of 27 km2 comprising primarily residential and industrial uses. The passive sampling device was deployed just downstream from the King William St and Bayswater Main Drain confluence in Bayswater, about 800 m upstream from where the drain discharges to the Swan River. The Bayswater Main Drain consistently had good water flows, while the King William St drain tended to dry out over summer. After heavy rainfall, water levels rose dramatically in the Bayswater Main Drain and sandy sediment accumulated around the base of the passive sampler. The passive sampler was also often fouled with leaves, sticks and other organic materials. On the first sampling deployment contractors were observed spraying herbicides on the ovals nearby. Large benthic macrophytes were present in the drain most of the year.

Bennett Brook

Bennett Brook sub-catchment has an area of 112 km^2 comprising primarily conservation and natural bushland, horticulture, residential and industry. The passive sampling device was deployed near the bridge where Benara Road crosses Bennett Brook in Caversham. This site is about 2.2 km upstream from where the drain discharges to the Swan River. Bennett Brook consistently had good water flows. On all occasions visited, suspended solids were evident in the water and large benthic macrophytes were present.

In April 2007, as part of a program to eradicate the pearl cichlid, a feral fish species, the Department of Fisheries placed a net across the Brook and treated a section upstream from this with the pesticide, rotenone.

Ellen Brook

Ellen Brook sub-catchment is 715 km^2 in area comprising significant areas of conservation, natural bushland and farming land uses. The site is situated at the end of Henry Street in Henley Brook. The passive sampling device was deployed about 20 m upstream of the Ellen Brook and Swan River confluence. Ellen Brook was sampled only during the first deployment. The water levels were low during this period and continued to drop to very low levels through the summer. The water was tannin stained during sampling.

Helena River

The Helena River sub-catchment is 176 km^2 in area comprising mostly conservation and natural bushland, with some industry, residential areas and farm land. The sub-catchment includes the Bellevue and Midland industrial areas. The passive sampling device was deployed under the bridge where the Great Eastern Highway crosses the Helena River, about 600 m upstream from the confluence of the Helena River and the Swan River. Water levels in the Helena River fluctuated dramatically over the year. In the winter months water levels were high and flowed from the upper catchment. However, in the summer months there was tidal influence from the Swan River with fluctuating water levels and directions of flow.

Perth Airport South

Perth Airport South sub-catchment is 25 km^2 in area largely comprising industry, conservation areas and natural bushland. The sub-catchment captures stormwater runoff from Perth Airport. The passive sampling device was deployed in the drain about 170 m upstream from where the drain discharges to the Swan River. Water levels in the drain fluctuated over the year. In summer, water levels were low and appeared to have some tidal influence from the Swan River. In winter, water levels were consistently high. After heavy rainfall events water levels in the drain rose rapidly.

Belmont South

Belmont South sub-catchment is 10 km^2 in area comprising predominantly residential and industrial areas. The passive sampling device was deployed in the drain approximately 160 m upstream from where it discharges to the Swan River. Belmont South drain consistently had good water flows, even through summer. This suggests that the drain may have some groundwater influence. The water was generally clear.

Liege Street Wetland

Liege Street Wetland is in the Lower Canning sub-catchment which is 47 km^2 in area and contains large areas of land for residential, conservation, natural bushland and industrial use. It receives major stormwater inputs from Liege Street and Cockram Street drains and includes the commercial areas of Cannington and the Westfiled Carousel Shopping Centre. The passive sampling device was deployed above the Liege Street Wetland Weir which is about 180 m from the Canning River. The wetland had some marginal fluctuations in water levels over the year but water flow through the wetland was consistently slow. In the summer months there were extensive build-ups of the aquatic weeds, *Lemna* and *Azolla*.

Mills Street

Mills Street sub-catchment is 13 km^2 in area comprising land used primarily for industrial and residential purposes. The sub-catchment is immediately surrounded by light industrial (e.g. car wreckers) and commercial property. The passive sampling device was deployed at the outlet of the Mills St compensating basin in Welshpool, about 3.1 km from the Canning River. Water levels in the Mills St compensating basin dropped over the summer months. Water at the site was typically shallow and clear.

Southern River

Southern River sub-catchment is 149 km^2 in area comprising large areas of conservation and natural bushland, farming, industrial and residential land. The passive sampling device was deployed near the bridge where Corfield Street crosses the Southern River, about 980 m from the Canning River. Water flowed all year in the Southern River but water levels were much higher in the winter months. The site was not sampled in summer due to the low water levels.

Bull Creek

Bull Creek sub-catchment is 42 km^2 in area comprising large areas of residential and industrial land. The passive sampling device was placed on the southern side of Leach Highway just before the creek passes underneath the Highway. The site is adjacent to All Saints College in Bull Creek and approximately 500 m upstream of the Canning River. The creek consistently had good water flows, even in summer suggesting that there may be some groundwater influence. The water was generally clear and the drain often had a petroleum-like odour.

2.5 Application of trigger values

There are currently no guidelines available specifically for comparison with surface waters within stormwater drains. However, consideration was given to the sensitive nature of the receiving environment downstream from the drainage systems in the selection of guidelines for this study. As such, data were compared to the Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand (ANZECC & ARMCANZ 2000) trigger values for 95% ecosystem protection. This level of protection is relevant for slightly to moderately disturbed ecosystems (ANZECC & ARMCANZ 2000).

It should be noted that the use of guidelines in this study was to provide a general frame of reference only as to the state of water quality in the drains. Where the referenced guidelines are exceeded, this does not indicate that standards are not being met. Rather, it indicates that further consideration should be given to the particular situation, most probably in the form of targeted impact studies in the downstream receiving environment

2.6 Quality control

Two replicate EDs, PDMSs and SPMDs were deployed at each site on each occasion (Figure 2). Sampling was conducted four times at most sites. One set of field blanks of each type of device was deployed at four of the selected sites.

The passive sampling devices each had a performance reference compound (PRC) loaded onto the sorbent material prior to deployment. The desorption of the PRC from the sorbent material during the period of sampling enables an accurate estimation of the water flow through the passive sampling device to be calculated from comparison with calibration data (Bartkow et al. 2006).

For comparison, water samples (grabs) were also collected from each location to determine contaminant concentrations. Two grab samples were collected for determination of polar organic compounds at each location on two occasions throughout the trial and two grab samples were collected for non-polar organic compounds at four locations on ten occasions during deployment.

2.7 Data analysis and presentation

Sample analysis was carried out by the Queensland Health Scientific Services laboratory (National Association of Testing Authorities - NATA accredited). The data was then compiled and analysed by EnTox. A summary is presented in Appendix C.

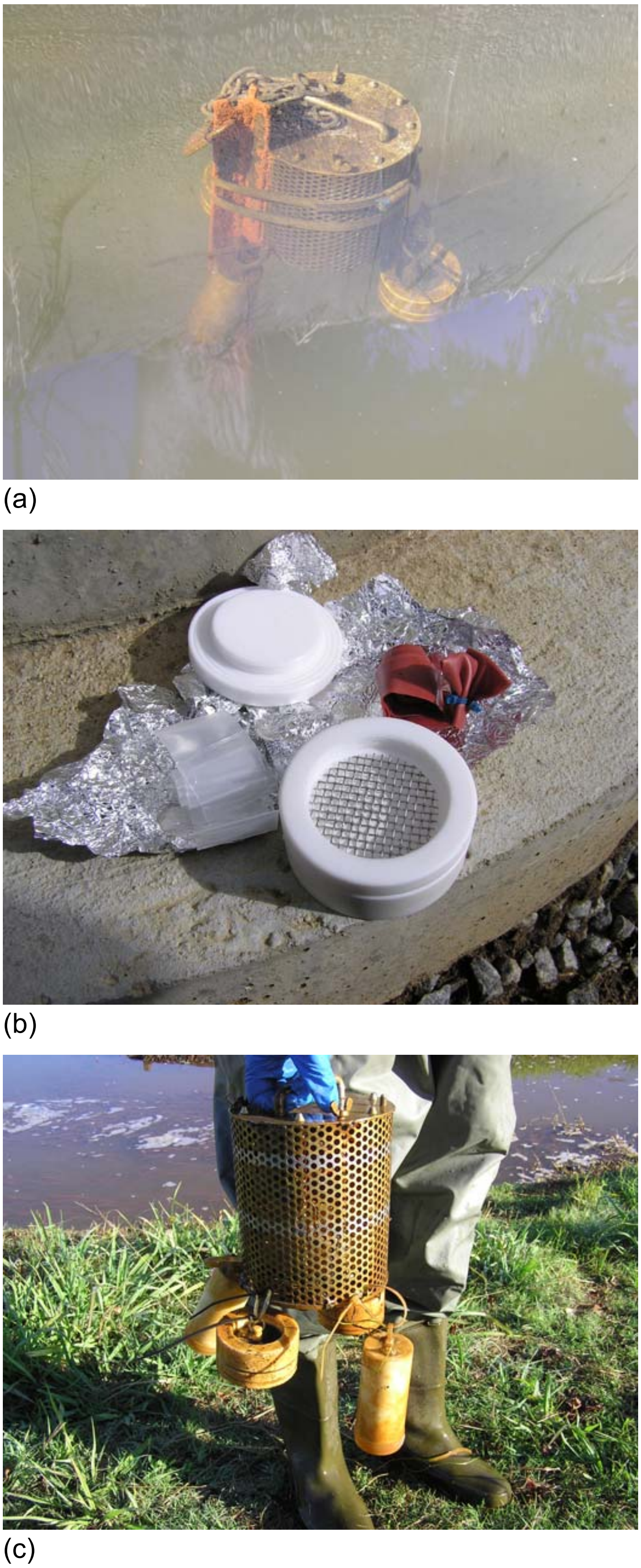


Figure 2. (a) Passive sampling device in situ (b) The components of an Empore Disk sampler used to collect a procedural field blank. (c) Passive sampling device after 1 month deployment in Bayswater Main Drain, April 2007.

3 Results

3.1 Water quality results

Table 1 summarises the compounds that were reported in the analysis of passive sampling devices and their associated ANZECC & ARMCANZ (2000) trigger values. Table 2 lists the six compounds that exceeded the trigger values and summarises their chemical and ecotoxological properties (ANZECC & ARMCANZ 2000). The comprehensive set of water quality data from this study is presented in Appendix C.

Table 1. The herbicides, insecticides and PAHs reported in the analysis of passive sampling devices and the corresponding ANZECC & ARMCANZ (2000) 95% freshwater ecosystem trigger values. Chemicals in bold exceeded 95% freshwater ecosystem trigger values on one or more occasion(s). Trigger values in brackets are for the parent compound in cases where the degradation products do not have guidelines established.

Herbicides	**Trigger Values (µg/L)**	**Insecticides**	**Trigger Values (µg/L)**	**PAHs**	**Trigger Values (µg/L)**
Diuron	0.2*	Trifluralin	4.4	Acenaphthylene	
Simazine	3.2	**Diazinon**	0.01	Acenaphthene	
Atrazine	13	Terbuthylazine		Fluorene	
Desthyl atrazine	(13)	Triallate		Phenanthrene	2*
Desisopropyl atrazine	(13)	**Chlorpyrifos**	0.01	Anthracene	0.4*
Hexazinone	75*	Heptachlor epoxide	(0.09)	Fluoranthene	1.4*
Tebuthiuron	2.2	Pendimethalin		Pyrene	
Ametryn		trans- Chlordane	0.08	Benz[a]anthracene	
Metolachlor	0.02*	Methidathion		Chrysene	
Oxadiazon		**Dieldrin**	0.01*	Benzo[k]fluoranthene	
Terbutryn		Piperonyl butoxide		Benz[e]pyrene	
Propiconazole		Benalaxyl		Benz[a]pyrene	0.2*
Propazine		Bifenthrin		Perylene	
		Rotenone		Indeno[1,2,3cd]pyrene	
				Benzo[ghi]perylene	

* represent calculated low reliability trigger values and should only be used as indicative interim working levels.

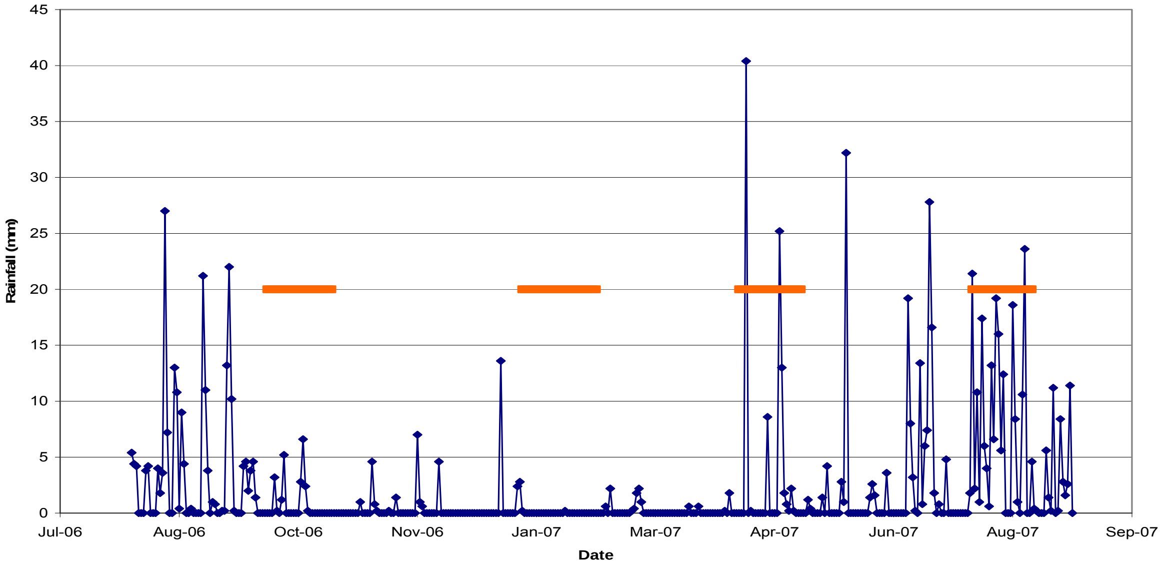
Table 2. Chemical and ecotoxicological properties of compounds that exceeded 95% ecosystem protection trigger values (ANZECC & ARMCANZ 2000).

	Solubility at 25°C (mg/L)	**Adsorption potential (to soil)**	**Ecotox testing freshwater fish**	**LC50* (µg/L)**	**Bioaccumulation potential**
Simazine	6.2	Strong	7 fish species for 24 – 96h	90 – 6,600	No
Diuron	42.0	Moderate	15 fish species for 48 - 96h	500 - 63,000	No
Metolachlor	488.0	Moderate	1 fish species for 48h in two different laboratories	20 - 8,600	No
Diazinon	60.0	Strong	23 fish species for 48 – 96h	22 - 24,000	No
Chlorpyrifos	1.4	Strong	16 fish species for 48 – 96h	1.3 - 542	Yes
Dieldrin	0.2	Strong	9 fish species for 48 – 96h	1 - 79	Yes

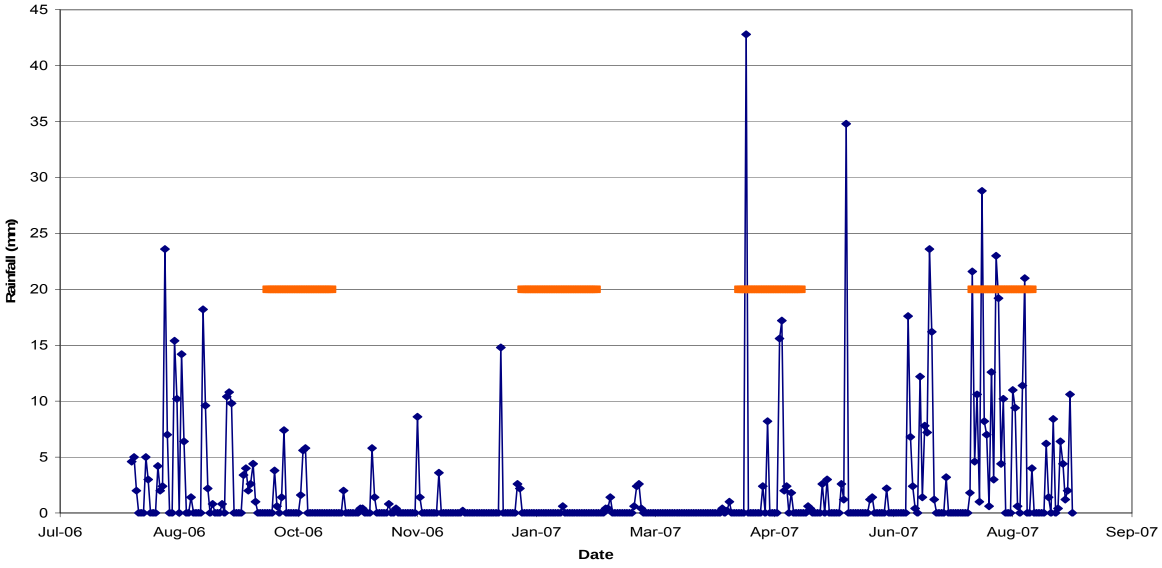
* LC50 represents the concentration of contaminant at which 50% of the test species suffer mortality.

3.2 Rainfall

The Perth Metropolitan area experienced its driest year on record in 2006 with an annual rainfall of 467 mm. The annual rainfall for 2007 was 703 mm, still well below the average annual rainfall of 855 mm. Rainfall records from the Perth Metropolitan and Perth Airport weather stations over the period from July 2006 to September 2007 are presented in Figure 3. Passive sampler deployments are indicated in orange.



(a)



(b)

Figure 3. Rainfall data from (a) Perth Metropolitan weather station and (b) Perth Airport weather station from July 2006 to September 2007.

The orange lines denote the duration of the passive sampler deployments.

3.3 Physical data

Physical data (water temperature, pH and specific electrical conductivity) were collected weekly during deployment periods. Five readings were collected per deployment. Median data are presented below.

Water temperature

Water temperatures at all sites peaked during the January sampling and dropped through the winter months, as shown in Figure 4. The largest variation in temperatures and the lowest median temperature occurred in Helena River.

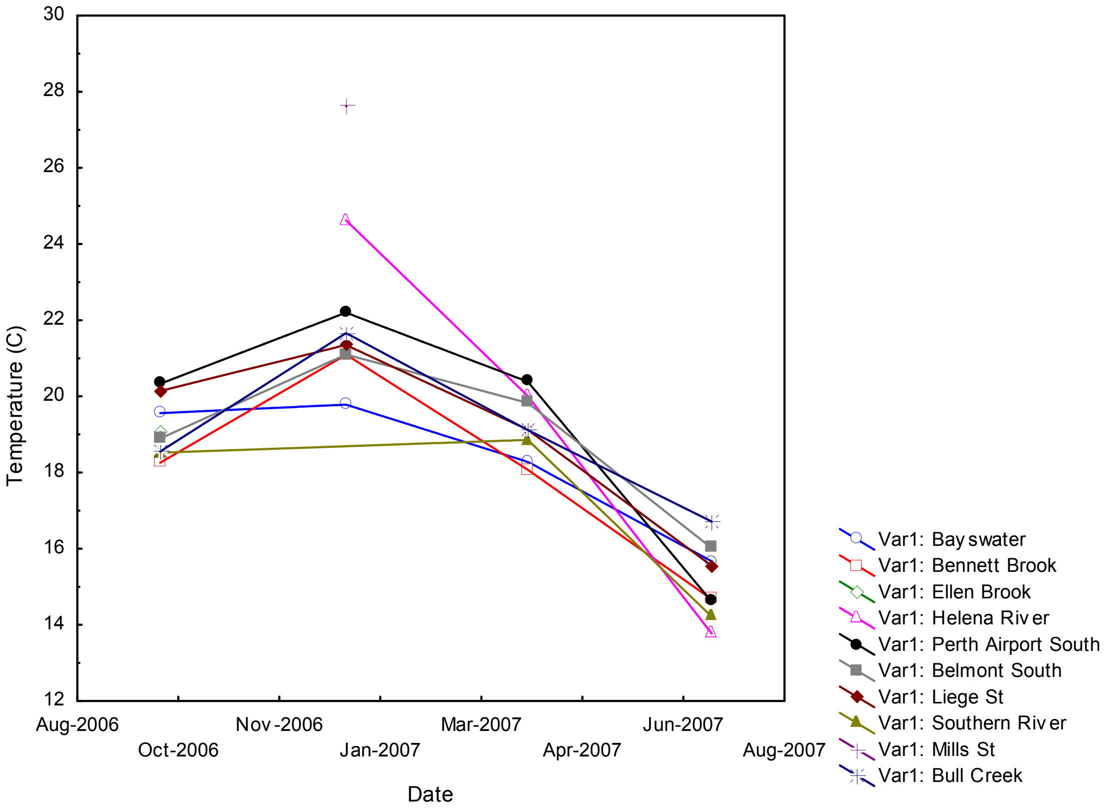


Figure 4. Median water temperatures (°C) in each drain during passive sampler deployment.

pH

The south west lowland trigger values for aquatic ecosystems for pH constitutes a range from 6.5 to 8.0 (ANZECC & ARMCANZ 2000), where values falling outside of this range should trigger further investigation. As shown in Figure 5, the most alkaline waters were recorded at Mills St compensating basin in January 2007, exceeding the upper trigger value. The most acidic waters were consistently recorded at Bayswater Main Drain and were below the lower trigger value on one occasion. There were no clear seasonal patterns.

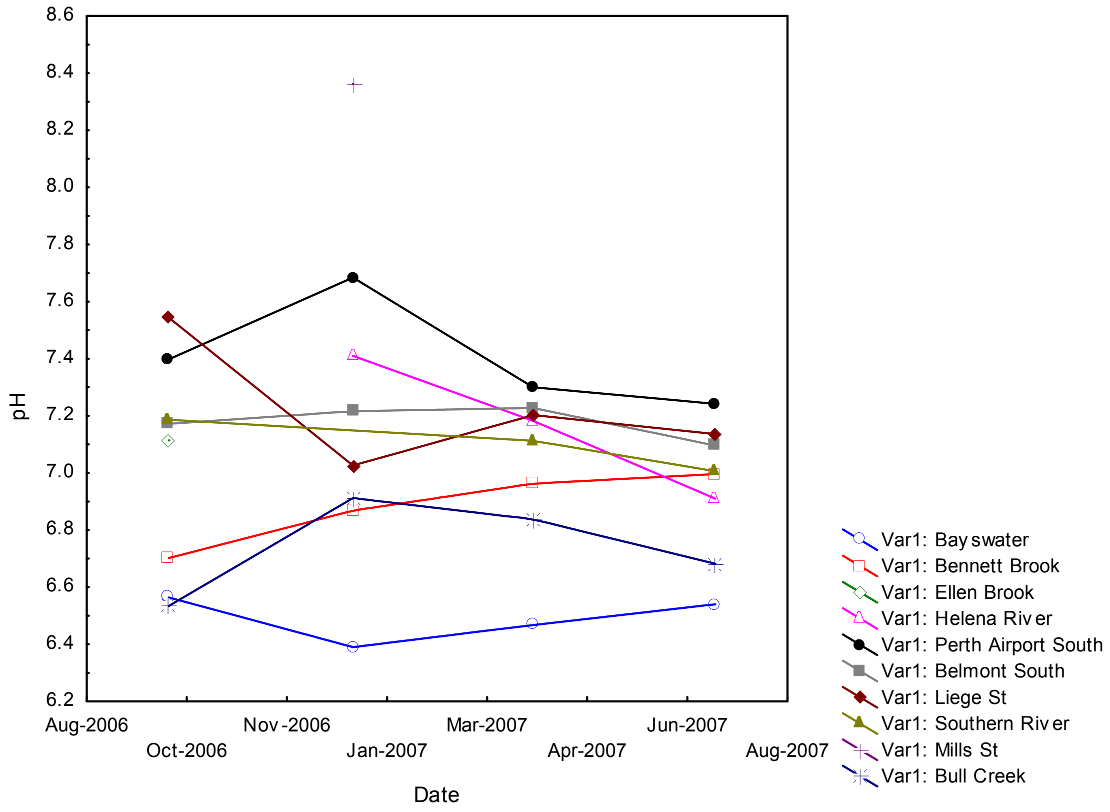


Figure 5. Median pH in each drain during the four passive sampler deployments.

Salinity (specific conductivity)

The south west lowland trigger values for aquatic ecosystems for electrical conductivity constitutes a range from 0.12 to 0.3 mS/cm, where values falling outside of this range should trigger further investigation (ANZECC & ARMCANZ 2000). Values at the lower end of the range are typically found in upland rivers, with higher values found in lowland rivers. Mean electrical conductivity exceeded the upper trigger value in all drains (Figure 6). The sites can all be classified as fresh or marginal with the exceptions of Helena River and Perth Airport South which are influenced by tidal activity from the Estuary during the summer months when water flows are low.

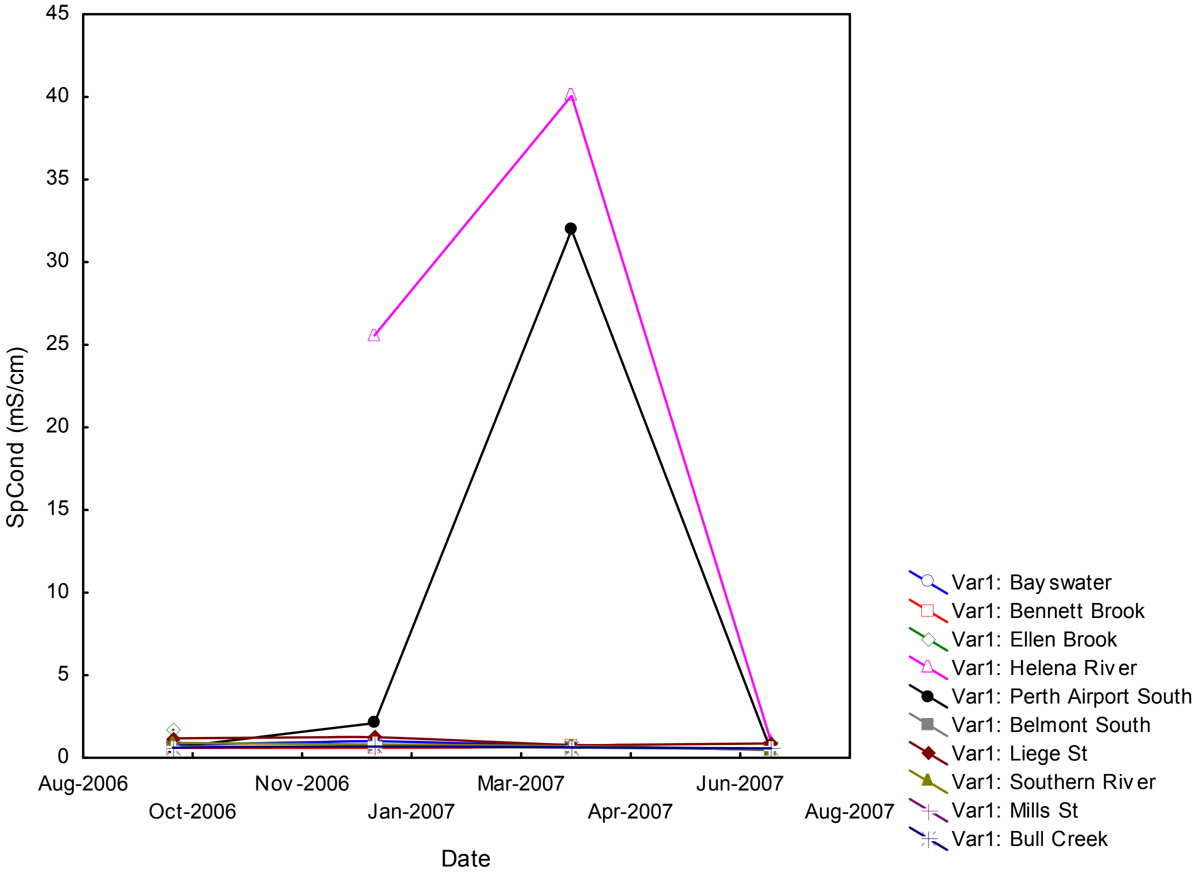


Figure 6. Median electrical conductivity (mS/cm) during passive sampler deployments.

4 Discussion

A wide range of herbicides, insecticides and PAHs were detected in the surface water drainage networks that discharge into the Swan and Canning rivers. Ten of the 16 herbicides,15 of the 26 insecticides and 15 of the 17 PAHs targeted in this study were detected. The low limits of reporting in this study allowed more of these compounds to be identified in the surface water than shown in previous studies (e.g. Nice et al. 2009).

Many of the compounds that were present in samples from this study are toxic to organisms at low levels. Of particular concern are the regular detections in surface water of organochlorine pesticides, namely chlordane, dieldrin and heptachlor and the metabolites of these pesticides. In 1995, the Governing Council of the United Nations Environment Programme called for global action to be taken on persistent organic pollutants. Following this, the 12 most harmful persistent organic pollutants were nominated, commonly referred to globally as the “Dirty Dozen”. All of the organochlorine pesticides detected in the current study are on the list of nominees. The Stockholm Convention, an internationally legally binding agreement for persistent organic pollutants, was enacted in 2004. As a result, the importation, manufacture and use of all organochlorine pesticides has been completely banned in Australia since 2004. Despite this, organochlorine pesticides and their metabolites may still be present in the environment due to their highly persistent nature (Department of the Environment, Water, Heritage and the Arts 1997).

Only a limited number of water quality guidelines are available for herbicides, insecticides and PAHs. The ANZECC & ARMCANZ (2000) guidelines for freshwater ecosystems provide trigger values for 95% protection for six of the herbicides that were reported as present, six of the insecticides and four of the PAHs. Low reliability values have been derived due to insufficient data being available for many of these compounds (denoted by an asterisk in Table 1), and these should only be used as indicative working levels. The herbicides simazine, metolachlor and diuron were present in concentrations above trigger values. The insecticides diazinon, chlorpyrifos and dieldrin also exceeded trigger values. None of the PAHs exceeded the trigger values.

Herbicides have been shown to be more concentrated in surface water, whereas the less water soluble insecticides and PAHs were shown to more likely to be concentrated in the sediment (Nice et al. 2009). By their nature many herbicides, particularly the systemic varieties, tend to be strongly polar compounds and hence have relatively high water solubility (Australian Academy of Technological Sciences 2002). This assists in their mode of action on the target plant through uptake of water through their roots or other parts with the herbicide in solution. The herbicide can then act upon the whole plant. These chemical properties enable the herbicides and other polar compounds to migrate offsite through leaching into groundwater and/or surface water after rainfall or irrigation.

Conversely, insecticides are often less polar and lipophilic in nature and will bind to sediment in preference to dissolving in water (Australian Academy of Technological Sciences 2002), increasing their persistence in the environment. Insecticides enter the body of an insect through ingestion, direct contact and/or inhalation as aerosols. PAHs are also generally non-polar in nature and will likewise bind strongly to sediment (Wilson et al. 2003). Many of the insecticides and PAHs will bind to suspended solids reducing their concentrations in the water column. However, high concentrations of these contaminants can enter stormwater after heavy rainfall when suspended solid loads are highest (Department of Water 2007).

Herbicides

Herbicides are a group of chemicals that are used to destroy, control or inhibit the growth of plant which are environmental pests. For the purpose of this discussion they also include fungicides. They can be harmful to both environmental and human health in trace concentrations. Simazine, diuron and metolachlor were all detected above 95% freshwater ecosystem trigger values at one or more sites. Simazine and diuron were also generally the herbicides found at the highest concentrations at most sites. The herbicides atrazine, hexazinone, oxadiazon, terbutryn, propiconazole, propazine and trifluralin were all measured but were below trigger values and were found more sporadically in the sub-catchments. Concentrations of all these herbicides were greater than 1.0 ng/L (i.e. the limit of reporting) on at least one occasion in the sub-catchments. A summary of the occurrence and use of each of these herbicides is as follows.

Simazine was the most frequently reported herbicide, detected in all sub-catchments on almost all occasions. Simazine is a triazine herbicide with a selective systemic action and is absorbed through the roots (Australian Academy of Technological Sciences 2002). It is used for control of a wide variety of grasses and broadleaf weeds in fruit, vines, vegetables, flowers, turf and forestry (Tomlin 1994). It is also commonly used in households, for instance it is the active ingredient in some paver sprays.

A freshwater moderate reliability trigger value of 3.2 µg/L has been derived for simazine (ANZECC & ARMCANZ 2000), which was exceeded on one occasion in a grab sample in the Belmont South Main Drain (ANZECC & ARMCANZ 2000). The high concentration of simazine in the sample suggests that it may be associated with applications of the herbicide in the sub-catchment prior to heavy rainfall events that occurred in April. Southern River consistently had the highest concentrations of simazine. Belmont South (April) and Bennett Brook (July) also recorded high concentrations. As simazine was widely detected across the sub-catchments, the sources are likely to be diffuse and not associated with any particular type of land use.

Diuron was reported in all sub-catchments on all occasions. Diuron is a selective urea herbicide which has a systemic mode of action being mainly absorbed through the roots (Australian Pesticide and Veterinary Medicines Authority 2006). Diuron has a variety of uses including selective control of grasses and broadleaf weeds in crops, and total weed control in commercial areas, roads, railways and buildings (Australian Academy of Technological Sciences 2002). In Australia, diuron is registered for use on commercial areas, crops, cereals, vegetables, orchards, flower nurseries, in flood mitigation channels, home ponds and as a boat antifouling agent (Australian Pesticide and Veterinary Medicines Authority 2006).

A freshwater low reliability trigger value of 0.2 µg/L has been derived for diuron (ANZECC & ARMCANZ 2000) which was exceeded in the water grab samples during the April deployment in the Bayswater Main Drain on one occasion and Liege St Wetland on both occasions. The high spikes of diuron in grab samples suggest that they may be associated with applications in the sub-catchment prior to heavy rainfall events that occurred in April. Similarly to simazine, because it was so widely detected across the sub-catchments the sources are likely to be diffuse and not necessarily associated with any particular type of land use.

Metolachlor is a herbicide with a selective action that inhibits weed germination after absorption by hypocotyls and shoots (Tomlin 1994). Metolachlor is used for control of annual grasses and broadleaf weeds in clover pasture, vegetable and cereal crops (Australian

Academy of Technological Sciences 2002). It was detected in a number of sub-catchments. A freshwater low reliability trigger value of 0.02 µg/L has been derived for metolachlor (ANZECC & ARMCANZ 2000). Metolachlor was detected above the trigger value in the PDMS samplers in Bayswater Main Drain in April.

Atrazine is one of the most widely used herbicides in Australian agriculture for the control of grasses and broadleaf weeds (Gaynor et al. 2001). In 1997, industrial and non-agricultural uses of atrazine (home garden uses and all commercial turf uses) were banned because of concerns over environmental impacts including the potential for contamination of ground and surface water, and residue and efficacy uncertainties (APMVA 2006). Atrazine is a known endocrine disruptor, having been found to induce hermaphtoditism in genetically male frogs at levels as low 0.1 µg/L. It also has potential phytotoxicity effects, is considered to be mutagenic and is a known carcinogen (Cox 2002). Most sub-catchments where atrazine was detected, such as Ellen Brook and Helena River, had farming or horticultural land uses within them. Bayswater and Mills Street were unusual, however, as they exhibited some of the highest concentrations of atrazine with very little agricultural land use in the sub-catchment.

Hexazinone is used in various situations for the control of annual and perennial weeds (Australian Academy of Technological Sciences 2002). It was detected across a number of the sub-catchments at low concentrations. Oxadiazon is used for pre-emergent control of grasses, broadleaf weeds, vines and trees (Australian Academy of Technological Sciences 2002). It was present in Bennett Brook, Helena River, Belmont South and Southern River. Both herbicides are likely to have originated from diffuse sources in the sub-catchments.

Terbutryn is a selective herbicide that is a pre-emergent and post emergent control agent for most grasses and many annual broadleaf weeds (Australian Academy of Technological Sciences 2002). It is also used as an aquatic herbicide for the control of submerged and free-floating weeds and algae. It was reported at the highest concentrations in Southern River and Bull Creek and is likely to be from point sources.

Propiconazole is a systemic foliar fungicide with a broad range of activity. It is used on grasses grown for seed, mushrooms, corn, cereals, nuts and a range of stonefruit (Australian Academy of Technological Sciences 2002). Mills St Compensating Basin had the highest concentrations on the one occasion it was sampled with samples from a number of other sub-catchments containing low concentrations.

Propazine is a herbicide used for control of broadleaf weeds and annual grasses. It is generally applied as a pre-emergent spray (Australian Academy of Technological Sciences 2002). Its occurrence was reported only in April 2007 in Bayswater Main Drain and is likely to be from a point source in the sub-catchment.

Trifluralin is a selective pre-emergent herbicide used to control many annual grasses and broadleaf weeds (Australian Academy of Technological Sciences 2002). Highest concentrations were detected in Southern River, but low concentrations were detected in a number of other sub-catchments. The sources of contamination are likely to be diffuse and may be associated with agriculture.

High concentrations of herbicides commonly appear to be linked to rainfall patterns as heavy rainfall or overhead irrigation soon after application can wash herbicides from foliage, causing loss with runoff. With time, residues on foliage are less likely to be washed off as they become incorporated in surface plant waxes. In agricultural areas, herbicides are strategically applied to protect crops, trees and pasture from weed invasion (MAFRA 2006). On annual crops, pre-emergent herbicides are sprayed in summer and spring to prevent weeds from emerging, selective herbicides are used during cropping in winter and nonselective herbicides are often applied after harvest to clear waste ground (MAFRA 2006). In urban areas, herbicides are commonly used to maintain lawns and gardens. Many common grass varieties used for lawns grow in the warmer months and become dormant over winter so herbicide application regimes can be quite different to those typical in the agricultural areas.

Measured concentrations from the September 2006 sampling event were comparatively high for all herbicides in the Perth Airport South Main Drain, for diuron and simazine at Bull Creek and for simazine at Liege St Wetland. Concentrations were consistently low in January 2007 sampling, coincident with low rainfall (herbicides are less likely to have been washed into the drainage system). Perth Airport South showed an increase in concentrations from January through to July 2007. Bayswater Main Drain showed increases in most herbicides, particularly atrazine during April 2007 followed by a decrease in July 2007. Also in April, a large increase was detected for diuron at Liege Street and simazine at Belmont South and Southern River. This is likely to be related to an intensive application during the spring pre-emergence season as was observed in a United States study for metolachlor and atrazine (Hines et al. 2001). In July 2007, the previous high concentrations of these herbicides subsequently decreased to similar levels that were measured in January, except at Southern River. Simazine concentrations also showed large increases in July 2007 at Bennett Brook, Helena River and Bull Creek.

Insecticides

Insecticides prevent, destroy, repel or mitigate insects. Therefore it is unsurprising that they are extremely toxic to aquatic organisms with which they come into contact. Many of the insecticides, such as the organochlorine pesticides, are lipophilic and so are bioaccumulated by the fatty tissue of aquatic organism (Department of the Environment, Water, Heritage and the Arts 1997). Consequently animals higher up the food chain such as predatory fish and birds of prey can accumulate higher levels of these chemicals. Some insecticides can have serious short-term and long-term impacts at low concentrations (Department of the Environment, Water, Heritage and the Arts 1997). The degradation products of many of these chemicals are even more toxic than the parent compound (Australian Pesticide and Veterinary Medicines Authority 2006). In addition, non-lethal effects such as immune system and reproductive damage can occur (Australian Pesticide and Veterinary Medicines Authority 2006). Several of the insecticides detected in this study including chlordane, dieldrin and heptachlor are known endocrine disruptors, having oestrogenic properties that are able to interfere with reproductive system function, inducing reproductive organ abnormalities and fertility problems (Ulrich et al. 2000). These pesticides are also carcinogenic, mutagenic and teratogenic (Fox 1995).

Diazinon, chlorpyrifos and dieldrin were all detected above 95% freshwater ecosystem trigger values at one or more sites and were also amongst the most commonly reported insecticides in this study. Methidathion, rotenone and the synergist piperonyl butoxide were all detected below trigger values and found more sporadically in the sub-catchments. They were all detected to concentrations of at least 10 ng/L at one or more sites, with the exception of rotenone which was just shown as being present. A summary on the use and occurrence of each of these pesticides or synergists follows.

Diazinon is an organophosphate pesticide. It is a non-systemic insecticide used for controlling sucking and chewing insects and mites on a wide variety of crops, for fruit flies on harvested fruit, as well as flies, cockroaches and other household pests (Tomlin 1994). In Australia, diazinon is also used on farm and pet animals, for pest control in buildings, vehicles and on ponds to control mosquito populations (Australian Academy of Technological Sciences 2002). Many organisms are extremely sensitive to diazinon and its metabolite is more toxic than the parent compound (Australian Pesticide and Veterinary Medicines Authority 2006). A moderate reliability freshwater trigger value of 0.01 ug/L has been derived for diazinon (ANZECC & ARMCANZ 2000) which was exceeded in the PDMS samplers in all sub-catchments on at least one occasion except Belmont South and Liege St Wetland. It was also detected above trigger values on all four grab sampling occasions (ANZECC & ARMCANZ 2000). The highest concentrations were reported in the Southern River, Helena River and Perth Airport South sub-catchments in April sampling. It is a widely used insecticide and likely to be entering the aquatic environment from diffuse sources.

Chlorpyrifos is an organophosphate pesticide with a non-systemic mode of action (Australian Academy of Technological Sciences 2002). Chlorpyrifos is used against subterranean termites, flies, mosquitoes, beetles, moths and cockroaches. Chlorpyrifos is used to protect wheat, vegetables, fruit, pasture, machinery, turf, gardens and pets (Australian Academy of Technological Sciences 2002). Chlorpyrifos is highly toxic to most organisms and the metabolite is more toxic than the parent compound (Australian Pesticide and Veterinary Medicines Authority 2006).

Chlorpyrifos was detected at all sites on almost all occasions. The freshwater high reliability trigger value of 0.01 µg/L derived for chlorpyrifos (ANZECC & ARMCANZ 2000) was exceeded in the PDMS samplers in Southern River and Bull Creek in April 2007.

In 1987, the use of the insecticide dieldrin was restricted to sub-floor use against termites. Prior to 1987 dieldrin also had agricultural appliations on fruit and pastures. Dieldrin is considered to be toxic to most organisms and has a low reliability trigger value of 0.01 µg/L (ANZECC & ARMCANZ 2000). Use ceased in 1994 (Australian Academy of Technological Sciences 2002). Dieldrin was consistently detected in the PDMS samplers above trigger values in the Belmont South Main Drain. It also exceeded the trigger value in April in the Bayswater Main Drain. As dieldrin has been banned in Australia since 1994, the source of contamination in surface waters is likely to be from historic use, such as the protection from termites of wooden poles carrying electricity and telephone cables; soil treatment in farm and industrial premises from termites; and buildings, fences and similar structures (Department of the Environment, Water, Heritage and the Arts 1997). Dieldrin may enter the drains through contaminated groundwater where it is particularly persistent (United States Geological Survey 2006). Concentrations were highest in Belmont South and Bayswater Main Drain, both of which appear to be influenced by groundwater.

Methidathion is a non-systemic organophosphate insecticide with stomach and contact action (Australian Academy of Technological Sciences 2002). The compound is used to control a variety of insects and mites in crops such as fruits and vegetables and also in greenhouses and on rose cultures. It is especially useful in combating scale insects. Methidathion was only detected on one occasion in July 2007 in the Helena River sub-catchment. Its occurrence is likely to be a result of a point source use prior to rainfall.

Piperonyl butoxide is a synergist used in a wide variety of insecticides (Australian Academy of Technological Sciences 2002). Synergists are chemicals that lack pesticidal effects of their own but enhance the properties of the active ingredients of a pesticide (United States Geological Survey 2006). Piperonyl butoxide can be used with pyrethrins, pyrethroids, rotenone and carbamates (Australian Academy of Technological Sciences 2002). It is often added to pyrethroid containing insecticides to enhance the effectiveness of mosquito control by preventing the insects from breaking down the pesticide. AbateR, containing temephos as the active ingredient, is typically used for mosquito control around Perth, however, it does not require piperonyl butoxide as a synergist.

Rotenone is used in solution as a piscicide and insecticide. It is commonly used in fisheries management to remove unwanted finfish species from waterways (Australian Academy of Technological Sciences 2002). It was not specifically targeted as an analyte in this study but nonetheless was reported in samples from Bennett Brook in April 2007. At this time, the Department of Fisheries was conducting a program using rotenone to eradicate feral pearl cichlids from the brook, so the result can be regarded as a positive control.

Insecticides are not applied as seasonally as herbicides. Insecticide applications are normally targeted at specific outbreaks of pests as they occur, so seasonal trends are less likely to be evident. However, in some cases they are applied pre-emptively to prevent outbreaks. Spring is the most active time of year for many insects but outbreaks can occur at any time (United States Geological Survey 2006). Occurrences in surface waters may also be linked closely with heavy rainfall events as a result of insecticide runoff.

The variable nature of insecticide application may have been reflected in the results. The highest concentrations were generally detected in April 2007 and were most evident at the Bayswater site. This concentration spike might be due to a combination of increased application through the spring months and heavy rainfall runoff. In general, the lowest concentrations of insecticides were measured in January 2007, with the exception of diazinon in Helena River and terbutryn in Bull Creek. Again this may be a result of the low rainfall during the summer months. Concentrations of pesticides in July and September 2007 varied depending on the compound and the site. For instance, some of the highest concentrations of pesticides were measured in Bennett Brook in September while the highest concentrations measured in Bull Creek occurred in July.

Polycyclic Aromatic Hydrocarbons

The PAHs determined in the current study are a subset of the PAH group and were limited to the 17 PAHs that were identified as being of greatest concern with regard to potential exposure and adverse human health (Department of Health 2004). In aquatic systems, the toxicity of PAHs has been shown to increase with increased molecular weight, and degradation time has been shown to decrease with increasing molecular weight (Eisler 1987). LMW PAHs such as phenanthrene are acutely toxic and several are described as being endocrine disrupting, mutagenic, carcinogenic and teratogenic (Fetzer 2000). Many of the HMW PAHs are considered to be mutagenic and carcinogenic (Fetzer 2000). PAHs have the potential for bioaccumulation and have been recorded in the tissues of plankton, vascular plants, molluscs and fish (Neff 1979). The ensuing toxicity to higher level organisms as a result of bioaccumulation is thought to constitute a significant ecological risk (Mosisch and Arthington 2001).

PAHs are common in the environment from petrogenic and pyrogenic sources. Petrogenic sources may include accidental spills and discharges, for example, from underground storage tanks, and from municipal and urban runoff. Pyrogenic sources include the combustion of fossil fuel (coal and petroleum) and biomass. In the Swan Canning sub-catchment, fumes from vehicle exhaust, coal, coal tar, asphalt, wildfires, agricultural burning and hazardous waste sites are all potential sources. PAHs such as fluorene, may also be used in the manufacture of dyes, plastics and pesticides (Agency for Toxic Substances and Disease 1990).

The factors controlling the mobility of colloids should be considered when assessing how PAHs are being transported through sub-catchments. Due to their hydrophobic nature, most PAHs in aquatic ecosystems bind to particulates (soil and sediments), rendering them less available for biological uptake. Jann et al. (2004) found that the release of LMW PAHs appears to be controlled by dissolution, while the high molecular weight PAHs were less soluble and transported in association with colloidal particles. Hernan et al. (2004) found that, in general, aquatic organisms are mainly exposed to the dissolved fraction of the LMW PAHs (two, three and four ringed aromatics) while the higher molecular ring systems (five and six ringed aromatics) were more bioavailable within the sediment.

Several PAHs were detected in all sub-catchments, however concentrations were low. The most commonly reported PAHs in the surface water were phenanthrene (3 aromatic rings), fluoranthene, pyrene and chrysene (all 4 aromatic rings). Menzies (2002) identified these same four compounds as the primary PAHs found in stormwater runoff in coastal Massachusetts. Unsurprisingly, acenaphthylene and acenaphthene (both LMW PAHs) were seldomly reported in samples from any of the sub-catchments. These PAHs are not commonly found in petroleum and are susceptible to degradation and weathering which may be occurring within the sub-catchment upstream of the sample sites. There were also very few instances where PAHs with five or more aromatic rings occurred, probably due to the low solubility of the HMW PAHs which typically accumulate in the sediment (Wilson et al. 2003). Sediment sampling would be required to assess the extent of the HMW PAHs in the system.

Anthracene (3 aromatic rings) was present in all sub-catchments except Bennett Brook and Southern River, and was only detected on one occasion at Bayswater. As anthracene is not normally found in petroleum its presence suggests that the sources of PAHs in these sub-catchments are likely to be pyrogenic (Brown and Peake 2005). Conversely, the sites where anthracene is absent are more likely to have been impacted by a petrogenic source. Profiling using the phenanthrene to anthracene ratio showed that the ratio is less than ten for most sites, from which it may be implied that pyrogenic sources of PAHs at least contribute to the total PAH concentration in most sub-catchments. Ellen Brook, a large sub-catchment dominated by farming and natural bushland was the exception.

The highest total PAH concentrations occurred in the Belmont South and Perth Airport South sub-catchments. These have a large percentage of industrial land uses within them as well as major roads which are likely to be contributing significantly to the PAH concentrations. This is supported by Hoffman (1984) who found that industry and highways contributed similarly high concentrations of PAHs, while residential and commercial areas both contribute lower levels in a study in Rhode Island’s Narragansett Bay.

The lowest total PAH concentrations were consistently reported at Bennett Brook. The Bennett Brook sub-catchment has large areas of natural bushland including Whiteman Park, which is unlikely to contribute significantly to PAH inputs. Bennett Brook also had high organic suspended solid loads that provide a substrate for adsorption (binding) of the PAHs and making them less available and more difficult to detect with the passive samplers.

The LMW PAHs acenaphthene, fluorene and phenanthrene were detected on several occasions in field blanks. These are three of the more volatile PAHs so airborne contamination is feasible, although we would expect the more commonly occurring naphthalene to co-occur if this was the case.

Patterns in the occurrence of PAHs in surface water appear to be linked to rainfall. In July 2007, high rainfall was accompanied by the highest concentrations and variety of PAHs in all sub-catchments. January 2007 had low rainfall and only five of the PAHs were present, and at relatively low concentrations. Notably, Bayswater had no reported occurrences of PAHs, while sampling of Bennett Brook and Bull Creek showed very low concentrations. This is likely to be a result of limited rainfall runoff restricting the transport of the PAHs into the drains. In October and April 2007, although concentrations were comparable, the diversity of PAHs was greater in April with almost twice as many of the target PAHs reported. The first flush occurred during the April 2007 deployment, so it is reasonable to assume that a large proportion of the more water soluble LMW PAHs entered the drains in runoff associated with this first flush.

Determining how to compare the time-averaged concentrations from the passive sampling devices with existing guidelines (ANZECC & ARMCANZ 2000) is the next important step in developing passive sampling as a routine operational technique. For example, in this study the time averaged concentration of six contaminants exceeded freshwater ecosystem values (ANZECC & ARMCANZ 2000), which implies that the sampler would have been exposed to transient concentrations very much higher than the guideline value. Thus we can conclude that high concentrations of these contaminants are entering waterways and will have both chronic and acute effects. Passive sampling data provides estimates of exposure that are critical to conducting ecological risk assessments as a basis for determining appropriate response actions.

5 Conclusion

This study has identified and quantified a range of surface water contaminants within the catchment drainage system around the Perth area using passive sampling devices. This technique has enabled herbicides, insecticides and PAHs to be sampled in a time-integrated manner and determined concentrations to low levels of reporting within each sub-catchment. The limits of reporting for concentrations of the contaminants are typically comparable to, or lower than, those specified as trigger values (ANZECC & ARMCANZ 2000). Although the appropriateness of comparing these trigger values to concentrations measured using passive sampling devices is yet to be established, results from the passive sampling technique are potentially more useful than those from grab sampling.

Concentrations of six contaminants exceeded freshwater ecosystem trigger values. Three of the organochlorine pesticides that were detected (dieldrin, chlordane and heptachlor epoxide) have been banned in Australia since 2004. Of these, only dieldrin exceeded the trigger value (on 3 occasions at the Belmont South site). Atrazine is only permitted for agricultural uses but was detected in Bayswater and Mills Street sub-catchments which have minimal agricultural land.

In addition, a wide variety of PAHs and pesticides were detected at low concentrations across the sites. However, some of these compounds have the potential to bioaccumulate resulting in harmful concentrations in biota. Many of the contaminants that were detected have chronic and/or acute toxic effects on aquatic organisms, with some known to have endocrine disrupting, phytotoxic, carcinogenic, mutagenic and teratogenic potential (Department of Health 2004). The information provided in this study is an important first step in determining the potential impact of drainage waters on the downstream receiving environments.

This study raises concerns about the management of herbicide and insecticide use in Perth. Indiscriminate use of these is likely to result in contaminants entering the Swan and Canning Estuary where they may impact aquatic organisms. Simple steps such as the application of pesticides in accordance with the manufacturer’s instructions (for example, not spraying before heavy rainfall or strong winds and ensuring there are vegetated buffers around watercourses) should assist greatly in reducing their inputs into water bodies. There is a continuing need for education of the community on the appropriate use of herbicides and pesticides.

Finally, this study has shown that passive sampling devices are effective in sampling a wide variety of organic compounds and their use may be applicable to further studies of organic compounds in surface waters. They are likely to capture transient events (although the transient signal is time averaged), whereas traditional grab sampling techniques are less able to capture such events.

6 References

Agency for Toxic Substances and Disease 1990, *Public health statement, polycyclic aromatic hydrocarbons,* Atlanta, GA, US Department of Health and Human.

Australian Academy of Technological Sciences 2002, *Pesticide use in Australia,* ANL Publishing.

ANZECC & ARMCANZ 2000, *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*, Australia and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand.

Australian Pesticide and Veterinary Medicines Authority 2006, *Diuron review – frequently asked questions,* http://www.apvma.gov.au/chemrev/diuron_FAQ.shtml

Bartkow, ME, Jones, KC, Kennedy, KE, Holling, N, Hawker, DW, & Müller, JF 2006, Evaluation of performance reference compounds in polyethylene-based passive air samplers*, Environmental Pollution,* 144, 365-370.

Bartkow, ME, Kapernick, A, Dunn, A, Komarova, T, Paxmans, C & Müller, JF in prep, *Evaluation of organic pollutants using passive samplers in subsub-catchments near Perth, Western Australia,* National Research Centre for Environmental Toxicology (EnTox), Report for Department of Water.

Boonchan, S, Britz, ML, & Stanley, GA 2000, *Degradation and mineralisation of high molecular weight polycyclic aromatic hydrocarbons by defined fungal bacterial communities,* Applied Environmental Microbiology 66(3), 1007-1019.

Brown, JN & Peake, BM 2005, *Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff,*. Science of the Total Environment 359 (2006) 145-155.

Chemistry Centre of WA 2007, *The determination and analysis of pesticides in the Swan and Canning Rivers in Western Australia*: a survey, Unpublished.

Chapman, D 2005, *The virtual fish: SPMD basics,* 6th International SPMD Workshop and Symposium.

City of Belmont 2007, *Belmont: City of opportunity*. Website: http://www.belmont.wa.gov.au/Pages/CityOfBelmont.aspx

Courtney, K & Foulsham, G 2007, *The determination and analysis of pesticides in Perth bore water: a survey,* Groundwater Quality Conference 2007: Securing Groundwater Quality in Urban and Industrial Environments.

Cox, C 2002, Fact Sheet atrazine, *Pesticide News*, pp 20-21.

Department of Environment 2003, *Assessment of water, sediment and fish quality in the Bayswater drains and adjacent Swan River,* Department of Environment, Government of Western Australia.

Department of the Environment, Water, Heritage and the Arts 1997, *Substance fact sheets for organic pollutants,* Australian Government, ACT.

Department of Health 2004, Information fact sheet on polycyclic aromatic hydrocarbons, Government of South Australia, Adelaide.

Department of Health 2006, Public Sector Circular. Use of herbicides in water sub-catchment areas, No. 88 (PSC88).

Department of Water 2006, *Sampling and Analysis Plan: Swan River Passive Sampling Assessment,* Water Science Branch, Department of Water.

Department of Water 2007, *Stormwater management manual,* Drainage and Waterways Branch, Department of Water.

Eisler, R 1987, *Polycyclic aromatic hydrocarbon hazards to fish, wildlife and invertebrates: a synoptic review,* Biological Report of the US Fish and Wildlife Service, 85 (1.1).

Evans, SJ 2009, *A baseline study of contaminants in groundwater at disused waste disposal sites in the Swan Canning catchment*, Water Science technical series report No. 4, Department of Water, Western Australia.

Fetzer, JC 2000, Large (C>=24) *Polycyclic aromatic hydrocarbons: chemistry and analysis. A Series of Monographs on Analytical Chemistry and its Applications,* JD Winefordner (Ed) Wiley Press.

Fox, R 1995, Male reproductive health and environmental oestrogens, *Lancet* 345, 933-935.

Gaynor, JD, Tan, CS, Drury, CF, Welacky, TW, Ng, HWF & Reynolds, WD 2001, Runoff and drainage losses of atrazine, metribuzin and metolachlor in three water management systems, *Journal of Environmental Quality,* 31, pp.300-308.

Jann, S, Totsche, KU & Kogel-Knabner, I 2004, Release and redistribution of polycyclic aromatic hydrocarbons in contaminated soil, *Geophysical Research Abstracts*, vol. 6, 02558.

Hayes, TB, Collins, A, Lee, M, Mendoza, M, Noriega, N, Stuart, A & Vonk, A 2002, Hermaphroditic, demasculinised frogs after exposure to the herbicide atrazine at low ecologically relevant doses, *Proceedings of the National Academy of Sciences*, 99, 5476-5480.

Hernan, PF, Adalberto, J, Asencio, P & Elena, G 2004, Polycyclic aromatic hydrocarbons in sediments and mussels of Corral Bay, south central Chile, *Journal of Environmental Monitoring,* no. 6, pp. 229-233.

Hines, C.J., Deddens, J.A., Tucker, S.P. & Hornung, R.W. 2001, Distributions and determinants of pre-emergent herbicide exposures among custom applicators, *The Annals of Occupational Hygiene*.

Hoffman, EJ 1984, Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters, *Environmental Science and Technology,* 18, pp. 580-587.

Kapernick, A, Dunn, A, Carter, S & Mueller, J 2003, *Western Australia Water Corporation passive sampling study site: Middle Helena Catchment,* Unpublished.

Kapernick, A, Komarova, T Mueller, J, Dunn, A & Beneken, C 2006, *Evaluation of organic pollutants in the water from urban drains using passive samplers: Report to the Western Australia Department of Environment,* Unpublished.

Kerle, EA, Jenkins, JJ, & Vogue, PA 2007, *Understanding pesticide persistence and mobility for groundwater and surface water protection*, EM 8561-E.

Linderfelt, WR, & Turner, JV 2001, Interaction between shallow groundwater, saline surface water and nutrient discharge in a seasonal estuary: the Swan Canning system. *Hydrological Processes,* 15(13), pp. 2631-2653.

Menzies, CA 2002, Urban and suburban stormwater runoff as a source of polycyclic aromatic hydrocarbons (PAHs) to Massachusetts estuarine and coastal environments, *Estuaries,* 25 pp. 165-176.

MAFRA 2006, *Principles of inte.grated weed management: use of chemicals to control weeds,* Ch.1, Pub. 75, Guide to Weed Control.

Mosisch, TD & Arthington, AH 2001, Polycyclic aromatic hydrocarbon residues in the sediments of a dune lake as a result of power boating, *Lakes and Reservoirs: Research and Management*, 6, pp. 21-32.

Neff, JM 1979, *Polycyclic aromatic hydrocarbons in the aquatic environment: sources, fates and biological effects,* Applied Science Publishers, London, UK.

Nice, HE 2009, *A baseline study of contaminants in the sediments of the Swan and Canning estuaries,* Water Science Technical Series Report No. 6, Department of Water, Western Australia.

Nice, HE, Grassi, M, Foulsham, G, Morgan, B, Evans, SJ & Robb M 2009, *A baseline study of contaminants in the Swan and Canning Catchment Drainage System*, Water Science Technical Series Report No. 3, Department of Water, Western Australia.

Pitt, R, Clark, S, Parmer, K, & Field, R 1996, *Groundwater contamination from stormwater infiltration,* Ann Arbor Press Inc.

Swan River Trust 1999a, *Action Plan: An action plan to clean up the Swan Canning Rivers and Estuary,* Swan River Trust, May 1999.

Swan River Trust 1999b, *Contaminants in the Swan Canning Rivers and Estuary,* Swan Canning Cleanup Program.

Tomlin, C 1994, The Pesticide Manual. Incorporating the Agrochemicals Handbook, The British Crop Protection Publications, pp.171-172.

Ulrich, EM, Caperell-Grant, A, Jung, SH, Hites, RA & Bigsby, RM 2000, Environmentally relevant xenoestrogen tissue concentrations correlated to biological responses, *Environmental Health Perspectives*, 108.

United States Geological Survey 2006, *Pesticides in the nation's streams and groundwater, 1992 – 2001: A summary*, Fact Sheet 2006–3028.

Vo, M, Porter, DE, Chandler, GT, Kelsey, H, Walker, SP, & Jones, BE 2004, Assessing photoinduced toxicity of polycyclic aromatic hydrocarbons in an urbanised estuary, *Ecology and Society,* 9(5): 3.

Wilson, C, Clarke, R, D'arcy, BJ, Heal, KV, & Wright, PW 2003, *Persistent pollutants urban rivers sediment survey: implications for pollution control,* Diffuse Pollution Conference, Dublin.

Shortened forms

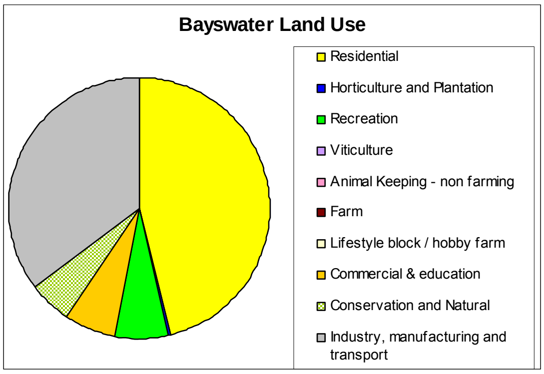
ANZECC	Australian and New Zealand Environment and Conservation Council
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
EDs	Empore discs
HMW	High molecular weight
LMW	Low molecular weight
NATA	National Association of Testing Authorities
NNCP	Non-nutrient contaminants program
PAHS	Polycyclic aromatic hydrocarbons
PDMS	Polydimethylsiloxane
PRC	Performance reference compound
SCCP	Swan Canning catchment program
SPMD	Semi-permeable membrane devices

Appendix A - Background to the sub-catchments within the Swan Canning system

The Swan Canning catchment is comprised of 31 sub-catchments, These contain different land uses, vary in size and discharge different volumes of water to the Swan and Canning rivers. The proportion of stormwater and groundwater influence also differs between sub-catchments.   The ten sub-catchments examined in this study are summarised below:

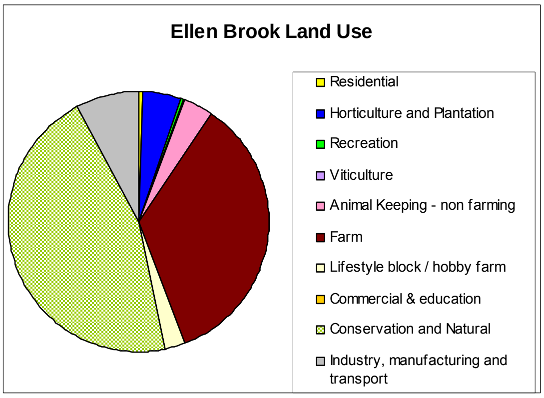
Bayswater

Bayswater sub-catchment is 27 km^2 in size and consists primarily of residential and industrial land uses.



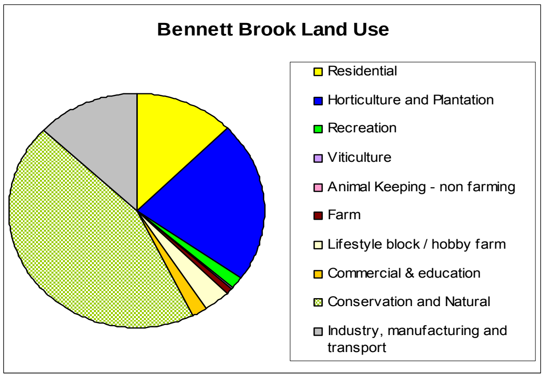
Ellen Brook

Ellen Brook sub-catchment is 715 km^2 in size and consists of significant areas of conservation and natural bushland, and farming.



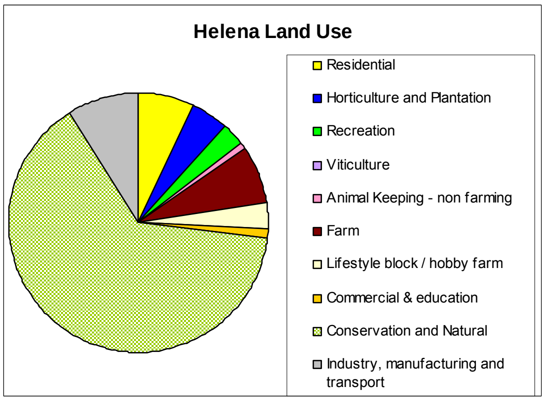
Bennett Brook

Bennett Brook sub-catchment is 112 km^2 in size and consists primarily of conservation and natural bushland, horticulture, residential and industry land uses.



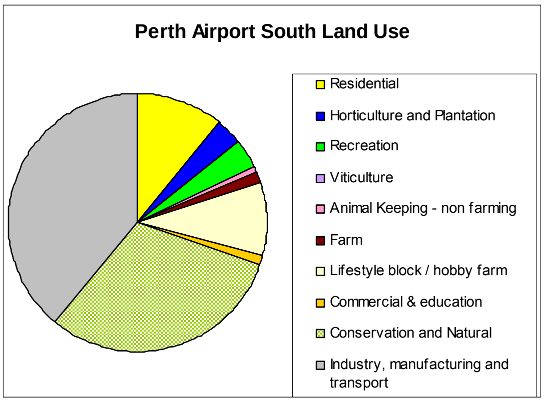
Helena River

Helena River sub-catchment is 176 km^2 in size and contains mostly conservation and natural bushland, with some additional industry, residential and farm land.



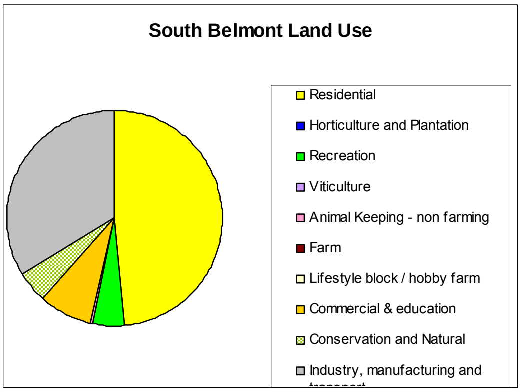
Perth Airport South

Perth Airport South sub-catchment is 25 km^2 in size and consists of largely industrial, and conservation and natural bushland land uses.



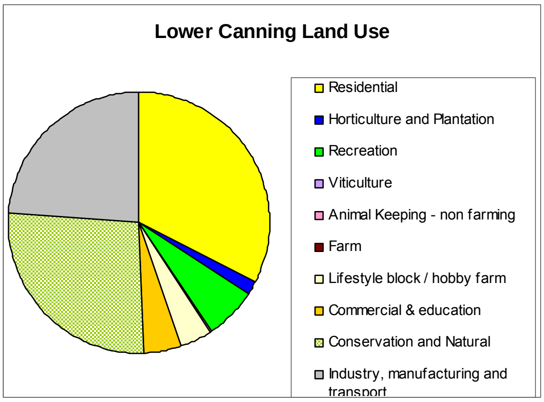
South Belmont

South Belmont sub-catchment is 10 km^2 in size and consists predominantly of residential and industrial land uses.



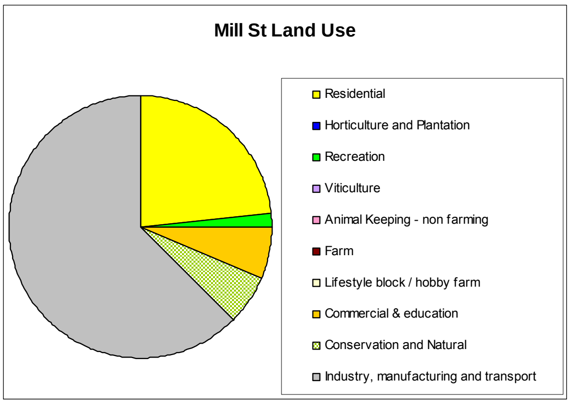
Liege St Wetland

Liege St Wetland is in the Lower Canning sub-catchment which is 47 km^2 in size and contains large areas of residential, conservation and natural bushland and industrial land uses.



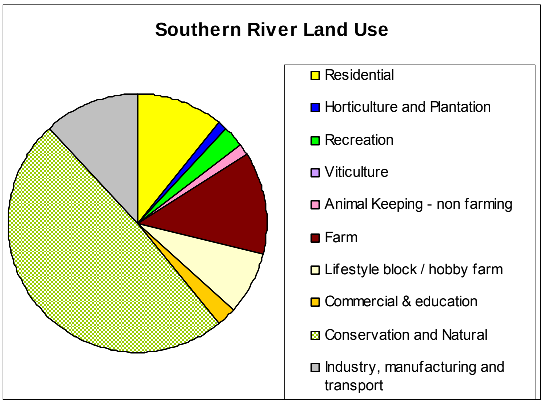
Mills Street

Mills St sub-catchment is 12 km^2 in size and contains primarily industrial and residential land uses.



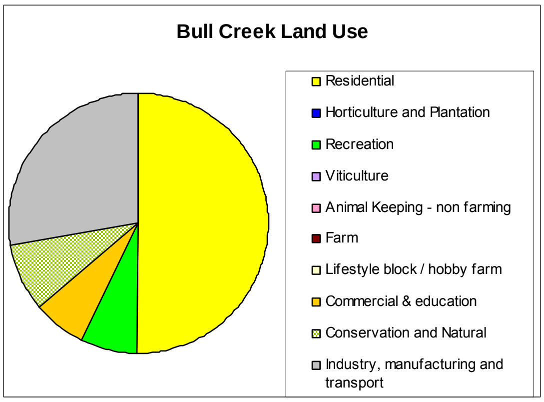
Southern River

Southern River sub-catchment is 149 km^2 in size and contains large areas of conservation and natural bushland, farming, industry and residential land uses.



Bull Creek

Bull Creek sub-catchment is 42 km^2 in size and contains large areas of residential and industrial land uses.



Appendix B - Site location photographs

Note: pink circle demarks the passive sampling point and yellow or red dots show nearby Water Information Network (WIN) sampling sites.

Bayswater Main Drain

Bennett Brook

Ellen Brook

Helena River

Perth Airport South Main Drain

South Belmont Main Drain

Liege St Wetland

Mills St Compensating Basin

Southern River

Bull Creek Main Drain

Appendix C - Summary of Results

Extracted from Evaluation of organic pollutants using passive samplers in sub-catchments near Perth, Western Australia (Bartkow et al., in prep).

Key:

BAY = Bayswter Main Drain
BEN = Bennett Brook
ELL = Ellen Brook
PAIR = Perth Airport South Main Drain
BEL = South Belmont Main Drain
LIE = Liege Street Wetland
SOU = Southern River
BULL = Bull Creek Main Drain
MILL = Mill Street Compensating Basin
HEL = Helena River

Deployment period one; September - October 2006

The estimated concentration in water (ng/L) of insecticides predicted from the accumulation in PDMS strips deployed during September-October 2006.

Site	**BAY**		**BEN**		**ELL**		**PAIR**		**BEL**		**LIE**		**SOU**		**BUL**	
Replicate	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Phosphate tri-n-butyl	7	5	4	4	<2	<2	<2	<2	19	19	11	14	10	9	20	20
Diazinon	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	44	37	14	13
Terbutryn	<3	<3	<3	<3	<3	<3	<3	<3	10	<3	<3	<3	7	6	<3	<3
Chlorpyrifos	2	2	2	2	1	1	0.6	0.7	2.5	2.8	0.6	1	7	6	4	4.5
Fenitrothion	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
Metolachlor	<7	<7	<7	<7	9	10	<7	<7	<7	<7	<7	<7	<7	<7	<7	<7
Heptachlor epoxide	1	1	<1	<1	<1	<1	<1	<1	1	1	<1	<1	2	1	<1	<1
Chlordane trans	<1	<1	<1	<1	<1	<1	<1	<1	0.6	0.7	<1	<1	0.7	0.6	<1	<1
Oxadiazon	<0.5	<0.5	0.9	1	<0.5	<0.5	<0.5	<0.5	5	5	<0.5	<0.5	2	2	<0.5	<0.5
Dieldrin	5	4	1.4	1.3	<0.5	<0.5	<0.5	<0.5	10	11	3	4	4	3	2	2
Piperonyl butoxide	0.6	0.5	1	1	<0.5	<0.5	<0.5	<0.5	2	2	1	2	9	8	4	4
Propiconazole	<2	<2	11	13	<2	<2	<2	<2	6	<2	<2	<2	<2	<2	<2	<2
Mean ND (%)	20		6		14		15		5		37		17		4	
LOR in water: based on a standard PDMS deployed for 30 days in standard conditions of flow and temperature																

The concentration in water (ng/L) of herbicides, detected in snapshot water samples collected during September - October 2006.

Site	**BAY**	**BEN**	**ELL**	**PAIR**	**BEL**	**LIE**	**SOU**	**BUL**
Diuron	44	8.1	1.5	18	22	36	32	7.7
Simazine	52	55	7.5	21	47	43	74	54
Atrazine	3.3	<1	5.5	6	<1	3.4	<1	<1
Hexazinone	4.9	<1	<1	11	<1	<1	6.8	<1

The estimated concentration in water (ng/L) of PAHs as predicted by SPMDs deployed during September - October 2006.

Site	**BAY**		**BEN**		**ELL**		**PAIR**		**BEL**		**LIE**		**SOU**		**BUL**	
Replicate	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Acenaphthylene	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.05	0.05	0.30	0.30	0.05	0.07	<0.03	0.03	<0.03	<0.03
Acenaphthene	0.20	0.20	0.07	0.07	0.09	0.07	0.10	0.10	0.20	0.20	0.10	0.10	0.07	0.10	0.06	0.04
Fluorene	0.10	0.09	0.04	0.04	0.06	0.05	0.08	0.07	0.15	0.15	0.30	0.40	0.04	0.05	0.05	0.03
Phenanthrene	0.40	0.30	0.10	0.10	0.70	0.60	0.50	0.60	0.60	0.70	<0.02	<0.02	0.40	0.30	0.20	0.20
Anthracene	0.05	0.04	<0.01	<0.01	0.06	0.06	0.07	0.06	<0.01	<0.01	0.80	0.90	<0.01	<0.01	<0.01	<0.01
Fluoranthene	0.60	0.50	0.20	0.20	0.70	0.60	1.50	1.50	2.00	2.00	<0.01	<0.01	0.80	0.80	0.30	0.20
Pyrene	1.10	1.00	0.60	0.60	0.40	0.30	1.70	1.90	<0.01	<0.01	<0.01	<0.01	1.00	1.00	0.60	0.50
Benz[a]anthracene	0.08	0.07	0.02	0.02	0.07	0.05	0.10	0.10	0.30	0.30	0.50	0.50	0.07	0.09	0.03	0.03
Chrysene	0.20	0.20	0.20	0.20	0.10	0.09	0.80	0.80	0.90	0.90	0.80	0.80	0.40	0.40	0.20	0.20
Benzo[b+k]fluoranthene	0.06	0.07	0.07	0.07	0.07	0.05	0.40	0.40	0.30	0.30	0.20	0.20	0.10	0.10	0.07	0.06
Benzo[e]pyrene	0.04	0.05	0.07	0.07	0.02	0.01	0.20	0.20	0.20	0.20	0.10	0.09	0.08	0.09	0.06	0.04
Benzo[a]pyrene	<0.02	0.02	0.02	0.01	0.01	<0.02	0.04	0.04	0.06	0.05	0.02	0.03	0.02	0.02	<0.02	<0.02
Perylene	<0.02	<0.02	0.01	0.01	0.04	0.03	0.02	0.02	0.04	0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mean ND (%)	14		6		25		4		3		14		12		23	
As all PAHs were run on the GC-MS in SIM mode, the data was not confirmed in a full-scale run.																

The concentration of PAHs (ng/L) in water at four different sites estimated from snapshot water samples and passive sampling (SPMD) data.

Site	**BAY**		**ELL**		**PAIR**		**LIE**	
Type of sampling	WATER	SPMD	WATER	SPMD	WATER	SPMD	WATER	SPMD
Acenaphthylene	<8	<0.03	<3	<0.03	<4	0.05	<2	0.06
Acenaphthene	<25	0.2	<17	0.08	<13	0.1	<12	0.1
Fluorene	<4	0.1	<2	0.06	<3	0.08	<2	0.4
Phenanthrene	<14	0.4	<11	0.7	<7	0.6	<7	<0.02
Anthracene	<0.1	0.05	<0.1	0.06	<0.1	0.07	<0.1	0.9
Fluoranthene	<3	0.6	<2	0.7	<3	2	<2	<0.01
Pyrene	<5	1	<0.1	0.4	<5	2	<4	<0.01
Benz(a)anthracene	<0.1	0.08	<0.1	0.06	<0.1	0.10	<0.1	0.50
Chrysene	<0.1	0.20	<0.1	0.10	<3.9	0.80	<0.1	0.80
Benzo(b+k)fluoranthene	<0.1	0.07	<0.1	0.06	<5.4	0.40	<0.1	0.20
Benzo(a)pyrene	<0.1	0.02	<0.1	0.02	<0.1	0.04	<0.1	0.03
Benzo(e)pyrene	<0.1	0.05	<0.1	0.02	<0.1	0.20	<0.1	0.10
Perylene	<0.1	<0.02	<0.1	0.04	<0.1	0.02	<0.1	<0.02
Indeno(123cd)pyrene	<0.1	<0.02	<0.1	<0.02	<0.1	<0.02	<0.1	<0.02
Benzo(ghi)perylene	<0.1	<0.03	<0.1	<0.03	<0.1	<0.03	<0.1	<0.03

Note – "<" symbols have been used on all snapshot detections due to uncertainties
"<0.1" indicates the LOR for snapshot water samples

Deployment period two; January - February 2007

The estimated concentration in water (CW) (ng/L) of herbicides predicted from ED passive samplers deployed in January - February 2007 in sub-catchments near Perth. The sampling rates used 0.12 L/day.

Site		**BAY**		**BEN**		**HEL**		**PAIR**		**BEL**		**LIE**		**MILL**		**BULL**	
Replicate		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Diuron	ng/ED	43	27	5.0	4.8	44	40	24	17	31	23	7.6	7.8	190	120	9.4	13
	Cw	12	7.1	1.3	1.3	12	11	6.4	4.4	8.4	6.2	2.0	2.1	50	33	2.5	3.5
	ND %	46		3.5		9.5		34		30		2.9		45		32	
Simazine	ng/ED	130	66	5.6	5.3	19	18	35	32	34	25	4.0	< 1	43	32	< 1	< 1
	Cw	35	18	1.5	1.4	5.1	4.7	9.3	8.5	9.2	6.6	1.1	< 0.3	11	8.6	< 0.3	< 0.3
	ND %	65		5.1		5.4		9.0		31		-		29		-	
Atrazine	ng/ED	150	66	< 1	< 1	5.0	2.1	8.1	6.7	< 1	< 1	< 1	< 1	160	110	< 1	< 1
	Cw	41	18	< 0.3	< 0.3	1.4	0.6	2.2	1.8	< 0.3	< 0.3	< 0.3	< 0.3	42	28	< 0.3	< 0.3
	ND %	78		-		83		19		-		-		37		-	
Desethyl Atrazine	ng/ED	3.7	2.7	< 1	4.2	< 1	< 1	14	13	2.0	2.3	1.0	< 1	31	14	< 1	< 1
	Cw	1.0	0.7	< 0.3	1.1	< 0.3	< 0.3	3.9	3.6	0.5	0.6	0.3	< 0.3	8.3	3.7	< 0.3	< 0.3
	ND %	30		-		-		7.4		14		-		76		-	
Desisopropyl Atrazine	ng/ED	5.4	< 1	< 1	< 1	< 1	< 1	6.6	5.1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
	Cw	1.4	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	1.8	1.4	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
	ND %	-		-		-		25		-		-		-		-	
Hexazinone	ng/ED	10	9.9	< 1	< 1	6.7	6.3	4.5	4.8	8.9	6.8	< 1	< 1	9.9	5.6	2.6	< 1
	Cw	2.8	2.7	< 0.3	< 0.3	1.8	1.7	1.2	1.3	2.4	1.8	< 0.3	< 0.3	2.7	1.5	0.7	< 0.3
	ND %	1.2		-		5.3		4.9		26		-		55		-	
Ametryn	ng/ED	1.9	3.1	< 1	1.5	< 1	2.5	< 1	< 1	< 1	< 1	< 1	< 1	32	16	< 1	< 1
	Cw	0.5	0.8	< 0.3	0.4	< 0.3	0.7	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	8.6	4.2	< 0.3	< 0.3
	ND %	46		-		-		-		-		-		70		-	
Mean ND %		44		4.3		26		17		25		2.9		52		32	

< 1 ng is the LOR in the sample; < 0.3 is the equivalent LOR in water.

The estimated concentration in water (ng/L) of insecticides predicted from PDMS passive samplers deployed during January - February 2007 in sub-catchments near Perth.

Site	**BAY**		**BEN***	**HEL**		**PAIR**		**BEL**		**LIE**		**MILL**		**BULL**	
Replicate	A	B	A	A	B	A	B	A	B	A	B	A	B	A	B
Phosphate Tri-n-Butyl	5.0	4.0	1.0	8.0	13.0	8.0	9.0	7.0	5.0	3.0	3.0	26	18	7.0	5.0
Trifluralin	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.5	0.3	<0.5	<0.5
Diazinon	<6	<6	<6	63	54	17	12	<6	<6	<6	<6	<6	<6	<6	<6
Terbuthylazine	<8	<8	<8	<8	<8	9.0	6.0	<8	<8	<8	<8	<8	<8	<8	<8
Triallate	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.9	0.7	<0.5	<0.5
Terbutryn	<3	8.0	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	27	26
Chlorpyrifos	0.8	0.5	0.2	<0.5	<0.5	<0.5	<0.5	0.4	0.4	<0.5	<0.5	2.0	<0.5	1.2	0.9
Chlordane trans	0.3	0.3	0.1	0.2	0.2	<1	<1	0.5	0.4	<1	<1	2.0	2.0	0.1	0.1
Dieldrin	4.0	3.0	<0.5	2.0	<0.5	1.0	1.4	11	10	<0.5	0.6	<0.5	<0.5	2.0	2.0
Propiconazole	<3	<3	<3	<3	9.0	<3	<3	<3	<3	<3	<3	90	72	<3	<3
Mean ND (%)	24			21		30		16		0		27		13	
LOR in Water: Based on a standard PDMS deployed for 30 days in standard conditions of flow and temperature (field blanks lost during processing) * One replicate lost during processing															

The estimated concentration in water (ng/L) of PAHs predicted from SPMDs deployed during January - February 2007 in sub-catchments near Perth.

Site	**BAY**		**BEN**		**HEL**		**PAIR**		**BEL**		**LIE**		**SOU**		**BULL**	
Replicate	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Acenaphthene	0.04	0.04	0.03	0.06	0.03	0.03	0.07	0.06	0.09	0.09	0.07	0.06	<0.03	<0.03	0.03	0.04
Fluorene	<0.01	<0.01	<0.01	0.02	0.02	0.03	0.04	0.04	0.05	0.05	0.1	0.1	<0.01	0.08	<0.01	0.01
Phenanthrene	0.05	0.04	0.03	0.03	0.20	0.3	0.4	0.3	0.20	0.20	0.2	0.10	<0.02	0.20	0.06	0.07
Anthracene	<0.01	<0.01	<0.01	<0.01	0.03	0.04	0.03	0.04	0.03	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fluoranthene	<0.01	<0.01	0.05	0.04	0.5	0.8	0.6	0.6	0.6	0.5	0.3	0.2	0.6	0.8	0.06	0.08
Pyrene	<0.01	<0.01	0.07	0.06	0.3	0.5	0.7	0.7	0.9	0.7	0.2	0.2	1.0	1.2	0.1	0.1
Mean ND %	11		21		34		12		7.2		24		7.8		18	
LOR in Water: Based on a standard SPMD deployed for 30 days in standard conditions of flow and temperature																

Deployment period three; April - May 2007

The estimated concentration in water (CW) (ng/L) of herbicides predicted from ED passive samplers deployed in April - May 2007 in sub-catchments near Perth. The sampling rates used 0.12 L/day.

Site		**BAY**		**BEN**		**HEL**		**PAIR**		**BEL**		**LIE**		**SOU**		**BULL**	
Replicate		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Diuron	ng/ED	490	360	170	170	72	61	46	46	34	51	162	138	96	107	48	36
	Cw	155	114	55	55	23	19	15	15	11	16	52	44	30	34	15	11
	ND %	30.1		1.2		16.9		0.1		39.6		16.4		11		28	
Simazine	ng/ED	150	110	96	92	110	110	110	110	3620	4260	27	26	5300	6680	43	40
	Cw	46	35	30	29	36	36	36	36	1160	1360	8.8	8.5	1700	2140	13	13
	ND %	27		4.1		1.2		0.3		16		3.1		23		5.8	
Atrazine	ng/ED	1040	760	3.0	3.5	15	19	30	29	16	< 1	14	15	< 1	< 1	8.4	10
	Cw	333	244	1.0	1.1	4.9	6.1	9.6	9.5	5.3	< 0.3	4.8	4.8	< 0.3	< 0.3	2.7	3.3
	ND %	30		12		21		0.9		-		1.3		-		20	
Desethyl Atr	ng/ED	13	9.6	< 1	< 1	< 1	< 1	11	4.3	< 1	1.1	< 1	< 1	0.8	< 1	< 1	< 1
	Cw	4.3	3.1	< 0.3	< 0.3	< 0.3	< 0.3	3.7	1.4	< 0.3	0.4	< 0.3	< 0.3	0.3	< 0.3	< 0.3	< 0.3
	ND %	32		-		-		92		-		-		-		-	
Desisopropyl Atr	ng/ED	17	16	< 1	< 1	7.7	10	11	10	49	77	< 1	< 1	82	88	< 1	< 1
	Cw	5.4	5.4	< 0.3	< 0.3	2.5	3.2	3.8	3.2	15	24	< 0.3	< 0.3	26	28	< 0.3	< 0.3
	ND %	1.0		-		26		16		44		-		6.7		-	
Hexazinone	ng/ED	12	8.6	< 1	< 1	3.1	4.6	2.9	2.3	4.8	8.7	< 1	< 1	< 1	< 1	< 1	2.3
	Cw	4.0	2.7	< 0.3	< 0.3	1.0	1.5	0.9	0.7	1.5	2.8	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.7
	ND %	37		-		39		24		57		-		-		-	
Mean ND%		26		6.0		21		22		39		6.9		13		18	
< 1 ng is the LOR in the sample; < 0.3 is the equivalent LOR in water																	

The concentration in water (ng/L) of herbicides, detected in snapshot water samples collected during April - May 2007.

Site		**BAY**		**BEN**		**HEL**		**PAIR**		**BEL**		**LIE**		**SOU**		**BULL**	
Date		16-Apr	23-Apr	16-Apr	23-Apr	16-Apr	23-Apr	16-Apr	23-Apr	16-Apr	23-Apr	16-Apr	23-Apr	16-Apr	23-Apr	16-Apr	23-Apr
Diuron	Replicates	630	82	5.1	1.7	39	54	19	72	25	8.5	220	199	59	47	10	10
	Mean		350		3.4		46		45		16		209		53		10
Simazine	Replicates	197	5	15	1.9	90	43	61	71	7655	74	18	22	48	12	19	29
	Mean		101		8.4		66		66		3870		20		30		24
Atrazine	Replicates	2900	41	<1	<1	8.3	5.1	8.3	22	43	<1	9.1	10	<1	<1	<1	4.4
	Mean		1470		<1		6.7		15		21		9.5		<1		2.2
Desethyl Atrz.	Replicates	<1	<1	<1	<1	<1	<1	<1	13	<1	<1	<1	<1	<1	<1	<1	<1
	Mean		<1		<1		<1		6.5		<1		<1		<1		<1
Desisopropyl Atrz.	Replicates	26	<1	<1	<1	9.2	7.1	3.7	11	49	1.7	<1	<1	1.5	<1	<1	<1
	Mean		26		<1		8.1		7.3		25		<1		<1		<1
Hexazinone	Replicates	0.8	3.6	<1	<1	<1	1.8	<1	2.7	2.1	1.8	<1	<1	<1	<1	<1	1
	Mean		2.2		<1		<1		1.3		1.9		<1		<1		<1
Ametryn	Replicates	<1	<1	<1	<1	1.4	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Mean		<1		<1		<1		<1		<1		<1		<1		<1

The estimated concentration in water (ng/L) of insecticides predicted from PDMS passive samplers deployed during April - May 2007 in sub-catchments near Perth.

Site	**BAY**		**BEN**		**HEL**		**PAIR**		**BEL**		**LIE**		**SOU**		**BULL**	
Replicate	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
PHOSPHATE TRI-n-BUTYL	9	8	1	1	>30	>30	>30	>30	14	16	14	12	15	12	16	16
TRIFLURALIN	<0.5	<0.5	<0.5	<0.5	1	0.9	1	1	<0.5	<0.5	<0.5	<0.5	8	10	<0.5	<0.5
DIAZINON	24	25	10	12	121	114	82	83	<6	<6	<6	<6	785	857	11	12
PROPAZINE	25	18	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
TERBUTRYN	<3	<3	<3	<3	<3	<3	<3	<3	58	54	<3	<3	8	7	<3	<3
CHLORPYRIFOS	4	4	1	1	<0.5	<0.5	2	2	3	4	3	3	11	12	12	11
METOLACHLOR	81	59	<8	<8	<8	6	14	9	<8	<8	13	9	8	7	<8	<8
HEPTACHLOR EPOXIDE	2	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	<1	<1
CHLORDANE trans	0.6	0.6	<1	<1	<1	<1	<1	<1	0.8	0.9	<1	<1	0.4	0.4	<1	<1
OXADIAZON	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	3	3	<0.5	<0.5	0.9	0.7	<0.5	<0.5
DIELDRIN	12	12	<0.5	<0.5	2	2	<0.5	<0.5	11	11	<0.5	<0.5	3	4	2	<0.5
PIPERONYL BUTOXIDE	3	3	<0.5	<0.5	<0.5	<0.5	<0.5	0.8	4	4	5	5	10	12	5	5
BENALAXYL	5	6	<3	<3	<3	<3	<3	<3	5	5	<3	<3	3	<3	<3	<3
PROPICONAZOLE	15	21	<3	<3	15	12	15	16	<3	<3	<3	<3	25	23	<3	<3
BIFENTHRIN	0.9	0.9	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	1	<1	<1
ROTENONE estimate only	<2	<2	present	present	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Mean ND%	14		10		16		8.3		7.3		10		16		3.5	

The estimated concentration in water (ng/L) of PAHs predicted from SPMDs deployed during April - May 2007 in sub-catchments near Perth.

Site	**BAY**		**BEN**		**HEL**		**PAIR**		**BEL**		**LIE**		**SOU**		**BULL**	
Replicate	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Acenaphthene	<0.03	<0.03	0.1	0.1	0.04	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.1	0.1
Fluorene	0.4	0.7	0.1	0.1	0.1	0.1	0.3	0.2	1.0	0.9	1.0	1.0	0.1	0.1	0.2	0.2
Phenanthrene	0.2	0.4	0.1	0.1	0.1	0.1	0.5	0.4	0.6	0.6	0.5	0.5	0.3	0.3	0.2	0.2
Anthracene	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.1	0.1	0.1	0.1	<0.01	<0.01	<0.01	<0.01	0.02	0.02
Fluoranthene	0.5	0.6	0.1	0.1	0.2	0.2	0.9	0.8	1.1	1.1	1.0	1.0	0.6	0.6	0.3	0.3
Pyrene	0.8	0.9	0.1	0.1	0.2	0.2	1.2	0.9	1.7	1.7	1.1	0.9	0.7	0.6	0.5	0.6
Benz[a]anthracene	0.1	0.1	<0.02	<0.02	0.02	0.02	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	<0.02	0.03
Chrysene	0.2	0.2	0.03	0.1	0.04	0.04	0.3	0.3	0.4	0.4	0.4	0.4	0.3	0.2	0.1	0.2
Benzo[b+k]fluoranthene	0.1	0.1	0.01	0.02	0.04	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.0	0.1
Benzo[e]pyrene	0.1	0.1	0.01	<0.02	<0.02	0.02	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.04
Benzo[a]pyrene	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Perylene	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02
Indeno[123cd]pyrene	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Benzo[ghi]perylene	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.03	0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Mean ND%	28		27		3		14		1		4		12		14	

The concentration in snapshot water samples (ng/L) of PAHs during April - May 2007 in select sub-catchments near Perth.

Site	**BLANK**	**BAY**	**HEL**	**PAIR**	**LIE**
Acenaphthylene	0.7	<0.03	<0.03	<0.03	<0.03
Acenaphthene	<0.03	<0.03	<0.03	<0.03	4.1
Fluorene	0.9	6	4.4	2.2	3.7
Phenanthrene	1.8	13	7.1	4.8	7.7
Fluoranthene	0.4	4.2	1.8	2.2	3.7
Pyrene	1	4.9	2.3	3	3.2
Benz(a)anthracene	0.2	<0.02	1.3	<0.02	<0.02
Chrysene	0.3	<0.02	2.9	<0.02	<0.02
Perylene	0.9	6.3	4.3	<0.02	<0.02
Indeno(123cd)pyrene	<0.02	<0.02	2.6	<0.02	<0.02
Benzo(ghi)perylene	<0.03	6.1	<0.03	<0.03	<0.03
Sum PAHs	6.2	41	27	12	22

Deployment period four; July - August 2007

The estimated concentration in water (ng/L) of herbicides predicted from ED passive samplers deployed in July - August 2007 in sub-catchments near Perth. The sampling rates used 0.12 L/day.

Site	**BAY**		**BEN**		**HEL**		**PAIR**		**BEL**		**LIE**		**SOU**		**BULL**	
Replicate	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Diuron	27	30	10	9.3	16	11	22	31	1.6	1.9	8.8	9.0	21	18	6.1	6.8
Simazine	37	40	410	380	150	110	41	50	15	15	12	13	630	620	130	140
Atrazine	13	16	3	3.2	17	14	9.8	12	0.4	0.2	2.2	2.5	4.3	4.1	1.3	1.5
Desethyl Atrz.	<1	<1	<1	<1	2.1	1.9	3.2	4.8	<1	<1	<1	<1	<1	<1	<1	<1
Desisopropyl Atrz.	5.4	5.6	9.8	11	8.3	9.1	8.5	8.5	0.4	<1	1.8	1.8	24	24	7.1	8.6
Hexazinone	5.0	5.5	<1	<1	3.7	2.5	<1	0.3	<1	<1	0.9	1.0	<1	0.3	<1	<1
Tebuthiuron	<1	<1	<1	<1	0.3	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

The estimated concentration in water (ng/L) of insecticides predicted from PDMS passive samplers deployed during July - August 2007 in sub-catchments near Perth.

Sample reference	**BAY**		**BEN**		**HEL**		**Pair**		**BEL**		**LIE**		**SOU**		**BULL**	
Replicate	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Phosphate tri-n-butyl	8	9	3	3	21	19	>30	>30	>30	>30	6	6	19	16	>30	>30
Trifluralin	1	2	<0.5	<0.5	1	1	1	1	<0.5	<0.5	<0.5	<0.5	9	8	1	1
Diazinon	6	7	<6	<6	<6	<6	<6	<6	<6	6	<6	<6	14	15	6	9
Triallate	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	3	3	<0.5	<0.5
Terbutryn	<3	<3	<3	<3	3	4	<3	<3	10	9	4	4	14	13	39	54
Chlorpyrifos	7	7	3	3	5	5	2	2	7	8	1	1	8	7	7	9
Metolachlor	10	10	<8	<8	11	8	<8	<8	<8	<8	<8	6	<8	<8	<8	<8
Heptachlor epoxide	1	1	<1	<1	1	1	<1	<1	<1	<1	<1	<1	2	1	<1	<1
Pendimethalin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	7	7	<1	<1
Chlordane trans	1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	1	<1	<1
Methidathion	<30	<30	<30	<30	102	100	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Oxadiazon	<0.5	<0.5	<0.5	<0.5	4	4	1	1	7	7	<0.5	<0.5	1	1	<0.5	<0.5
Dieldrin	8	10	2	1	5	5	5	4	5	6	2	2	4	4	3	4
Piperonyl butoxide	<0.5	<0.5	4	4	1	2	9	9	6	7	2	2	31	30	7	7
Benalaxyl	<3	<3	<3	<3	<3	<3	3	4	<3	6	3	3	7	7	3	3
Propiconazole	16	13	<3	<3	9	8	13	13	<3	<3	<3	<3	<3	11	<3	<3
Bifenthrin	<1	<1	<1	<1	<1	<1	1	1	1	1	<1	<1	1	1	<1	1
Mean ND%	16		7		10		10		11		5		11		17	

The estimated concentration in water (ng/L) of PAHs predicted from SPMDs deployed during July - August 2007 in sub-catchments near Perth.

Sample Reference	**Helena River**	**Helena River***	**Bays-water**	**Bays-water***	**Belmont South**	**Belmont South***	**Perth airport south**	**Perth airport south***	**Bennett Brook**	**Bennett Brook***	**Liege St**	**Liege St***	**Southern River**	**Southern River***	**Bull Ck**	**Bull Ck***
Units	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
Acenapylene	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Acenaphthene	0.10	0.09	<0.03	<0.03	<0.03	0.20	<0.03	0.05	0.06	0.08	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Fluorene	0.20	0.10	<0.05	<0.05	<0.05	0.40	0.20	0.30	0.10	0.10	0.80	1.00	0.20	0.20	0.20	0.20
Phenanthrene	0.30	0.40	0.20	0.10	0.40	0.50	0.40	0.50	0.30	0.30	1.30	1.40	0.70	0.60	0.30	0.30
Anthracene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fluoranthene	0.50	0.50	1.00	0.80	1.40	1.90	2.10	2.30	0.60	0.60	0.70	0.80	1.50	1.60	0.90	1.00
Pyrene	0.50	0.40	2.80	2.80	3.40	3.90	2.50	2.80	1.30	1.40	1.80	1.70	1.80	1.60	1.80	1.80
Benz(a)anthracene	0.04	0.04	0.20	0.20	0.30	0.40	0.30	0.20	0.07	0.08	0.10	0.10	0.20	0.20	0.10	0.10
Chrysene	0.10	0.10	0.60	0.60	0.80	0.90	1.10	0.90	0.30	0.30	0.40	0.40	0.50	0.50	0.40	0.40
Benzo (b+k) Fluoranthene	0.06	0.07	0.30	0.30	0.30	0.40	0.60	0.50	0.08	0.08	0.20	0.10	0.20	0.20	0.20	0.20
Benz(e)pyrene	0.02	0.02	0.09	0.10	0.10	0.20	0.10	0.10	0.06	0.07	0.08	0.07	0.10	0.08	0.09	0.08
Benz(a)pyrene	<0.02	<0.02	0.03	<0.02	0.02	0.06	0.06	0.03	<0.02	<0.02	0.03	0.02	<0.02	0.02	<0.02	<0.02
Perylene	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.02	0.02
Dibenz(ah)anthracene	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Indeno(123cd)pyrene	<0.02	<0.02	0.03	0.02	0.04	0.05	0.05	0.03	<0.02	<0.02	0.02	<0.02	<0.02	0.03	0.02	0.02
Benzo[ghi]perylene	<0.03	<0.03	0.04	0.03	0.04	0.06	0.04	0.03	0.06	0.04	0.03	<0.03	<0.03	<0.03	0.03	<0.03

Summary data

Summary data for ED-based water concentrations of herbicides. Results from all sampling periods summarised according to site.

	BAY	BEL	BEN	LIE	HEL	SOU	PAIR	BUL	ALL SITES
Number of values	21	13	13	14	20	15	22	13	131
Minimum	0.70	0.21	0.20	0.10	0.30	0.16	0.16	0.0	0.0
25% Percentile	3.5	1.2	1.2	0.99	2.0	4.2	2.8	1.2	2.0
Median	9.4	2.1	9.8	3.7	5.5	20	7.0	6.4	6.4
75% Percentile	34	11	43	10	15	33	21	18	22
Maximum	289	20	396	48	131	42	45	131	396
Mean	34	6.0	46	10	15	18	12	19	20
Std. Deviation	66	6.5	108	16	29	15	13	35	47

Summary data for PDMS-based water concentrations of pesticides. Results from all sampling periods summarised according to site.

	BAY	BEL	BEN	LIE	HEL	SOU	PAIR	BUL	ALL SITES
Number of values	22	21	11	17	10	32	11	15	130
Minimum	0.60	0.90	1.0	1.0	0.80	0.40	0.70	1.0	0.40
25% Percentile	1.0	3.0	1.0	2.6	1.7	1.4	1.0	4.0	2.0
Median	4.2	6.9	1.0	9.5	3.5	7.0	8.5	11	6.0
75% Percentile	9.3	11	3.0	25	7.7	13	30	20	13.5
Maximum	70	56	12	120	13	81	82	46	117.5
Mean	9.2	10	2.7	24	5.2	10	17	13	12
Std. Deviation	15	12	3.2	37	4.5	15	24	12	20

Summary data for SPMD-based water concentrations of total PAHs. Results from all sampling periods summarised according to site.

Site	**BAY**	**BEL**	**BEN**	**LIE**	**HEL**	**SOU**	**PAIR**	**BUL**	**ALL SITES**
Number of values	4	4	4	4	4	4	4	4	32
Minimum	0.0	0.065	1.3	1.7	1.4	0.70	2.1	0.17	0.0
25% Percentile	0.67	0.17	1.3	2.1	2.2	1.3	2.1	0.49	1.4
Median	2.7	0.95	2.5	4.4	5.1	3.6	2.5	1.5	2.8
75% Percentile	4.5	2.6	4.4	7.1	7.5	5.2	4.6	3.5	4.8
Maximum	5.1	3.0	4.8	7.6	8.2	5.6	5.2	4.1	8.2
Mean	2.6	1.2	2.7	4.5	4.9	3.4	3.1	1.8	3.0
Std. Deviation	2.1	1.3	1.7	2.6	2.8	2.1	1.4	1.6	2.1

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