



# Environmental monitoring of selected pesticides and organic chemicals in urban stormwater recycling systems using passive sampling techniques



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## ABSTRACT

Water recycling via aquifers has become a valuable tool to augment urban water supplies in many countries. This study reports the first use of passive samplers for monitoring of organic micropollutants in Managed Aquifer Recharge (MAR). Five different configurations of passive samplers were deployed in a stormwater treatment wetland, groundwater monitoring wells and a recovery tank to capture a range of polar and non-polar micropollutants present in the system. The passive samplers were analysed for a suite of pesticides, polycyclic aromatic hydrocarbons (PAHs) and other chemicals. As a result, 17 pesticides and pesticide degradation products, 5 PAHs and 8 other organic chemicals including flame retardants and fragrances were detected in urban stormwater recharging Aquifer Storage and Recovery (ASR) and an Aquifer Storage Transfer and Recovery (ASTR) system. Of the pesticides detected, diuron, metolachlor and chlorpyrifos were generally detected at the highest concentrations in one or more passive samplers, whereas chlorpyrifos, diuron, metolachlor, simazine, galaxolide and triallate were detected in multiple samplers. Fluorene was the PAH detected at the highest concentration and the flame retardant Tris(1-chloro-2-propyl)phosphate was the chemical detected in the greatest abundance at all sites. The passive samplers showed different efficiencies for capture of micropollutants with the Empore disc samplers giving the most reliable results. The results indicate generally low levels of organic micropollutants in the stormwater, as the contaminants detected were present at very low ng/L levels, generally two to four orders of magnitude below the drinking water guidelines (NHMRC, 2011). The efficiency of attenuation of these organic micropollutants during MAR was difficult to determine due to variations in the source water concentrations. Comparisons were made between different samplers, to give a field-based calibration where existing lab-based calibrations were unavailable.

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**Abbreviations:** ASE, Accelerated Solvent Extraction; ASR, Aquifer Storage Recovery; ASTR, Aquifer Storage Transfer Recovery; DOC, Dissolved Organic Carbon; DEET, N,N-Diethyl-meta-toluamide; ED, Empore™ disc; GPC, Gel Permeation Chromatography; MAR, Managed Aquifer Recharge; PAH, Poly Aromatic Hydrocarbons; PDMS, polydimethylsiloxane; PCBs, polychlorinated biphenyls; PFM, Passive Flow Monitor; PRCs, performance reference compounds; PTFE, polytetrafluoroethylene; SPMD, semi-permeable membrane device; TDCPP, Tris(1,3-dichloro-2-propyl)phosphate; TCPP, Tris(1-chloro-2-propyl)phosphate; XAD, Amberlite™ resin.

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## 1. Introduction

The effects of a drying climate and limited opportunities for further expansion of conventional water resources in urban areas have necessitated new approaches to urban water management and supply. Stormwater harvesting depends on the ability to effectively capture, treat and store the urban stormwater, and thereby reduce demand on conventional sources during extended dry periods. Increasingly, Managed Aquifer Recharge (MAR) systems have been constructed in

urban areas as a cost effective method to store and improve the quality of harvested stormwater (Dillon et al., 2009).

In 2003, the Parafield stormwater harvesting system was constructed which incorporates two detention basins and a wetland that serve to improve stormwater quality (Page et al., 2010). The Parafield stormwater harvesting system is designed to capture urban stormwater and treat the water to a suitable standard for water recycling via Aquifer Storage and Recovery (ASR) (recovery from the injection well) and Aquifer Storage Transfer and Recovery (ASTR) systems (recovery from a separate well). The water is recovered for public open space irrigation, industrial use and for blending with more brackish recycled waters for non-potable reticulated urban water supplies for garden watering and toilet flushing at the nearby Mawson Lakes development. The current study was undertaken as part of a project to assess the viability of use of stormwater for potable supplies.

Urban stormwater runoff may contain significant quantities of contaminants including herbicides (Marks et al., 2005). However, traditional one litre grab sampling gives an isolated point-in-time concentration, and without frequent collection, can miss chemicals due to their occurrence below detectable limits, varying concentrations or sporadic presence.

In response to these challenges, time-integrated passive sampling techniques are increasingly being used to provide a representative picture of the suite of trace-level contaminants that may be present in the environment, over a given deployment period (e.g. Bartkow et al., 2005; Kingston et al., 2000; Komarova et al., 2006; Page et al., 2010; Rusina et al., 2007). Passive samplers accumulate a broad range of organic chemicals (from air or water) via passive diffusion into a sorbing material placed in a passive sampler device. The mass sorbed is assumed to be in equilibrium with the time-averaged concentration in the environmental water over the period of deployment, accounting for the adsorption isotherm of the chemical sorbent. These generally give considerably lower detection limits than grab samples and enable detection of sporadically present chemicals.

The aim of this study was to demonstrate the use of passive samplers to characterise the range of trace-level organic micropollutants present in wetland-treated urban stormwater before injection, during storage and after recovery from an aquifer system.

## 2. Methods

### 2.1. Site description

Located at the Parafield Airport within the City of Salisbury in Adelaide, South Australia, the Parafield stormwater harvesting scheme collects and treats stormwater from urban catchments via the ASR and ASTR well fields (subsurface storage and treatment) (Fig. 1). Urban stormwater from a mixed residential and industrial catchment is harvested from the stormwater network, before passing through two settling basins and a constructed wetland (Marks et al., 2005). The wetland-treated water is then injected into the target aquifer via either an ASR or ASTR configuration.

For ASR, the wetland treated stormwater is injected into a confined limestone aquifer ~60 m thick (from 160 to 220 m below ground) within the Tertiary Port Willunga formation

known as the T2 aquifer. The T2 aquifer is overlain by 7 m thick clay aquitard, the Munno Para Clay, which prevents migration of injected water to the overlying aquifers. Beneath the T2 aquifer is the lower permeability Ruwaring member. Water is recovered from the same injection well when required.

The ASTR system is a six-well system consisting of two inner recovery wells (RW1 and RW2), and four outer injection wells, with inter-well spacing of 50 m between each injection well and its nearest recovery well and providing a mean aquifer residence time of 240 days between injection and recovery (Page et al., 2012). The six ASTR wells are completed over an open interval of about 17 m from 165 to 182 m below ground to preclude a zone of high hydraulic conductivity in the lower part of the aquifer (intersected in ASR wells) which could reduce travel times and compromise recovery efficiency in this initially brackish aquifer (Pavelic et al., 2004).

In the period March 2003 to January 2012, 2,768,000 m<sup>3</sup> of harvested stormwater was injected into the T2 aquifer via the ASR system. From August 2006 to January 2012, 902,000 m<sup>3</sup> were injected via the ASTR system, of this 399,000 m<sup>3</sup> was injected into the RW wells during the initial flushing phase and subsequently 503,000 m<sup>3</sup> was injected into the four surrounding IW wells during the operational phase. A combined total of 2,231,000 m<sup>3</sup> was recovered, 1,843,000 m<sup>3</sup> from ASR and 388,000 m<sup>3</sup> from ASTR over the same period leaving a net volume of 1,439,000 m<sup>3</sup> within storage in the aquifer.

For the period of this study, 31st August 2011 to 9th January 2012, 205,000 m<sup>3</sup> was injected into the ASR wells and 41,000 m<sup>3</sup> was extracted while 0 m<sup>3</sup> was injected and 2500 m<sup>3</sup> was extracted from the ASTR well field. Water quality was assessed using passive sampling techniques, applied at the outlet of the wetland (WE02), the ASR observation well (ASRO), two ASTR observation wells (PP1 and PP3) and mixed ASR and ASTR recovered water quality (MT1, in a mixing tank). Distances of sampler locations from injection wells are given in Table 1 and shown schematically in Fig. 1.

A numerical solute transport model (Miotliński et al., in press) was used to simulate the contributions of stormwater injected through the IW and RW wells and ambient groundwater and estimate groundwater residence times at the ASTR piezometers PP1 and PP3. The hydraulic conductivity and storage coefficients for groundwater modelling were collected through pumping tests whereas vertical heterogeneity in hydraulic conductivity was estimated by using downhole electromagnetic flowmeter. Average porosity of the aquifer material was determined from seven (200 cm<sup>3</sup>) aquifer cores collected between 166 and 189 m depth. Each core was weighed wet (saturated) and then dried overnight in a laboratory oven at 105 °C for 24 h. Porosity was calculated by dividing the total wet minus dry weight by the volume of the core, with an average used as a representative porosity for the target aquifer. Dispersivity of the aquifer was determined by using a solute transport groundwater model through calibration of salinity breakthrough at observation wells (Miotliński et al., in press). The model was calibrated for the period (September 2006 to June 2008) during which 390 × 10<sup>3</sup> m<sup>3</sup> of freshwater was injected using the inner RW1 and RW2. Subsequently, the model was used to predict minimum, maximum and mean residence times for the period 25 June–29 August. At that time, recharge water was injected through

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