Chemosphere 81 (2010) 394–399

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Quantification of herbicide removal in a constructed wetland using passive samplers and composite water quality monitoring

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ARTICLE INFO

Article history:
Received 2 March 2010
Received in revised form 6 July 2010
Accepted 6 July 2010
Available online 3 August 2010

Keywords:
Passive samplers
Stormwater quality
Diuron
Simazine
Atrazine
Constructed wetlands

ABSTRACT

Constructed wetlands used as treatment for urban stormwater have the potential to improve water quality. This study aimed to estimate the removal of selected herbicides in stormwater by a constructed wetland using composite water quality monitoring and passive samplers. For the four week duration of the study the wetland was effective in reducing the concentrations of diuron, simazine and atrazine. Mean estimated concentrations over a 28 d period were 192, 70 and 5 ng L^{-1} at the inlet and 94, 30 and 2 ng L^{-1} at the outlet for diuron, simazine and atrazine, respectively. Concentrations of these herbicides generally halved as a result of passage through the constructed wetland with a design hydraulic retention time of 7 d. Simple ratios of the inlet and outlet herbicide concentrations as well as hydraulic load-based methods of measuring the wetland's removal efficiency resulted in a range of estimations 33–51% for diuron and 20–60% for simazine. Due to their lower detection limits, the use of passive samplers provides a more efficient technique than conventional sampling for assessment of stormwater wetland treatment.

1. Introduction

Increasingly wetlands have been constructed in urban areas to detain and improve the quality of stormwater (Terzakis et al., 2008; Imfeld et al., 2009; Janzen et al., 2009). In 2002, the Parafield stormwater harvesting system was constructed which incorporates a series of detention basins and a constructed wetland that serves to improve stormwater quality (Page et al., 2008). The Parafield stormwater harvesting system is designed to capture urban stormwater and treat the water to a suitable standard for water recycling via an aquifer storage and recovery (ASR) system (Marks et al., 2005).

Urban stormwater runoff is often presumed to contain significant quantities of contaminants including herbicides (Kohler et al., 2004; Page et al., 2008; Imfeld et al., 2009). However, monitoring the concentrations of organic chemicals remains a challenge as many herbicides in urban stormwater occur at trace levels that are very difficult to detect and quantify. This coupled to their sporadic detections in the stormwater result in limitations in the quantification and assessment of urban stormwater treatment systems such as constructed wetlands.

In response to these difficulties, time integrated passive sampling techniques were developed for the monitoring of organic chemicals at low concentrations in water by various researchers (e.g. Kingston et al., 2000; Bartkow et al., 2005; Rusina et al., 2007). These techniques are based on the diffusion of chemicals from the aqueous phase into a sampling phase that has a relatively high sorptive capacity for the chemicals of interest. When deployed for an extended period of time the sequestration of chemicals in these passive samplers makes for easier detection. Initially, these techniques were applicable only for non-polar chemicals such as organochlorine insecticides. More recently samplers have also been developed for polar organic chemicals including herbicides (e.g. Stephens et al., 2005; Hyne and Aistrope, 2008; Mazzella et al., 2008). Passive sampling techniques provide a time-weighted average water concentrations during the period of the passive sampler deployment. The concentrations are calculated from the amount of chemical sequestered in the sampler using sampling rates determined either by calibrations conducted in the laboratory or via field deployments (Shaw et al., 2009).

The aims of this study were to determine the average herbicide concentrations in urban stormwater water moving through the constructed wetland, assess water quality changes, and compare the calculated removal efficiency of herbicides using passive samplers and conventional techniques.

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doi:10.1016/j.chemosphere.2010.07.002

2. Methods

2.1. Site description

The Parafield stormwater harvesting system is located on the Parafield airport in the city of Adelaide, Australia. The system receives stormwater from a 16.2 km^2 mixed light industrial and residential catchment (annual rainfall averages 461 mm which results in an average runoff of 1 520 000 $m^3 y^{-1}$). The harvesting system is designed to provide treatment for an average annual supply of 1 100 000 $m^3 y^{-1}$ (Marks et al., 2005). The system treats urban stormwater and is currently configured to provide water for non-potable uses, including irrigation and for use by a wool processing plant. The wetland operates in conjunction with two aquifer storage and recovery (ASR) wells for storage of excess water.

A weir diverts water from the Parafield drain into the in-stream basin (50 000 m^3), which is the first of three stages of the stormwater harvesting system. The in-stream basin serves as an initial settling basin for sediments and gross pollutants. Water flows into the in-stream basin during a storm event and is pumped at ~3000 $m^3 h^{-1}$ to the holding storage until capacity (50 000 m^3) is reached or the in-stream basin is drained. Water flows by gravity from the holding storage into the constructed wetland (25 000 m^3). Water flow into and through this wetland with mean flows of ~1000 $m^3 d^{-1}$ (Page et al., 2008). The wetland is diamond shaped with the inlet and outlet at the apexes, a total land area of 0.11 km^2, standing water depth of 30–60 cm and has been vegetated with including different species of reeds (*Phragmites australis*, *Eleocharis sphacelata*, *Schoenoplectus validus*, *Baumea articulate* and *Typha orientalis*), planted in parallel rows that are perpendicular to flow (Marks et al., 2005). The wetland is designed to achieve a minimum holding time of 7 d. Water flows through the wetland were measured at the outlet and the water level of the wetland was monitored. During the period of the study the wetland was operated to have a constant volume (~21 000 m^3) with an average depth of 0.2 m.

Water quality sampling was undertaken using two methods, composite sampling and passive sampling, applied at the inlet and outlet of the wetland over a 28 d period, from the 18/09/2007 to 15/10/2007. During this spring period temperatures ranged from 3.8 to 32.9 °C for air and 13.3 to 15.6 °C for water.

2.2. Composite water quality sampling

Sampling locations were selected in the direct flow of the water through the inlet or outlet structures. ISCO automated water samplers (6700 series) were used to collect daily samples of water for four weeks (28 d total). Daily samples were collected by sampling 1 L every 4 h and were combined to form weekly composites as well as a monthly composite for direct comparison with the passive sampler deployment times. Samples were kept refrigerated whilst in the field at 4 °C. Water samples were collected at the same point where the passive samplers were deployed to represent water moving through the system.

Samples were stored at 4 °C and transported to NATA accredited analytical laboratory (National Measurement Institute, Sydney, Australia) and analysed using a multi-residue method (US FDA, 1994) on an Agilent 5973 GC/MS using an MSD set to scan mode (70 eV) with a reporting limit of 100 ng L^{-1} and method uncertainty set at 1000 ng L^{-1}. Analytical conditions: injection volume: 20 μL; GC column: ZB5 (30 m × 0.25 μm × 0.25 mm): carrier gas helium 2.2 mL min^{-1}; temperature profile: 50 °C for 3 min, ramp 25 °C min^{-1} to 150 °C, ramp 3 °C min^{-1} to 200 °C, ramp 8 °C min^{-1} to 320 °C, hold for 5 min. Samples were analysed for diuron, atrazine, simazine, tebuthiuron, flumeturon, hexazinone, ametryn, prometryn, bromacil and metolachlor (Table 1).

2.3. Passive samplers

The monitoring of polar chemicals by the "Chemcatcher" passive sampler employs the use of a high surface area adsorptive sequestering phase, the styrenedivinylbenzene-reverse phase sulfonated (SDB-RPD) Empore™ disk (ED). The SDB-RPD ED (47 mm diameter, 16 μm particle size, 0.008 μm pore size, Phenomenex, Australia) was first employed in the determination of time-weighted average concentrations of polar organic water pollutants (Kingston et al., 2000). The 47 mm diameter EDs were housed in a patented Teflon sampling device (Kingston et al., 2001) used with permission. This device exposes the inside 45 mm of a single side of the ED to the water, giving a total exposed area of 15.9 cm^2.

Disks were prepared by conditioning in methanol (HPLC grade) followed by ultra-pure water (18.2 M ohm conductivity). Polyethersulfone Z-bind membranes (0.2 μm nominal pore diameter, 146 μm thickness, Pall Corporation) were soaked in methanol and ultra-pure water before being fitted to samplers.

Naked Empore disks (ED) samplers (without membranes) were deployed by suspending them face down approximately 30 cm below water level at the main inlet structure of the wetland, over four consecutive 7 d periods; exactly matching the composite samplers. Passive samplers with membranes were deployed for a concurrent 28 d period. 28-d passive samplers with membranes were deployed in triplicate (Table 2).

Retrieved samplers were transported on ice back to the laboratory within 24 h of the time of collection and spiked with a deuterated standard (simazine-d5) then extracted with 5 mL acetone followed by 5 mL methanol (HPLC grade) in an ultrasonic bath. The extracts were combined and reduced in volume under nitrogen before being filtered through a 0.45 μm PTFE syringe driven filter unit (Minisart 0.45 μm, Sartorius, Göttingen, Germany). They were then reduced to 0.5 mL under nitrogen and made up to 1 mL with ultra-pure water. Samples were spiked with another deuterated standard (atrazine-d5) prior to analysis.

Passive sampler extracts were analysed by liquid chromatography–triple quadruple mass spectrometry (AB/Sciex API 300 mass spectrometer, Applied Biosystems, Concord, Ontario, Canada) for the same ten herbicides: diuron, atrazine, simazine, tebuthiuron, flumeturon, hexazinone, ametryn, prometryn, bromacil and metolachlor using the sample preparation and analytical method reported by Shaw et al. (2009) (Table 1). Quantification criteria were as presented by Shaw et al. (2009) and included comparison of ion mass ratios.

Results from passive samplers were converted to water concentrations (ng L^{-1}) according to the following equation:

$$C_W = \frac{N_{ED}}{R_S \times t} \quad (1)$$

where C_W is the water concentration (ng L^{-1}), N_{ED} is the mass of chemical in the ED (ng ED^{-1}), R_S is the compound-specific sampling

Table 1
Limit of detection and physicochemical properties of studied herbicides.

Herbicide	Chemical group	LOD (ng L^{-1})	LOD (ng ED^{-1})	Log K_{ow}[a]	Log K_{oc}[a]
Ametryn	Triazine	100	1	2.98	2.59
Atrazine	Triazine	100	1	2.61	2.24
Bromacil	Uracil	100	1	2.11	1.60
Diuron	Urea	100	1	2.68	2.40
Fluometuron	Urea	100	1	2.42	2.00
Hexazinone	Triazine	100	1	3.40	1.57
Metolachlor	Anilide	100	1	2.90	3.01
Prometryn	Triazine	100	1	3.51	2.85
Simazine	Triazine	100	1	2.18	2.10
Tebuthiuron	Urea	100	1	1.62	1.83

LOD limit of detection.
[a] Log K_{ow} and log K_{oc} values compiled from Sabljic et al. (1995) and EXTOXNET (1998).