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Monitoring pesticides in the Great Barrier Reef

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ABSTRACT

Pesticide runoff from agriculture poses a threat to water quality in the world heritage listed Great Barrier Reef (GBR) and sensitive monitoring tools are needed to detect these pollutants. This study investigated the utility of passive samplers in this role through deployment during a wet and dry season at river mouths, two near-shore regions and an offshore region. The nearshore marine environment was shown to be contaminated with pesticides in both the dry and wet seasons (average water concentrations of 1.3–3.8 ng L^{-1} and 2.2–6.4 ng L^{-1}, respectively), while no pesticides were detected further offshore. Continuous monitoring of two rivers over 13 months showed waters flowing to the GBR were contaminated with herbicides (diuron, atrazine, hexazinone) year round, with highest average concentrations present during summer (350 ng L^{-1}). The use of passive samplers has enabled identification of insecticides in GBR waters which have not been reported in the literature previously.

1. Introduction

Intensive agriculture is a major land use in northern Queensland Wet Tropics river catchments, with most of the cropping activity occurring on the coastal floodplains adjacent to the Great Barrier Reef (GBR) Marine Park. The proximity of the GBR to these intensive agricultural land uses places the Reef, an ecosystem of great ecological and economic importance (Productivity Commission, 2003), under threat of exposure to pesticides used widely in modern agricultural practices. Off-site movement of pesticides is typically 1–2% of the total applied mass (Kookana et al., 1998; Carter, 2000) and this fraction has been shown to increase (e.g. 2–3% (Glofelty et al., 1984); >10% (Baker et al., 1978)) under the higher rainfall scenarios likely to be consistent with conditions in the northern Australian Wet Tropics region. Integral to the effective management of water quality entering the GBR is the implementation of a monitoring program to provide feedback on the effectiveness (or otherwise) of land management strategies designed to minimize off-site transport of applied pesticides. A successful monitoring program calls for robust and sensitive tools that can be utilized in remote areas to detect low levels of organic pollutants.

Pesticides represent a useful marker of the distribution of dissolved agricultural pollutants since there are no natural or pre-development levels to distinguish with current levels, as is the case with nutrients. A survey of sediments and seagrass along the Queensland coast identified pesticide residues of the currently used herbicide diuron and the insecticide dieldrin in the nearshore environment of the Wet Tropics (Haynes et al., 2000), and a range of organic pollutants have been detected in local marine mammals (Haynes et al., 2005). Recent surveys of pesticides have been conducted in river and flood plume waters in the Burdekin (Lewis et al., 2007, 2009), Mackay-Whitsunday (Mitchell et al., 2005; Rohde et al., 2006; Lewis et al., 2009) and Tully–Murray (Faithful et al., 2007; Lewis et al., 2009) regions of the GBR catchment with herbicides detected in each instance. Studies employing grab sampling techniques generally report pesticide detection limits of 10 ng L^{-1} (Rohde et al., 2006; Faithful et al., 2007; Lewis et al., 2009) for the commonly sampled photosynthesis inhibiting herbicides (e.g. diuron, atrazine, hexazinone) and 50–1000 ng L^{-1} for pesticides such as organophosphates (e.g. Hunter et al., 2001; Lewis et al., 2007; Rohde et al., 2006), although these compounds are less commonly included in the analysis suite. While the lower detection limits (10 ng L^{-1}) are often suitable for the photosynthesis inhibiting herbicides, these studies will not detect many commonly

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applied insecticides at concentrations consistent with Australian water quality guidelines (ANZECC, 2000) (e.g. chlorpyrifos and diazinon, 10 ng L^{-1}). There is evidence that pesticides from agricultural land uses are entering the GBR environment, however, it is clear that improved monitoring tools are required to effectively track long-term trends in concentrations of a broad suite of pesticides.

Over the last decade passive samplers have gained wide acceptance as effective tools for monitoring organic pollutants in aquatic environments (Stuer-Lauridsen, 2005; Seethapathy et al., 2008). Passive samplers sorb analytes into a collection phase via molecular diffusion from the environment. Their robust, simple designs which do not require maintenance or intervention allow the samplers to be deployed for extended periods in remote locations such as the GBR. Long *in situ* accumulation periods (relative to grab samples) mean passive samplers enable low concentrations of analytes to be detected. Uptake into the samplers is initially governed by linear first order kinetics, providing a time weighted average of the exposure concentration incorporating fluctuations in the environmental concentration as opposed to grab samples which provide information on environmental pollutant concentrations for only one point in time (Shaw and Mueller, 2009). These characteristics represent considerable advantages over grab sampling techniques for monitoring in the GBR environment where low pollutant concentrations are the norm and waterways are characterized by episodic flows associated with monsoonal rainfall events during which pesticide concentrations may fluctuate dramatically (Cooper and Riley, 1996; Mitchell et al., 2005).

A preliminary survey of pesticides in the GBR utilizing passive samplers demonstrated the potential for these tools to effectively monitor pesticides in the GBR environment (Shaw and Mueller, 2005) and passive samplers have since been adopted into a pesticide monitoring program by the Great Barrier Reef Marine Park Authority (Haynes et al., 2007). This paper describes the application and evaluation of passive samplers as tools for broad-scale monitoring in the GBR environment. An extensive survey of pesticides was conducted with samplers deployed at river mouth and nearshore Reef sites in the Wet Tropics in both a dry and wet season and in a cross-shelf transect from river source to the outer Reef. Local spatial variation of pollutant concentrations was investigated by monitoring at three stations around two nearshore islands. In addition, continuous monitoring of two Wet Tropics rivers was conducted over a 13 month period to investigate the seasonality of pollutant inputs to the GBR lagoon. Pesticides in the analysis suite included herbicides and insecticides registered for common agricultural land uses in the wet tropics region of the GBR catchment (sugarcane, bananas, grazing, forestry and other horticultural crops) (APVMA, 2009) with properties that allowed detection using passive sampling tools (log K_{OW} 1.8–6.4, non-ionic compounds).

2. Methods and materials

2.1. Survey

The 2000 km long Great Barrier Reef (GBR) borders the continental shelf of the tropical North Queensland coast of Australia and is the world's largest coral reef system. Inshore reefs and the mouths of major rivers were sampled in the Wet Tropics region of the GBR in both dry (October 2004) and wet seasons (January 2005) (Fig. 1 and Table 1). Chemcatchers® (using SDB-RPS Empore™ disks as the sorbent phase) and semi-permeable membrane devices (SPMDs) were deployed in triplicate at each site. Sampling in the wet season included deployment of samplers on a cross-shelf transect from approximately 1 km upstream in the Russell River to the Russell–Mulgrave River mouth then to the inshore reef site of High Island, the mid-shelf site of Green Island and outer reef sites at Michaelmas and Hastings Reefs (Fig. 1). A nearshore island in Princess Charlotte Bay, Hannah Island, situated offshore from a river draining a relatively undisturbed catchment in far north Queensland, was also sampled for comparison to the agricultural areas of the Wet Tropics in the dry season (October 2004) and in the following wet season (March 2005).

Logistical considerations dictated relatively short (4–13 days) sampling periods. Therefore, the Chemcatchers® were deployed without a polyethersulfone membrane covering the sampling phase to meet the requirement for low detection limits. Grab water samples (2 L) were collected from the High Island site on the day of deployment and day of retrieval to validate passive sampler derived water concentrations. These samples were extracted using solid phase extraction on a Waters Oasis® cartridge (HLB 60 μm (LP) 12cc) then eluted twice with MeOH and analysed for herbicides using HPLC-MSMS.

Seasonal trends in pesticide inputs to the GBR lagoon were investigated by time-series monitoring at 2 upstream river sites in the Russell (17°27.409S 145°94.934E) and Mulgrave Rivers (17°21.759S 145°92.916E). Chemcatchers® were deployed continuously over a 13 month period from January 2005 to January 2006 and exchanged ~ monthly while non-polar samplers (SPMDs and polydimethyl siloxane (PDMS)) were deployed for 2 periods of 1 month each in December 2004 and January 2005. As the samplers were deployed for an extended period, the Chemcatchers® were deployed with a polyethersulfone membrane to extend the integrative period of uptake. Good reproducibility in co-deployed triplicate samplers was observed in the initial survey results and in a preliminary study (mean coefficient of variation = 0.3, $n = 29$) (Shaw and Mueller, 2005). Therefore the time-series sampling was conducted with duplicate samplers to minimize the cost of ongoing analysis. Daily river flow monitoring data was obtained from the Queensland Department of Natural Resources and Water at a monitoring point upstream of the passive sampling site in the Russell (Gauging Stn 111101D, 17°23S 145°58E) and Mulgrave (Gauging Stn 111005A, 17°08S 145°46E) Rivers. Pollutant load estimates were derived using a volume-weighted average method which multiplied the average water concentration (passive sampler results) by the average flow rate (mean for the period of sampler deployment, megalitres) for a given period. This approach is often employed as a first estimation method (Quilbe et al., 2006).

2.2. Spatial variation

The variation of pollutant concentrations was measured by monitoring at three replicate sampling locations around Normanby Island and Fitzroy Island. Duplicate membrane covered Chemcatchers®, SPMDs and PDMS strips were deployed for 29 and 27 days at Normanby and Fitzroy Islands, respectively, in January 2006. Due to the remote nature of the sites being sampled it was not logistically practical to measure flow across the sampler surface throughout the deployment period so variations in environmental factors that influence uptake were instead inferred through the comparative loss of performance reference compounds (PRCs) from SPMDs at each sampling station.

2.3. Passive sampler preparation and extraction

SDB-RPS Empore™ extraction disks for the Chemcatchers® were sourced from Phenomenex, Australia and the 0.2 μm polyethersulfone Z-bind™ membranes from Pall Corporation, Michigan. SPMDs were prepared using ~90–95 μm barefoot, layflat tubing of low density polyethylene (Brentwood Plastics, USA) and 99% purity triolein (1,2,3-tri[cis-9-octadecenoyl]glycerol) (Sigma–Aldrich, Australia). PDMS sheets (Purple Pig, Australia) were cut into strips