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Pesticide contamination and phytotoxicity of sediment interstitial water to tropical benthic microalgae

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ARTICLE INFO

Article history:
Received 23 January 2013
Received in revised form
27 May 2013
Accepted 1 June 2013
Available online 12 June 2013

Keywords:
Sediment
Pore water
Microalga
Diuron
Herbicide
Pesticide

ABSTRACT

Many organic compounds including some herbicides concentrate in sediment, thus it may be expected that interstitial waters contain higher concentrations of these contaminants than the water column. To estimate benthic microalgal exposure to pesticides, sediment and interstitial water sampled in the dry season from four major rivers in north Queensland, Australia, were analysed for these contaminants. Interstitial water extracts from the sediments were tested for acute phytotoxicity to benthic microalgae using PAM fluorometry and the results were compared with chemical analyses of the same water samples. A range of pesticides were detected in both sediment and interstitial waters from all sites, notably the herbicide diuron at concentrations ranging from 0.3 to 11 $\mu g\ kg^{-1}$ dry weight sediment, and up to 68 ng L^{-1} in interstitial waters. Herbicide concentrations estimated from partition coefficients and the sediment concentrations typically overestimated analytically determined concentrations present in interstitial water by an order of magnitude. The analytically determined herbicide concentrations in the interstitial water explained most of the phytotoxicity measured with the bioassay; however, photoinhibition was slightly higher than expected based on analytical results, indicating the presence of unidentified phytotoxins. These results demonstrate the presence of pesticides in interstitial waters in the Tropical dry season, sometimes at concentrations that may affect sensitive benthic organisms, and supports the use of the I-PAM bioassay as a valuable tool in exposure- and environmental risk- and impact-assessments.

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0043-1354/$ – see front matter
http://dx.doi.org/10.1016/j.watres.2013.06.003

1. Introduction

1.1. *Herbicide contamination in coastal marine environments*

Herbicide contamination of surface water and sediments is common along the Queensland coast in Australia (Davis et al., 2012; Kennedy et al., 2012; Lewis et al., 2009, 2012; Packett et al., 2009; Shaw et al., 2010). Many pesticides are persistent to varying extents, and their continued and growing use poses a potential threat to marine communities *via* chronic exposure even when environmental concentrations are not acutely toxic. For instance, when chemicals are present in low concentration mixtures, there is the potential for the combined toxicities to be additive (or even synergistic) exceeding toxic thresholds (Knauert et al., 2008; Magnusson et al., 2010). Nevertheless, there remains a lack of environmental studies focussing on the effects of agrochemicals to relevant aquatic organisms in Australia. An exception is the herbicide diuron, which has been investigated in laboratory experiments in relation to its effects on seagrasses (Haynes et al., 2000b), phototrophic biofilms (Magnusson et al., 2012), and coral reef communities (Negri et al., 2011) in the Great Barrier Reef (GBR), and has subsequently been proposed to exhibit negative effects at existing environmental concentrations (Lewis et al., 2009). However, very few studies have explored the influence of herbicides on the less conspicuous benthic estuarine communities of microalgae in the Australian tropics (Magnusson et al., 2008, 2012) despite their high primary productivity and recognised central role in sediment chemistry, nutrient fluxes and benthic/pelagic coupling (Forster et al., 2006).

1.2. *Bioassays for environmental monitoring*

Research has demonstrated the potential of polar or non-polar organic extracts of fresh- and seawater containing pesticides to inhibit photosynthesis in microalgae (Escher et al., 2006). Natural water samples tested to date have generally been sampled from the water column, either using a time integrated approach with passive organic samplers (POS) (Shaw et al., 2009, 2010), or by traditional grab sampling followed by clean-up and concentrating using solid phase extraction before analysis (Lewis et al., 2009; Muller et al., 2008). As many herbicides and other organic compounds can concentrate in sediment due to their relative hydrophobicity it can be expected that interstitial waters may contain higher concentrations of these contaminants than the overlying water (Dueri et al., 2008), therefore exposure of microphytobenthos living in the top few centimetres of sediment to contaminants may be underestimated using traditional water column sampling. It is, however, often not practical to collect the volumes of interstitial water that are required for sufficient preconcentration of the sample to reach reliable analytical detection limits of the compounds of interest. Instead, analysis of whole sediment is commonly performed to provide an approximation for contaminant exposure experienced by organisms in this habitat (Haynes et al., 2000a). Approximations are typically based on assuming equilibrium partitioning of the compound of interest between sorption to solid (SOM) or dissolved organic matter (DOM), and dissolved in the water phase (Dueri et al., 2008).

More recently bioassays have been used for effect-based monitoring of pollution of receiving waters from agrochemicals, hormones and genotoxic substances to complement analytically determined pollutant loads (Escher et al., 2008a; Muller et al., 2007, 2008; Vermeirssen et al., 2009). Combined and interactive effects of toxicants that are present near or below the analytical detection limits are taken into account using effect-based monitoring and a stronger biological response than expected based on analytically determined concentrations of selected target analytes can indicate the presence of unidentified pollutants with the same mode of action (Shaw et al., 2009). The application of bioassays to environmental monitoring has mainly been applied to test the toxicity of effluent from sewage treatment plants (Escher et al., 2008b; Vermeirssen et al., 2009), surface waters (Bengtson Nash et al., 2006; Muller et al., 2008) or drilling mud (Heimann et al., 2002), but has not been previously applied to investigate the toxicity of estuarine sediment interstitial waters.

1.3. *Aims*

The objectives of this study were therefore to determine the exposures of microphytobenthos to common herbicides and to use bioassays to assess the environmental significance of these exposures during low-flow dry season conditions, while simultaneously evaluating the applicability of using equilibrium partitioning to estimate pesticide concentrations in interstitial water based on concentrations in whole sediment. Specifically, the exposure of microphytobenthos to pesticides (herbicides and insecticides) from agricultural runoff was estimated in the Herbert, Johnstone and Tully Rivers in north Queensland, Australia, by analysing their concentrations in interstitial waters and sediments. These river systems were selected due to their reported high contribution of sediment and pesticide runoff to the Great Barrier Reef (GBR) lagoon (Bainbridge et al., 2009; Kapernick et al., 2006). Sediment and interstitial water samples from the Daintree River in the far north World Heritage Area were included to investigate pesticide pollution in a less impacted area. Interstitial water extracts from all river sediments were tested directly for acute phytotoxicity using a Maxi Imaging PAM (I-PAM) fluorometry bioassay as an effect-based biomonitoring tool (Muller et al., 2008).

2. Materials and methods

2.1. *Sediment sampling*

Triplicate sediment samples (1 L) from six sites in four rivers (Fig. A1) were collected in acetone-washed glass bottles using a modified Ponar grab equipped with a sliding hatch on the top of the grab enabling access to the undisturbed sediment surface layer, or by collecting the surface layer of sediment with a stainless steel spoon if the site was accessible. Sampling was carried out over two days in the dry season (June 2008) and the samples were transported chilled to the laboratory where they