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Pesticide occurrence and spatio-temporal variability in urban run-off across Australia

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A B S T R A C T

Stormwater is a major driving factor of aquatic ecosystem degradation as well as one of the largest untapped urban freshwater resources. We present results from a long-term, multi-catchment study of urban stormwater pesticides across Australia that addresses this dichotomous identity (threat and resource), as well as dominant spatial and temporal patterns in stormwater pesticide composition. Of the 27 pesticides monitored, only 19 were detected in Australian stormwater, five of which (diuron, MCPA, 2,4-D, simazine, and triclopyr) were found in >50% of samples. Overall, stormwater pesticide concentrations were lower than reported in other countries (including the United States, Canada and Europe), and exceedances of public health and aquatic ecosystem standards were rare (<10% of samples). Spatio-temporal patterns were investigated with principal component analysis. Although stormwater pesticide composition was relatively stable across seasons and years, it varied significantly by catchment. Common pesticide associations appear to reflect 1) user application of common registered formulations containing characteristic suites of active ingredients, and 2) pesticide fate properties (e.g., environmental mobility and persistence). Importantly, catchment-specific occurrence patterns provide opportunities for focusing treatment approaches or stormwater harvesting strategies.

1. Introduction

Worldwide application of pesticides for agricultural and urban purposes totaled more than 2 million tonnes in 2007, at a cost of more than 39 billion U.S. dollars (2007 equivalents) (U.S. EPA, 2011). Given the magnitude of global pesticide use, it comes as no surprise that pesticide contamination of surface water, groundwater, sediments, and soils is widespread. For instance, long-term studies by the U.S. Geological Survey detected pesticides in >95% of streams and rivers across the continental U.S. (1992–2011; Stone et al., 2014), and >50% of shallow groundwater wells beneath urban or agricultural areas (1992–2001; Gilliom, 2007). In European countries, including Germany and Italy, pesticide contamination in groundwater is likewise prevalent (Guzzella et al., 2006; Vonberg et al., 2014). Pesticides have also been reported in marine waters, and are listed amongst the leading causes of coral reef degradation in Honduras, Belize, Guatemala, and Australia (King et al., 2013).

While much of today's pesticide contamination can be traced

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Abbreviations

AICc	Akaike information criterion corrected for small sample sizes
CI	confidence interval
DCA	dichloroaniline
DEA	desethyl atrazine
K_{oc}	the organic carbon partition coefficient
LC-MS/MS	liquid chromatography tandem mass spectrometry
MRM	multiple reaction monitoring
NA-EU	North America and Europe
NRMSD	normalized root mean square deviance
NSW	New South Wales
PC	principal component
PCA	principal component analysis
QHFSS	Queensland Health Forensic and Scientific Services
QLD	Queensland
U.S.	United States
VIC	Victoria
WA	Western Australia

back to pesticide use in the agricultural sector, there is growing recognition that urban pesticide use presents its own environmental and human health challenges. Indeed, while the percentage of U.S. agricultural-impacted streams exceeding aquatic ecosystem benchmarks has held fast at 65% over the past two decades, the percentage of urban-impacted streams with exceedances has increased from 53 to 90% (U.S. EPA, 2011). This increase, combined with growing concern that urban pesticide exposure elevates the risk of lung cancer, non-Hodgkin lymphoma, and immune dysregulation (Hardell and Eriksson, 2003; Arya, 2005; Mokarizadeh et al., 2015), suggests that our attention to urban pesticides has come none too soon. However, despite growing recognition of urban pesticide impacts, large, multi-catchment studies that directly evaluate pesticide concentrations in urban stormwater runoff remain rare. This omission is important because urban stormwater is increasingly being viewed as a resource to combat water scarcity and security challenges, making its quality a priority (Roy et al., 2008; Askarizadeh et al., 2015; Walsh et al., 2016).

Perhaps nowhere is this viewpoint more front and center than in Australia, where a prolonged drought (the Millennium Drought) lingers in recent memory, and the sustainable water movement (including efforts to harvest and treat stormwater for potable substitution) is in full swing (Grant et al., 2013; Low et al., 2015; Radcliffe, 2015). Indeed, Australia's growing interest in stormwater as an urban water resource prompted a recent literature review of stormwater micro-pollutants by Zhang et al. (2015) which identified pesticides as a key knowledge gap. To date, stormwater-specific pesticide studies include early work by the U.S. Geological Survey (Oltmann and Shulters, 1989), which revealed elevated concentrations of organophosphorous and organochlorine pesticides in rain and road runoff in Fresno, California. Subsequently, other studies have focused on quantifying current-use pesticides (particularly atrazine, simazine, and diuron) in urban road runoff (Polkowska et al., 2001; Huang et al., 2004a,b; Lamprea and Ruban, 2008; Stachel et al., 2010), roof runoff (Bucheli et al., 1998; Polkowska et al., 2009; Bollmann et al., 2014), and within the storm sewer system (Rule et al., 2006; Wittmer et al., 2010; Zgheib et al., 2011a,b; Birch et al., 2011; Ensminger et al., 2013; Becouze-Lareure et al., 2016) (see Table S1). This body of work points to pesticides as a common (and highly variable) constituent in urban stormwater, with reported concentrations ranging from below the limit of quantitation to > 100 μg/L (Gasperi et al., 2014). However, it is not clear what is causing this variability, since studies that focus on the key drivers behind pesticide generation in stormwater are rare (Zhang et al., 2015). This could be regarded as the key knowledge gap in the development of control measures for pesticides in stormwater, which is important both for ecosystem protection and the future of stormwater as an urban water resource.

Here we present results from the first long term, multi-state and multi-catchment study on the prevalence of pesticides in urban stormwater. This study was conducted across several states in Australia and designed to characterize spatial and temporal variability in stormwater pesticide concentrations as well as likely chemical and human-use related drivers of that variability. The work is novel in several respects. First, it places broad-scale variability in Australian stormwater pesticides in a global context (e.g., via comparisons with the U.S., Canada and Europe, as well as public health standards and aquatic life benchmarks), the first study to do so. Furthermore, this study is one of few that quantifies the relative contribution of different spatial (state and catchment) and temporal (season and year) scales to urban stormwater pesticide variability. This information will help guide future questions about drivers of variability, which often have distinct spatial and temporal fingerprints. Finally, this study connects both continent-wide pesticide formulation information and fate properties (e.g., mobility and persistence) back to prevailing stormwater pesticide patterns. Although evaluation of the former is relatively uncommon, our results suggest that it may be an important determinant of pesticide co-occurrence in urban Australian stormwater.

2. Methods

2.1. Site description and sample collection

Stormwater samples (n = 62) were collected during wet weather events between 2011 and 2014 at 10 sampling stations, each located in a different urban or peri-urban catchment. Stations were distributed across 4 Australian states: Queensland (QLD, 2 stations), Victoria (VIC, 3 stations), New South Wales (NSW, 3 stations), and Western Australia (WA, 2 stations) (Fig. 1). Note that a large share of the samples were collected during spring and summer months and in 2012 and 2013 (see Table S1). Stormwater was collected at storm drain outlets, stormwater control measure inlets,

Fig. 1. Map of Australia showing the location of stormwater sampling stations in Queensland (QLD; red symbols), Victoria (VIC; blue symbols), New South Wales (NSW; cyan symbols) and Western Australia (WA; white symbols). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)