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

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31 **ABSTRACT:** Stormwater is a major driving factor of aquatic ecosystem degradation as well as one of
32 the largest untapped urban freshwater resources. We present results from a long-term, multi-catchment
33 study of urban stormwater pesticides across Australia that addresses this dichotomous identity (threat
34 and resource), as well as dominant spatial and temporal patterns in stormwater pesticide composition.
35 Of the 27 pesticides monitored, only 19 were detected in Australian stormwater, five of which (diuron,
36 MCPA, 2,4-D, simazine, and triclopyr) were found in > 50% of samples. Overall, stormwater pesticide
37 concentrations were lower than reported in other countries (including the United States, Canada and
38 Europe), and exceedances of public health and aquatic ecosystem standards were rare (< 10% of
39 samples). Spatio-temporal patterns were investigated with principal component analysis. Although
40 stormwater pesticide composition was relatively stable across seasons and years, it varied significantly
41 by catchment. Common pesticide associations appear to reflect 1) user application of common
42 registered formulations containing characteristic suites of active ingredients, and 2) pesticide fate
43 properties (e.g., environmental mobility and persistence). Importantly, catchment-specific occurrence
44 patterns provide opportunities for focusing treatment approaches or stormwater harvesting strategies.
45

46 **Keywords:** pesticide, urban runoff, stormwater management, alternative water source, spatio-temporal
47 pattern, principal component analysis

48 **ABBREVIATIONS:**

49 AICc: Akaike information criterion corrected for small sample sizes

50 CI: confidence interval

51 DCA: dichloroaniline

52 DEA: desethyl atrazine

53 K_{oc} : the organic carbon partition coefficient

54 LC-MS/MS: liquid chromatography tandem mass spectrometry

55 MRM: multiple reaction monitoring

56 NA-EU: North America and Europe

57 NRMSD: normalized root mean square deviance

58 NSW: New South Wales

59 PC: principal component

60 PCA: principal component analysis

61 QHFSS: Queensland Health Forensic and Scientific Services

62 QLD: Queensland

63 U.S.: United States

64 VIC: Victoria

65 WA: Western Australia

66 1. INTRODUCTION

67 Worldwide application of pesticides for agricultural and urban purposes totaled more than 2 million
68 tonnes in 2007, at a cost of more than 39 billion U.S. dollars (2007 equivalents) (**U.S. EPA, 2011**).
69 Given the magnitude of global pesticide use, it comes as no surprise that pesticide contamination of
70 surface water, groundwater, sediments, and soils is widespread. For instance, long-term studies by the
71 U.S. Geological Survey detected pesticides in > 95% of streams and rivers across the continental U.S.
72 (1992-2011; **Stone et al., 2014**), and > 50% of shallow groundwater wells beneath urban or agricultural
73 areas (1992-2001; **Gilliom, 2007**). In European countries, including Germany and Italy, pesticide
74 contamination in groundwater is likewise prevalent (**Guzzella et al., 2006; Vonberg et al., 2014**).
75 Pesticides have also been reported in marine waters, and are listed amongst the leading causes of coral
76 reef degradation in Honduras, Belize, Guatemala, and Australia (**King et al., 2013**).

77 While much of today's pesticide contamination can be traced back to pesticide use in the
78 agricultural sector, there is growing recognition that urban pesticide use presents its own environmental
79 and human health challenges. Indeed, while the percentage of U.S. agricultural-impacted streams
80 exceeding aquatic ecosystem benchmarks has held fast at 65% over the past two decades, the
81 percentage of urban-impacted streams with exceedances has increased from 53 to 90% (**U.S. EPA,**
82 **2011**). This increase, combined with growing concern that urban pesticide exposure elevates the risk of
83 lung cancer, non-Hodgkin lymphoma, and immune dysregulation (**Hardell and Eriksson, 2003; Arya,**
84 **2005; Mokarizadeh et al., 2015**), suggests that our attention to urban pesticides has come none too
85 soon. However, despite growing recognition of urban pesticide impacts, large, multi-catchment studies
86 that directly evaluate pesticide concentrations in urban stormwater runoff remain rare. This omission is
87 important because urban stormwater is increasingly being viewed as a resource to combat water
88 scarcity and security challenges, making its quality a priority (**Roy et al., 2008; Askarizadeh et al.,**
89 **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 a 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., 2015**) (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 $> 100 \mu\text{g/L}$ (**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, or receiving waters downstream of drain outlets (details in **Fig. S1**). At all stations except those in WA (where logistical constraints limited stormwater collection to grab samples), flow-proportioned composite samples were collected for each rain event. Sampling occurred as described in Tang et al., (2013). Briefly, stormwater samples were collected over the storm hydrograph at flow proportioned intervals using non-refrigerated autosamplers. Because the aquatic half lives (DT50s) of the pesticides evaluated

during this study typically exceed 7 days (median of 12.5 days) (PAN, 2015; USDA, 2001; PPDB, 2017) losses within the autosampler (timescale of hours - 1 day) are expected to be minimal. Note that haloxyfop esters are an exception (DT50 of 0.25 days, PPDB, 2017), and could have decayed markedly during sample collection. Intake rinses were performed between samples, and in QLD, an additional wash step for intake tubing was also performed. Samples were either composited automatically (VIC, NSW) or manually from smaller subsamples (QLD) into high density polyethylene barrels. All sampling containers used during this study were large volume (25-60 L) high density polyethylene containers; this translates to a low surface area to water volume ratio, reducing the risk of pesticide loss through adsorption to the container. In addition, pesticide sorption to high density polyethylene is expected to be negligible for the range of compounds evaluated (Topp and Smith, 1992, Fischer et al., 2008). All samples not collected in QLD (grab and composite) were shipped on ice by overnight freight to the University of Queensland, where they were filtered using 1.2 µm glass fiber filters (GF/C Whatman). Filtrate samples were stored frozen at -18 °C until sent out for pesticide analysis (see Fig. S1 for a schematic representation of the sample collection procedure).

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2.2. Analytical Procedures

Stormwater samples were analyzed for 27 pesticides with a limit of reporting of 0.01 µg/L. This includes two insecticides (carbaryl and propoxur) and 25 herbicides, including triazines and triazine derivatives (atrazine, desethyl atrazine (DEA), simazine, ametryn, terbutryn, prometryn), phenoxy herbicides (MCPA, MCPB, mecoprop, dichloroprop, 2,4-D, 2,4-DB, haloxyfop-2-ethyl, haloxyfop-methyl), polyureas and urea derivatives (diuron, DCA, tebuthiuron), pyridine herbicides (triclopyr, fluroxypyr), amide herbicides (metolachlor, flamprop-methyl), aromatic acid herbicides (dicamba), carbamate herbicides (asulam), substituted uracils (bromacil), and triazinones (hexazinone). The majority of these pesticides are used in consumer and/or professional markets for the following five

162 purposes: turf management (e.g., lawn care, landscaping, golf courses, parks, and cemeteries; most
163 notably MCPA, 2,4-D, simazine, dicamba, and mecoprop), industrial and rights-of-way vegetation
164 control (e.g., roads, railways, drainage pipelines, and industrial or commercial facilities; most notably
165 MCPA, MCPB, 2,4-D, dicamba, simazine, ametryn, diuron, bromacil, triclopyr, fluroxypyr,
166 hexazinone, and carbaryl), public health programs (e.g., related to weed/pest control in rangeland or
167 aquatic systems; most notably MCPA, 2,4-D, atrazine, simazine, terbutryn, prometryn, hexazinone,
168 triclopyr, and dicamba), non-agricultural crops (e.g., forestry and horticulture; most notably atrazine,
169 simazine, dicamba, triclopyr, fluroxypyr, hexazinone, haloxyfop esters, and asulam), and to a lesser
170 extent pest control (e.g., in-home pests like fleas, ticks, mites, and cockroaches and in-yard pests like
171 aphids, caterpillars, slugs, and ants; most notably carbaryl and propoxur) (**Hodge, 1993; AVPMA**
172 **PubCRIS, 2016**) (more details in **Table S2**). Although the emphasis of this study is on herbicides,
173 which constitute the bulk of the professional urban pesticide market, at least in the U.S. (similar data
174 for Australia is unavailable), this emphasis is not intended to suggest a lesser importance of insecticides
175 in urban environments. Indeed, Hoffman *et al.*, 2000 identified elevated insecticide relative to
176 herbicide concentrations in several U.S. urban streams. Rather, our intent is to expand the dialogue
177 concerning herbicides in Australia to include urban areas, focusing on herbicides with broad urban or
178 urban + agricultural use, including both frequently (e.g., triazines) and less frequently monitored (e.g.,
179 phenoxy and aromatic herbicides) active ingredients (**CAPIM, 2014**).

180 Sample extraction and pesticide analysis was performed by Queensland Health Forensic and
181 Scientific Services (QHFSS), a National Association of Testing Authorities laboratory accredited to
182 International Organization for Standardization 17025 standards for chemical testing. Water soluble
183 pesticides were quantified using solid phase extraction followed by liquid chromatography – tandem
184 mass spectrometry (LC-MS/MS), as per QHFSS method QIS27701 (adapted from US EPA Method
185 1694). Solid phase extraction was performed on a Gilson ASPEC system (Middleton, WI, USA) with

Phenomenex StrataX 200mg/3mL cartridges (Torrance, CA, USA). Two aliquots of each water sample were extracted; one acidified with HCl to pH3 and one without pH adjustment, to be analysed later in negative and positive ionization mode, respectively, using a Shimadzu Ultra-Fast Liquid Chromatography system (Kyoto, Japan) coupled to an Applied Biosystems 4000 Q-trap mass spectrometer (Framingham, MA, USA). The analytical column used was a Phenomenex Luna C18 (2), 150 x 2.1mm, 3 micron (Torrance, CA, USA). Pesticides were detected using scheduled multiple reaction monitoring (MRM). Positive detection required 1) MRM ratios (i.e., peak area ratios between primary and secondary ion transitions) within $\pm 30\%$ of one-another, and 2) comparable run times (≤ 15 seconds) between analytes and calibration standards. A minimum of four calibration standards prepared at four concentrations (between 5 and 100 $\mu\text{g/L}$) and a reagent blank were included in each sample batch. Five compounds (caffeine D₃, carbamazepine D₁₀, atrazine D₅, diclofenac D₄ and ¹³C₆ 2,4-dichlorophenoxyacetic acid) were added prior to extraction to monitor the solid phase extraction efficiency. A spike of four internal standards (acetyl-sulfamethoxazole D₅, fluoxetine D₅, 2,4-dichlorophenylacetic acid, and simazine D₁₀) was added to each sample prior to analysis by LC-MS/MS for internal calibration purposes and to correct for instrument drift. One in every ten samples was run in full duplicate (i.e. including sample pre-treatment) to assess analytical precision, with a mean relative standard deviation among duplicate samples typically below 25% (additional information provided in **Table S3**).

2.3. Data Analysis and Statistical Methods

2.3.1. Pesticide Occurrence in Stormwater

Pesticide concentrations occurring in urban stormwater were assessed across 4 years, 4 states, and 10 catchments (i.e. sampling stations). All measurements classed as below the limit of reporting were set to half its value, i.e. 0.005 $\mu\text{g/L}$. Where possible, Australian stormwater pesticide concentrations were

210 compared to reported values from the United States, Canada and Europe, henceforth referred to jointly
211 as North America – Europe (NA-EU) catchments. Only pesticides evaluated in five or more NA-EU
212 catchments, ten or more discrete stormwater samples, and three or more studies were included in this
213 comparison (see **Table S4** for information regarding the studies evaluated for each pesticide).
214 Percentile concentration values (5th, 50th, and 95th) were estimated for comparison to Australian data
215 following the procedure of Zhang et al., (2015). Briefly, a triangular cumulative distribution function
216 was generated for each pesticide using the minimum, maximum, and median concentrations reported in
217 literature. This distribution form reflects the scarcity of available urban stormwater pesticide data.
218 Censored minima were set to zero, as pesticide quantitation limits were inconsistently reported.
219 Percentile concentration values for each pesticide were calculated from their respective distributions.

220 To place Australian stormwater pesticide concentrations in a broader societal and environmental
221 context, pesticide concentration data were also compared to established public health and aquatic
222 ecosystem standards. Public health standards for recycled water intended to augment the potable
223 supply are from the Queensland Public Health Act (**QPHA, 2005**). These standards are consistent with
224 the National Australian guidelines for water recycling (**NWQMS, 2008**), but cover a broader range of
225 pesticide compounds. Ecosystem standards are Aquatic Life Benchmarks for algae, vascular plants,
226 invertebrates, and fish from the U.S. Environmental Protection Agency (**U.S. EPA, 2015**).

227

228 *2.3.2. Dominant Patterns in Stormwater Pesticide Concentration*

229 Principal Component Analysis (PCA) was employed in order to identify dominant patterns in
230 stormwater pesticide concentration in space (state and station) and time (season and year). Only
231 pesticides detected > 3 times (13 total) were included in this analysis, as PCA is sensitive to singletons
232 and rare events (**Babamoradi et al., 2013**). PCA reduces data dimensionality by replacing variables
233 (in this case pesticides) with linear combinations of variables (PC modes, also known as loadings) that

are 1) orthogonal to one-another and 2) retain the maximum amount of possible variance from the original dataset. Each mode has a corresponding vector of scores that indicate the position of individual samples (from different states, stations, seasons and years) in principle component space, and a latent value (or eigenvalue) that reflects the percent variance explained by that PC mode. The first mode captures the largest fraction of data variance, with each subsequent mode explaining a progressively smaller fraction (**Abdi and Williams, 2010**).

A resampling-based stopping rule was used to identify PC modes that explained significantly ($p < 0.05$) more variance in stormwater pesticide concentration than expected by chance (hereafter referred to as dominant modes). The stopping rule employed is analogous to the Rand-Lambda rule defined by Peres-Neto et al., (2005) which is purported to perform well for environmental data where variables can be weakly correlated (details in SI).

Following identification of dominant modes, a non-parametric bootstrap approach was used to determine the uncertainty about those modes and their corresponding scores. This provides an estimate of statistical confidence in pesticide pattern structure that is distinct from overall mode significance (defined above). 95% confidence limits were calculated as specified by Babamoradi et al. (2005), using the nonpara-boot-pca function in Matlab, Mathworks, MA (details in SI).

It is noteworthy, that all random error introduced by sampling and chemical analysis will contribute to the noise of the data analyzed by the statistical approach described. Noise in the data may lead to false negatives, when conducting hypothesis testing, but is less likely to increase the risk of false positive error.

2.3.3. Interpreting Dominant Pesticide Patterns: Spatial vs Temporal Variability

A series of four resampling-based statistical models were used to identify the dominant spatial and temporal factors contributing to observed stormwater pesticide variability. These models were coined

the year-model, season-model, state-model, and station-model as they were designed to evaluate the contribution of year-year, season-season, state-state, or station-station variability to dominant stormwater pesticide patterns, respectively. In each case, mean-centered and standardized pesticide concentration data were randomized across all spatial or temporal categories except the one of interest (for instance, in the year-model, randomization occurred across all states, stations and seasons within each year sampled, but not between years). These model-specific randomization procedures were executed 10,000 times for each model, PCA was performed on each realization, and percentile-based 95% confidence intervals were calculated for eigenvalues, modes, and scores. Note that because randomization was performed over space and time, but not across different pesticides, the dominant modes recovered by the four resampling-based statistical models were identical to data modes: model-data differences were limited to PC scores. Three criteria were used to identify the model (or models) that best explained observed scores: 1) Akaike's Information Criterion with a bias correction for small sample sizes (AICc), 2) the coefficient of determination (i.e., Pearson's R^2), and 3) normalized root mean squared deviance (NRMSD) (statistical details in SI).

2.3.4. Interpreting Dominant Pesticide Patterns: Use Groups and Fate Properties

Pesticide concentrations in runoff are controlled by a myriad of factors including, but not limited to, rainfall characteristics (intensity, duration), pesticide fate properties (mobility, persistence), properties of the application surface (soil conditions, percent imperviousness, topography), and herbicide use patterns (particularly application time, application concentration, and product use preferences; i.e., formulation) (**Huang et al., 2004a**). Here we focus on two of these drivers 1) pesticide fate properties (which, alongside runoff volume, can be a strong determinant of pesticide concentrations in runoff over a season; **Huang et al., 2004a, Gouy et al., 1999**) and 2) product use preferences, which are less frequently evaluated, and yet strongly indicative of the pesticide composition in urban receiving waters

282 (USGS, 1998). Importantly, as information regarding pesticide application concentration and time
283 (relative to storm events) was unattainable given the large spatio-temporal scale of this study, these
284 drivers (whilst important) are not considered further here.

285 Given our focus on use preferences and fate properties the following information was compiled
286 and assessed: 1) the registered pesticide formulations in QLD, NSW, VIC, and WA (see SI for details)
287 and 2) pesticide chemical properties such as the terrestrial field dissipation half-life, an indicator of
288 pesticide persistence that reflects dominant degradation and transport processes, and the organic carbon
289 partition coefficient ($\log K_{oc}$), a mobility indicator that describes the affinity of pesticides for soil
290 organic carbon. All pesticide formulation information used in this study is freely available from
291 PubCRIS, a database maintained by the Australian Pesticide and Veterinary Medicines Authority
292 (AVPMA PubCRIS, 2016). While this database is primarily intended for registration of pesticides
293 with agricultural applications, industrial, commercial, and residential-use pesticides are also included.
294 This suggests that it may be useful for first-order evaluation of urban pesticide use, specifically the
295 identification of “use groups” (e.g., types of pesticides that are likely to occur together due to co-
296 inclusion in commercial products).

297

298 3. RESULTS

299 3.1. Pesticide Variability in Stormwater

300 Of the 27 pesticides evaluated, 8 were never detected above the limit of reporting ($0.01 \mu\text{g/L}$). These
301 include asulam, prometryn, flamprop-methyl, and terbuthiuron as well as four phenoxy herbicides
302 (MCPB, 2,4-DB, haloxyfop-2-ethyl, and haloxyfop-methyl). Recall from section 2.1 that the absence
303 of both haloxyfop esters may reflect their rapid microbial-mediated hydrolysis rate (DT50 of 0.25 days;
304 PPDB, 2017) relative to our sample collection timeframe (over a storm hydrograph) rather than any
305 true absence from stormwater. Concentrations of the remaining pesticides were low (median

concentration $< 0.1 \mu\text{g/L}$) and variable, spanning ~ 3 orders of magnitude (range: $\leq 0.01 - 23 \mu\text{g/L}$) (Fig. 2, Table S5). The fraction of stormwater samples testing positive for a given pesticide also varied, with diuron detected near ubiquitously (in 59 of 62 samples) and metolachlor, hexazinone, fluroxypyr, dichloroprop, carbaryl, and DCA detected rarely (1-3 times each) (Fig. 3). Five pesticides were detected in $>50\%$ of samples; diuron $>$ MCPA $>$ 2,4-D $>$ simazine $>$ triclopyr.

Median stormwater pesticide concentrations were lower than those from the United States, Canada and Europe (NA-EU) (Fig. 2). This pattern was significant ($p < 0.05$ level) for atrazine, mecoprop, terbutryn, and metolachlor. Australian stormwater pesticide concentrations rarely exceeded Queensland public health standards for recycled water intended for potable purposes, the exception being MCPA, where 4 out of 62 samples were in excess of the $2 \mu\text{g/L}$ standard (Figs. 2, 3). The same standards were more frequently exceeded by NA-EU stormwater, with violations observed for diuron and mecoprop, as well as MCPA. Aquatic life benchmarks were also exceeded more frequently by NA-EU stormwater. These exceedances include invertebrate benchmarks (diuron), vascular plant benchmarks (diuron), and algal benchmarks (simazine, atrazine, mecoprop, and diuron). Only vascular plant and algal benchmarks (2,4-D and atrazine, respectively) were exceeded by Australian stormwater (see outliers in Fig. 2).

3.2. Dominant Pesticide Patterns

Two significant PC modes (e.g., dominant patterns) were identified in our stormwater pesticide concentration data (see black circles $>$ red dashed lines in Fig. S2). These modes explain approximately 30% and 22% of data variance, respectively (total variance explained: 52%, 95% CI: 43-62%). The primary pattern in our stormwater pesticide data (e.g., PC1) was that samples with high concentrations of mecoprop, dicamba, MCPA, and 2,4-D had low concentrations of bromacil, ametryn, terbutryn, atrazine and desethyl atrazine (see pesticide loading vectors for PC1 in Fig. 4a). Notably,

diuron, simazine, propoxur, and triclopyr did not contribute significantly to PC1, although diuron was marginally significant at the $p < 0.10$ level (grouping with mecoprop, dicamba, MCPA, and 2,4-D in **Fig. 4a**). Interestingly, our secondary mode, (PC2), grouped diuron with ametryn, terbutryn, atrazine, and desethyl atrazine, suggesting co-occurrence of diuron and triazines in a subset of stormwater samples. No other pesticides contributed significantly to PC2.

Evaluated together, PC1 and 2 delineate four major pesticide groupings: the triazine herbicides (ametryn, terbutryn, atrazine, and desethyl atrazine: - PC1, + PC2); the phenoxy and aromatic herbicides (MCPA, 2,4-D, mecoprop and dicamba: + PC1 only); the uracil, bromacil (- PC1 only); and the urea, diuron (marginal + PC1, + PC2) (**Fig. 4a**). Although simazine, propoxur and triclopyr were not significant for either dominant mode, the contribution of these pesticides (specifically simazine and propoxur) to overall stormwater pesticide variability was captured in two marginal modes (see **Fig. S3**). Each marginal mode explained $< 12\%$ of pesticide variability, and had a $> 50\%$ chance (but $< 95\%$ chance) of being significantly different than random (see black circles $>$ blue line in **Fig. S2**).

3.3. Interpreting Dominant Patterns: Temporal and Spatial Variability

Dominant pesticide patterns in Australian stormwater were not obviously seasonal, as evidenced by the absence of season-specific sample clustering in PC space (**Fig. S4**). Year specific patterns were also weak, although more samples were positive for mode 2 in 2013 and 2014 than 2011 and 2012. This may reflect the addition of new sampling stations in 2013 (see WA1 in the upper left quadrant of **Fig. 4a, Fig. S4c**) as well as true temporal shifts in pesticide composition at stations like QLD2, where higher concentrations of MCPA, 2,4-D, dicamba, and mecoprop were detected in 2013/2014 (**Fig. 3**). Notably, resampling-based statistical models that resolved only season or year-specific variability, were unable to reproduce the dominant pesticide patterns observed during this study (see large error bars about sample scores, **Fig. 4b, c**). This is reflected in relatively poor model-data fits (Variance

354 Explained: 1 – 5% vs. > 50% for the best-fit model; NRMSD: 0.22 – 0.28 vs. < 0.15 for the best-fit
355 model) and low AICc weights (e.g., a low probability (<< 1%) that year or season-specific models best
356 explain observed stormwater pesticide patterns) (**Table S6**).

357 Although temporal patterns in stormwater pesticide concentration were relatively weak, spatial
358 patterns (particularly station-specific patterns) were strong, as evidenced by the presence of station-
359 specific sample clustering in PC space (see **Fig. 4a**). While pesticide patterns were comparable for
360 some stations (see overlap of sample scores for NSW2 and NSW3 in **Fig. 4a**), others were unique,
361 including VIC1, WA1, and QLD2. State-specific patterns were less evident, with all states exhibiting
362 sample clustering in the lower left quadrant of PC space, and most also exhibiting clustering in the
363 upper right quadrant. The exception was WA, where no samples were positive for PC1, indicating
364 reduced concentrations of MCPA, 2,4-D, dicamba and mecoprop in WA relative to other states.
365 Although both spatially-resolved statistical models reproduced observed PC scores better than
366 temporally-resolved statistical models (see reduced error in **Fig. 4** panels **d,e** relative to **b,c**), the station
367 model had significantly higher model-data fits for pesticide scores (> 50% variance explained; 95% CI:
368 37-76%) and the highest overall probability of being the best model (~100%) across all spatial and
369 temporal models evaluated (**Table S6**). Indeed, in order of decreasing importance, urban stormwater
370 pesticide variability was catchment specific (37 – 76% of PC1 and 2, 16 – 47% overall), then state-
371 specific (0 – 48% PC1 and 2; 0 – 30% overall), year-specific (0 – 28% PC1 and 2; 0 – 17% overall),
372 and season-specific (0 – 18% PC1 and 2; 0 – 11% overall) (see 95% CIs in **Table S6**).

373

374 **3.4. Interpreting Dominant Patterns: Common Use Groups and Fate Properties**

375 The four dominant stormwater pesticide groups delineated by PC1 and 2 are consistent with “common
376 use groups” (e.g., pesticides that co-occur in registered AU products, **Fig. 5**, **Table S2**). For instance,
377 the phenoxy and aromatic herbicides (+ PC1 pesticides; delineated by the blue triangle in **Fig. 5**) are a

use group. They co-occur in multiple products (1-47; see numbered black lines connecting different phenoxy and aromatic herbicides (blue circles) in **Fig. 5**), and are infrequently associated with other pesticides (e.g., triazines (red): 8 products shared, bromacil (green): 0 products shared, and diuron (cyan): 0 products shared, **Fig. 5**). Diuron and bromacil represent single compound use groups, as they are typically applied in isolation (63 products only contain diuron and another three only contain bromacil; see numbered circles, **Fig. 5**). The exception is 1 shared product intended for pest control in pineapple. The triazines (- PC1, + PC2; delineated by the red square in **Fig. 5**) may also constitute a use group, as most occur with each other (or in isolation), but not with other pesticides. Evidence for this group is weaker, however, as intra-group pesticide associations are few (e.g., only 1-3 products contain multiple triazines), and one triazine, terbutryn, is found more frequently in association with the phenoxy herbicide MCPA than other triazines. A detailed breakdown of these relationships can be found in **Table S2**.

Dominant pesticide groups can also be distinguished by pesticide fate properties related to environmental persistence (e.g., field dissipation half life) and mobility (e.g., $\log K_{oc}$, where low values indicate relatively mobile pesticides with low soil affinity) (**Fig. 6**). $\log K_{oc}$ explains 54% of the variance in PC2, with high mobility pesticides such as bromacil and the phenoxy and aromatic herbicides ($\log K_{oc} \leq 1.6$) separating out from lower mobility pesticides such as the triazines and diuron ($\log K_{oc} > 2$). Similarly, field dissipation half-life explains 59% of the variance in PC1, separating out recalcitrant pesticides (e.g., bromacil; average half-life > 200 days) from those that are less persistent (e.g., the phenoxy and aromatic herbicides; average half life < 50 days. Notably, the triazines and diuron cluster together in a single “moderately persistent” group (half life 90-100 days) rather than forming separate groups, as observed in our original pesticide PCA (compare **Fig. 4a** and **6**).

400

401 **4. DISCUSSION**

402 The five pesticides detected > 50% of the time in Australian stormwater (i.e., diuron, MCPA, 2,4-D,
403 simazine, and triclopyr) are common urban (as well as agricultural) herbicides, several of which have
404 been previously reported in urban runoff or receiving waters across Australia (**CAPIM, 2014; Allinson**
405 **et al., 2015**), Europe (**Gasperi et al., 2014; Blanchoud et al., 2004**), Canada (**Glozier et al., 2012**),
406 and the U.S. (**USGS, 1998; Hoffman et al., 2000; Phillips and Bode, 2004; Ensminger et al., 2013**).
407 A subset of these pesticides are active ingredients in commercial products available for use in
408 Australian home gardens (e.g., simazine, MCPA, and triclopyr) or aquaria/ponds (e.g., simazine and
409 diuron), and most can also be applied in urban industrial and commercial settings or along roads (e.g.,
410 simazine, MCPA, 2,4-D, and triclopyr) (**Table S2**). Diuron is the only member of the top five
411 pesticides that is currently not approved for home garden, commercial, or industrial use in Australia;
412 these uses were suspended in 2011 and banned in 2012, half way through our study (**APVMA, 2012**).
413 Notably, the effects of this ban are not evident in our 2013/2014 stormwater samples. Indeed, similar
414 (if not higher) concentrations of diuron are observed in 2013/2014 (see QLD2, VIC3, and NSW1 in
415 **Fig. 3**). This could reflect 1) application of leftover diuron stocks following the ban, or 2)
416 environmental persistence of diuron from prior application events (half-life range in water and soil: 43
417 – 2180 days, depending on the degradation processes involved) (**DPR, 2004**).

418 Although 19 individual pesticides were detected in Australian stormwater (5 frequently, as
419 discussed above), absolute concentrations were lower than those observed in other developed countries
420 (e.g., the U.S., Europe, and Canada) (see **Fig. 2**). Given that Canada's overall use of pesticides on
421 arable and agricultural land is below Australia's (0.8 vs. 2.5 tonnes/1000 Ha), and values for the U.S.
422 and Europe (averaged across all countries) are comparable to Australia (2.4 and 3.0 tonnes/1000 Ha,
423 respectively), it seems unlikely that Australia's low stormwater pesticide concentrations reflect low
424 overall pesticide usage (**FAOSTAT, 2015**). However, as these usage statistics primarily reflect
425 agricultural rather than urban practices, it remains possible that low urban pesticide use is responsible

426 for the relatively low pesticide concentrations in Australia's urban stormwater.

427 Although low across the board, Australian stormwater pesticide concentrations were more
428 similar to those in other countries for some compounds (e.g., MCPA, triclopyr, and dicamba) than
429 others (e.g., atrazine) (**Fig. 2**). The former might reflect similar commercial availability of home-
430 garden products containing MCPA, triclopyr, and dicamba across countries (except some provinces of
431 Canada where urban use is restricted; **Pesticides Act Ontario, 2009; Pesticides Act Quebec, 2003**).
432 However, further research quantifying country-specific pesticide formulations, availability, and sales is
433 required in order to adequately evaluate this supposition. Regarding atrazine, it is notable that different
434 countries have regulated use of atrazine-containing products to various degrees; the European Union
435 formally banned all atrazine use in 2004 due to groundwater contamination concerns (although several
436 constituent countries had already done so in the early 90's; **Vonberg et al., 2014; Jablonowski et al.,**
437 **2011**), Australia banned atrazine for urban use in 1997 (**APVMA, 2008**), and the U.S. and Canada
438 generally allow atrazine use for urban and agricultural purposes (save Quebec and Ontario, which
439 restricted home-garden, school, and municipal use of atrazine in 2003 and 2008, respectively;
440 **Pesticides Act Ontario, 2009; Pesticides Act Quebec, 2003**). Thus, one explanation for the low
441 atrazine concentrations observed in Australian stormwater relative to average concentrations across
442 Canada and the U.S., is Australia's relatively early urban atrazine ban. However, it should be noted that
443 banning atrazine does not necessarily eliminate atrazine contamination in soils, surface water, or
444 groundwater (**Jablonowski et al., 2008, 2011**); indeed, pre and post-ban atrazine concentrations in
445 groundwater are comparable in some areas of Europe (Germany for instance, which banned atrazine in
446 1991), perhaps reflecting low rates of microbial degradation in anaerobic conditions (**Vonberg et al.,**
447 **2014**). Thus, while the 1997 ban represents a possible explanation for the differences in stormwater
448 atrazine concentrations between Australia and other countries, it is likely not the complete explanation.

449 One consequence of Australia's low stormwater pesticide concentrations is that they are unlikely

450 to pose an acute threat to 1) downstream aquatic ecosystems or 2) human health, if stormwater is
451 harvested for potable substitution in urban centers (e.g., toilet flushing or outdoor irrigation). This is
452 not to say that stormwater is necessarily safe, only that acute toxic effects related to pesticide exposure
453 are unlikely. Note that our results do not inform our understanding of chronic pesticide exposure levels
454 because chronic exposure reflects both wet and dry weather conditions (our focus was storms) as well
455 as the physico-chemical state of the pesticide (e.g., dissolved in water (our focus) or bound to sediment
456 particles, which more directly impact benthic ecosystems) (**Allinson et al., 2014, 2015**).

457 Despite low overall pesticide levels, public health standards and aquatic ecosystem benchmarks
458 were occasionally exceeded for MCPA, 2,4-D, and atrazine (**Fig. 2**), suggesting that some degree of
459 stormwater treatment is warranted to protect downstream ecosystems and public health. Furthermore,
460 routine monitoring of phenoxy herbicides (especially MCPA and 2,4-D) in stormwater is called for.
461 Currently, these pesticides are monitored less frequently in Australia than their triazine counterparts
462 (**CAPIM, 2014**), which given their prevalence in urban stormwater, and growing concerns about their
463 health effects globally (**Hardell and Eriksson, 2003; Arya, 2005; Mokarizadeh et al., 2015**), is
464 potentially ill advised.

465 One of the more interesting patterns our study revealed is that the urban pesticide composition
466 of Australian stormwater is more stable in time (season and year) than across catchments (e.g., station
467 to station) (see **Figs 4 and S4**). This may in part reflect the temporal limitations of our data, as no
468 single catchment was sampled during all years and only three were sampled during all seasons, limiting
469 our ability to detect coherent temporal trends (see **Table S1**). However, other studies have also
470 reported low levels of coherent temporal variability (particularly seasonal variability) in urban
471 pesticides at the national scale (**Phillips and Bode, 2004**). Because urban pesticide temporal signatures
472 are complex (reflecting multiple application events, products, and storms), persistent pesticide
473 detection both during and post growing season, as well as pesticide-specific temporal signatures, are

frequently observed (**Hoffman et al., 2000; Phillips and Bode, 2004; Johnson et al., 2011; Glozier et al., 2012**). Importantly, the latter would not necessarily be detected using resampling-based statistics and PCA, which are best suited for identifying patterns that are common amongst multiple pesticides.

While reports of urban stormwater pesticide seasonality vary, pesticide composition is often found to be catchment specific, likely reflecting some combination of regional product preferences, climatic differences, population density, and land use characteristics (**USGS, 1998; Hoffman et al., 2000; Blanchoud et al., 2004; Phillips and Bode, 2004; Glozier et al., 2012**). This said, the broad geographic scope of this study makes the degree of catchment specificity (up to ~50% of overall pattern) somewhat surprising, as one might expect broad climate gradients (e.g., the subtropical-to-temperate gradient from QLD to NSW) to render stations within QLD more similar to one-another than to stations from NSW (indeed the opposite is observed; **Fig. 4a**). This suggests that future research into dominant drivers of stormwater pesticide variability should focus on drivers that resolve catchment-level rather than state-wide pattern.

Although a detailed analysis of the possible drivers of catchment-specific pattern is beyond the scope of this paper, our findings do suggest that across all catchments, stormwater pesticide composition is governed by some combination of pesticide fate properties and user application of common pesticide formulations (**Figs. 5, 6**). Take mecoprop, for instance. Across Australia, mecoprop appears to be registered only in products containing other pesticides (specifically the phenoxy or aromatic herbicides MCPA, 2,4-D, or dicamba) (**Fig. 5, Table S2**). This means that in catchments where mecoprop is detected, one or another of these compounds must also be detected (see, for example, QLD2 in **Fig. 3**, where high concentrations of mecoprop coincide with the highest concentrations of dicamba, MCPA and 2,4-D of any sample). Use groups of this sort may go a long way towards explaining why certain pesticides tend to co-occur within catchments. Pesticide fate properties provide another key piece of the puzzle, particularly in regards to compounds like diuron and

498 atrazine that are no longer applied, but linger in the environment (in some cases across many
499 catchments; see diuron in **Fig. 3**). These compounds (and others) occupy the upper-middle section of
500 **Fig. 6**, and are problematic from a water quality perspective because they are 1) of moderate-low
501 mobility relative to other current-use pesticides, meaning that they have the potential to reside in soils
502 and sediments and dissociate/leach out over time, and 2) relatively stable in the environment (e.g.,
503 characterized by moderate field dissipation half-lives), making them persistent enough to be
504 transported by multiple storm events (**Jablonowski et al., 2011; USGS, 2000**). Importantly, pesticide
505 fate properties and use groups needn't be thought of as competing alternative explanations of dominant
506 pesticide pattern. Indeed, in practice, the two may be linked, with preferential application of common
507 pesticide use groups underlying patterns in fate properties (at least for pesticides that remain in
508 common use; e.g., all pesticides evaluated here save diuron and atrazine). For restricted-use (or
509 banned) compounds fate properties are more likely to control observed pattern than current use
510 formulations, although historical product composition (e.g., prior to a restriction or ban) could still play
511 an important role.

512 Australia's catchment-specific pesticide patterns point to the utility of catchment-specific
513 management approaches for urban pesticide regulation. Importantly, management must be flexible, as
514 catchments (or user practices within catchments) can and do change. For instance, although pesticide
515 patterns were relatively stable during our study, some variability between years was detected at QLD2
516 (**Fig. 3, and S4a**), and future change is only to be expected as new pesticides are developed and old
517 ones fall out of favor. An additional challenge facing catchment-specific management is that pesticide
518 prevalence in individual catchments does not necessarily translate into obvious management
519 trajectories. For instance, many urban catchments contain both banned and permitted current use
520 pesticides (**Figs. 3, 6**); the latter being more mobile and biodegradable than their predecessors.
521 Managing both is likely to call for a diversity of treatment approaches, as well as collaboration amongst

management entities responsible for different water types (e.g., stormwater, receiving water, and groundwater) and state and local governments (which have their own mandates concerning pesticides and watershed protection; **Roy et al., 2008**). Forging collaborative relationships between these entities and translating them into management programs capable of delivering consistent quality stormwater for human and environmental use, is a necessary step towards our sustainable water future both in Australia, and abroad.

5. CONCLUSIONS

- Australian stormwater pesticide concentrations are low relative to U.S., Canadian, and European public health standards for potable water and aquatic life benchmarks. Ergo it is unlikely that the compounds evaluated here (primarily herbicides) pose an acute threat to downstream aquatic ecosystems or human health, if stormwater is harvested for potable substitution or potable reuse.
- While overall pesticide concentrations are low, certain compounds warrant further attention due to widespread detection and environmental persistence (e.g., diuron) or high variability (e.g., MCPA, which occasionally exceeds public health standards).
- A substantive fraction of pesticide variability (up to ~50% of overall pattern) occurs at small spatial scales (e.g., catchment rather than state), suggesting that catchment-specific management approaches must supplement state-wide programs.
- Pesticide use practices and product formulation warrant consideration alongside traditional chemical, meteorological and land-use-related drivers of variability. In our study both formulation and chemistry (e.g., mobility in the environment and persistence metrics) constituted viable explanations for pesticide occurrence patterns.

545

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569 **FIGURE CAPTIONS**

570 **Figure 1:** Map of Australia showing the location of stormwater sampling stations in Queensland (QLD;
571 red symbols), Victoria (VIC; blue symbols), New South Wales (NSW; cyan symbols) and Western
572 Australia (WA; white symbols).

573
574 **Figure 2:** Urban stormwater pesticide concentrations in Australia (box and whisker plots: box width is
575 scaled by pesticide detection frequency, asterisks represent outliers), and across Europe, the U.S., and
576 Canada (blue squares are median concentrations with 95% confidence bounds). Green dots show
577 Queensland public health standards for recycled water intended to augment the potable supply (QLD
578 PHS) for each pesticide, and red symbols show US-EPA aquatic life benchmarks for fish (dot), plants
579 (diamond), invertebrates (plus sign), and algae (triangle).

580
581 **Figure 3:** Heat map of Australian stormwater pesticide concentrations ($\log \mu\text{g/L}$) organized by state
582 (red lines), station (solid white lines), and year (dashed white lines). The x -axis is pesticide type and the
583 y -axis indicates sample location and year.

584
585 **Figure 4:** Biplots of Australian pesticide concentration in principal component (PC) space. Dominant
586 mode PC1 is on the x -axis, and secondary mode PC2 is on the y -axis. Data observations are shown in
587 panel **A**) and resampling-based statistical model results in panels **B-E**; **B**) resolves yearly variability, **C**)
588 resolves seasonal variability, **D**) resolves state-specific variability, and **E**) resolves station-specific
589 variability. Across all panels, pesticide loading vectors are shown in black, with vector significance ($p <$
590 0.05 level) shown using vector markers (dot: significant in both PC modes, vertical diamond:
591 significant in PC1 only, horizontal diamond: significant in PC2 only, horizontal and vertical diamonds:
592 not significant in either mode. Scores for individual pesticide samples are shown using colored symbols

(red = Queensland, blue = Victoria, cyan = New South Wales, white = Western Australia), with different symbol shapes corresponding to different sampling stations (see legend). Grey error bars represent 95% resampling-based confidence intervals about sample scores. Colored stars in panel A) identify the location of dominant pesticide groups in PC space: blue = the phenoxy and aromatic herbicides, red = the triazines, green = the substituted uracil bromacil, and cyan = the polyurea diuron.

Figure 5: Flow diagram of registered Australian product formulations containing one or more of the 13 pesticides included in our stormwater PCA. Circles represent individual pesticides, and circle size reflects the number of products containing only one of the 13 pesticides evaluated. Solid lines connect pesticides that co-occur in one or more products. The line weight (and boxed number) indicate the number of products shared. In instances where three or more pesticides co-occur, the shared product number is centered (see MCPA, dicamba and mecoprop). Degradation products such as desethyl atrazine (DEA), which are not purposefully added to registered formulations, are connected to parent pesticides by dotted lines. Phenoxy and aromatic herbicides, triazines, substituted uracils, and polyureas are shown in color (blue, red, green, and cyan, respectfully), consistent with the star color in **Fig. 4a**. Boxes of corresponding color delineate pesticides within a group that are connected by shared products. ^a: Note that while the insecticide propoxur has no single-compound products or shared products with herbicides, it is found in three products with other insecticides (e.g., flumethrin, tetramethrin, and piperonyl butoxide), not diagrammed here.

Figure 6: Cross plot of pesticide chemical characteristics related to environmental persistence (the field dissipation half life, x -axis) and mobility ($\log K_{oc}$, y -axis). Field dissipation half lifes are from **USDA, 2001** and **PPD, 2015**. $\log K_{oc}$ values are from **USDA, 2001**, **PPD, 2015**, and **PAN, 2015**. Pesticides belonging to the four dominant groups in PC space (**Fig. 4a**) are identified using the same color scheme

as **Fig. 4a** (see colored stars) and **Fig. 5**.

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