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Potentially Toxic Concentrations of Synthetic Pyrethroids Associated with Low Density Residential Land Use

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Trace organic compounds associated with human activity are now ubiquitous in the environment. As the population becomes more urbanized and the use of pesticides and person care products continues to increase, urban waterways are likely to receive higher loads of trace organic contaminants with unknown ecological consequences. To establish the extent of trace organic contamination in urban runoff, concentrations of emerging chemicals of concern were determined in sediments from 99 urban wetlands in and around Melbourne, Australia between February and April, 2015. As a preliminary estimation of potential risks to aquatic biota, we compared measured concentrations with thresholds for acute and chronic toxicity, and modeled toxic units as a function of demographic and land use trends. The synthetic pyrethroid insecticide bifenthrin was common and widespread, and frequently occurred at concentrations likely to cause toxicity to aquatic life. Personal care products DEET and triclosan were common and widely distributed, while the herbicides diuron and prometryn, and the fungicides pyrimethanil and trifloxystrobin occurred less frequently. Toxic unit modeling using random forests found complex and unexpected associations between urban land uses and trace organic concentrations. Synthetic pyrethroid insecticides were identified as emerging compounds of concern, particularly bifenthrin. In contrast with previous surveys, the highest bifenthrin concentrations were associated with lower housing and population density, implicating low-density residential land use in bifenthrin contamination. We discuss the implications for pesticide regulation and urban wetland management in a global context.

Keywords: synthetic pyrethroids, bifenthrin, population density, urbanization, trace organics

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INTRODUCTION

Synthetic organic compounds are ubiquitous in modern society. Biocides such as disinfectants and pesticides have revolutionized agriculture and sanitation; however, their persistence in the environment may be harmful to aquatic life. Emerging chemicals of concern include personal care products and pesticides which persist in the environment with the potential to cause significant toxicity to aquatic life. These chemicals of concern have been detected in rivers worldwide (Schäfer et al., 2011a; Nowell et al., 2013) and in Australia (Scott et al., 2014), but their occurrence and distribution in the urban environment remain poorly characterized.

Synthetic pyrethroid insecticides currently fulfill many of the residential needs previously met by organochlorines and organophosphates. Their efficacy, persistence, and perceived safety to users have made them popular with consumers worldwide. For example, many persistent insecticides sold for domestic use in Australia now contain synthetic pyrethroids (APVMA, 2016), and these products are popular with both residents and professional pest controllers. Urban use of pyrethroids has been linked with high concentrations in urban streams and wetlands (Amweg et al., 2006b; Nowell et al., 2013; Sun et al., 2015). Based on international surveys of urban streams, residues of synthetic pyrethroids are likely to enter Australian urban water bodies, yet most monitoring to date has measured only concentrations in water (Scott et al., 2014), where they rarely occur due to their extreme hydrophobicity. A recent survey of urban wetlands which sampled both matrices, found synthetic pyrethroids were rare in water, but occurred in sediments at potentially toxic concentrations (Allinson et al., 2015). As the urban population continues to grow there is an urgent need to understand the sources, transport and fate of these emerging chemicals of concern.

Personal care products such as triclosan are widely used in consumer cleaning and personal care products. Triclosan is a persistent anti-bacterial with the potential to accumulate in the aquatic environment (Halden and Paull, 2005). The long-term effects of this biocide are not yet well known, however, it has the potential to alter bacterial communities and contribute to the spread of resistant bacterial strains (Drury et al., 2013). Triclosan and related personal care products have been detected in urban waterways internationally (Halden and Paull, 2005; Chen et al., 2014), and are widespread in Australian rivers (Scott et al., 2014), yet primary sources and transport are poorly understood. Given the limited monitoring of sediment to date, there is a need to understand the spatial distribution of these contaminants in the urban environment.

The composition of urban runoff provides a snapshot of contaminants in the built environment, so improved understanding of the factors influencing contaminant loads has important implications for human exposure, chemical regulation, and urban planning. Constructed wetlands for stormwater treatment have become popular worldwide (Vyamzal, 2010), and are effective traps for nitrogen, phosphorus and hydrophobic pollutants (Malaviya and Singh, 2012). This makes them ideal for surveying the distribution of hydrophobic trace organics in the urban environment. Our study area was Melbourne, Australia, which has grown rapidly in both population and urban area over the last 30 years. During this time, approximately 600 wetlands have been constructed to treat urban runoff, providing an ideal opportunity to evaluate spatial trends and impacts of changing land use patterns on emerging chemicals of concern.

Our aims were:

1. to establish the extent of trace organic contamination of wetland sediment across a representative sample of urban wetlands;
2. to conduct a preliminary risk assessment of their ecological significance;
3. to evaluate the land use and demographic factors linked with their occurrence and distribution.

MATERIALS AND METHODS

Site Selection

A collection of 111 urban wetlands in the greater Melbourne metropolitan area (GMA) were selected to represent a broad range of urban land use. For the purpose of site selection, catchment geology was classed as either sedimentary or basalt based on the prevailing underlying substrate. Geology can influence the accumulation of heavy metals associated with urban development (Pettigrove and Hoffmann, 2003), and so could conceivably influence the accumulation of organic contaminants. Sites were selected to represent a range of land uses, geological substrates and recent growth in population across the metropolitan area. From the initial 111 sites, 12 were excluded due to unsafe access or difficulty in determining catchment boundaries. The location of the remaining 99 sites in relation to housing density is summarized in **Figure 1**, while geographic coordinates and detailed catchment characteristics are provided in Table S1.

Catchment Land Use

Individual wetland sub-catchments were first determined from their primary catchment 10 m flow-weighted digital elevation models (DEMs) in ArcGIS 10.3 using methods adapted from Kunapo et al. (2009). Using the spatial analyst extension, a DEM was derived using TOPOGRID from LiDAR 5 m contours, with flows conditioned to stream layers and wetlands. Sinks were removed and flow direction and accumulation layers were created using spatial analyst. Watersheds were calculated from flow and accumulation layers using the hydrology toolbar. Quality control checks were performed by comparing to streams, drains, and watersheds derived for sediment ponds managed by the regional water authority. Catchment boundaries were adjusted to conform to higher resolution watershed layers and align with subterranean stormwater drains where necessary. Catchment land use was determined from the mesh block counts from the 2011 Australian population census (ABS, 2011). The category "Transport" represented only major roads and motorways with a large proportion of this area dominated by the reserve surrounding the road. Because it did not include the minor roads which represented the vast majority of road surface in the dataset, "Transport" was not included in the analysis. The category "Water" was excluded, as it was present at very low frequency in the dataset, and in most cases represented only the sampled wetland. The categories "Hospital/Medical" and "Education" were pooled into the single category "Institutional." Catchment population and housing density were estimated by

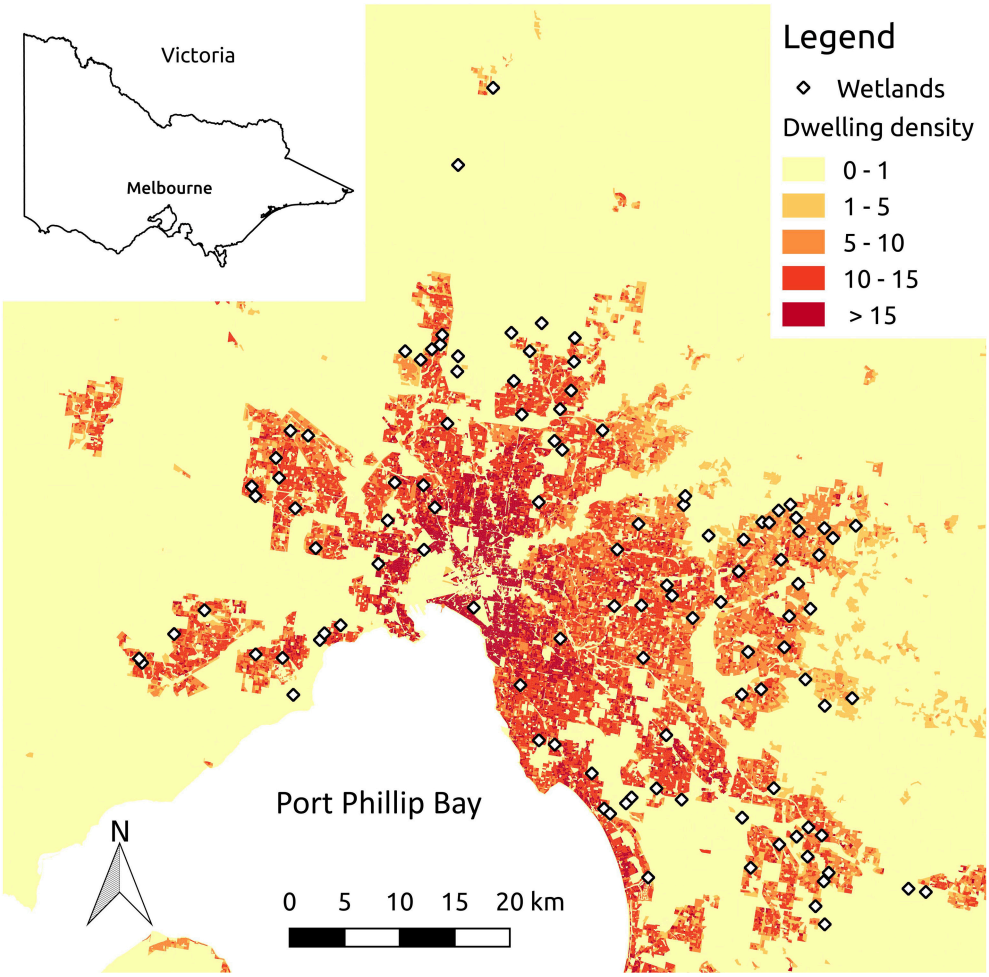

FIGURE 1 | Site locations in relation to the distribution of housing density across Melbourne. Housing density is measured as the number of dwellings per hectare derived from 2011 census (ABS, 2011).

calculating the population and housing density for census mesh block polygons, intersecting these with catchment polygons, and then recalculating the area of mesh blocks intersecting the catchment boundary. Assuming population and housing distribution was homogeneous within mesh blocks, densities were converted back to counts per mesh block, summed for each catchment, then divided by catchment area in hectares. This process was performed for both the 2006 and 2011 census data. Trends in land use, population and housing density were then estimated per catchment using the difference between the 2011 and 2006 census (ABS, 2006).

Sediment Collection and Chemical Analysis

Wetlands were visited between February and May 2015. At each wetland, a composite sample of surficial sediment (<5 cm) was collected with a shovel and sieved through 63 μm nylon mesh with ambient water. Nets and buckets were rinsed with extran between sites, and blank rinse samples tested for contamination.

Sieved samples were refrigerated, allowed to settle overnight in 10 L buckets, the overlying water decanted, and sediment stored in acid-washed oven-baked glass jars at 4°C until extraction and analysis. The concentration of 29 compounds (11 fungicides, 6 herbicides, 10 insecticides, and 2 personal care products) was determined by GC-MS. Program details are provided in Supplementary Information, and summarized in Tables S2, S3. Total organic carbon was determined by a wet oxidation method (Heanes, 1984).

Data Preparation

Quality control procedures included the analysis of laboratory blanks, spikes, and duplicates. Duplicate analyses were also performed on 5% of field sediments. Duplicates were averaged by site for data analysis. Where both duplicates were below the limit of reporting (LOR), the result was taken to be less than the LOR. Where one result was below and one equal to or above the LOR, the result was taken to be above the LOR. Where one result was TRACE and one result was less than the LOR, the result was taken to be detected, but with the concentration equal to the LOR × 0.75.

Data Analysis

Due to the high proportion of results below the LOR, descriptive statistics such as mean and median for trace organic compounds were summarized with an empirical cumulative distribution function (ECDF) for censored data using the Kaplan-Meier method (Lee, 2013). Contaminants not detected at any site were excluded from further analysis. To determine the environmental significance of the observed concentrations, we compared the concentration of each compound with a low and high environmental effect threshold as follows: Risk categories were "ND" for not detected, "low" where detected but below low/chronic guideline values, "moderate" between low/chronic and high/acute guidelines, and "high" above high/acute guidelines for benthic invertebrates. A concentration exceeding the high threshold indicates significant adverse effects are likely, while a concentration between the low and high thresholds indicates possible adverse effects (Simpson et al., 2013).

Category thresholds were based on local (ANZECC/ARMCANZ, 2000) and international (Nowell et al., 2014; Lewis et al., 2016) chronic and acute toxicity thresholds. Low thresholds were based on chronic effects such as observable effect concentration (NOEC), while high thresholds were based on acute effects such as median lethal concentrations (EC50). Category thresholds and sources are provided in Supplementary Material (Table S6).

Toxic units (TU) were calculated by dividing the measured compound concentration by the high threshold effect concentration, following the method of Nowell et al. (2014). All concentrations were normalized to 1% organic carbon to account for the effect of sediment carbon on bioavailability. Where no sediment high threshold effect concentration was available, a pore-water concentration was estimated using equilibrium partitioning (Di Toro et al., 1991) for comparison with a water high threshold effect concentration. This approach estimates the concentration present in pore water at equilibrium with sediment, based on the sediment organic carbon content and the carbon-water partitioning coefficient (KoC), and has been previously used to estimate toxic units of organic compounds (Di Toro et al., 1991; Schäfer et al., 2011b).

Modeling Framework

All modeling and statistical analysis was performed in R (version 3.3.0). We used random forests to model associations between organic contaminants as response variables, and catchment land use and demographic properties as predictor variables. These models are well suited to non-linear associations with a high degree of co-correlation between predictor variables (Breiman, 2001), are robust to data distribution and variance properties, and can incorporate both continuous and categorical variables. We tested the effect of variable transformation using log-transformed response variables, log-transformed population and dwelling densities and square-root arc-sin transformed land use proportions, but this had negligible impact on model performance (results not shown), therefore all variables were used untransformed to facilitate interpretation of results. Correlations between catchment demographic and land use variables were explored visually using scatterplot matrices and the significance of any correlations tested using the non-parametric Kendalls tau statistic (Sen, 1968). To explore the significance of changes in catchment demographics and land use, all compounds were summed as toxic units to yield a total toxic unit score (TU), and by class to yield a class-specific TU score for each of insecticides, herbicides, fungicides and personal care products. The model response variables were therefore: first, the TU sum per site; second, the TU summed for each class; and third, the TU contributed by each frequently detected organic compound. We then applied random forest models (Liaw and Wiener, 2002) to explore associations between TUs and spatial and temporal trends in catchment demographics and land use.

Spatial and Temporal Trends in Catchment Demographics and Land Use

To explore the significance of spatial trends in catchment demographics and land use, we used the 2011 matrix of catchment properties as predictor variables. A matrix of temporal change was produced by subtracting the 2006 matrix from the 2011 matrix. The resulting temporal change matrix summarized the proportion change in each land use and demographic variable, with each variable identified with the prefix "d_" for delta. To evaluate the significance of both spatial and temporal trends, each response variable was then modeled as a function of the full set of spatial and temporal demographic and land use properties. Model performance was evaluated using pseudo R-squared (pR-squared) as a measure of percent variance explained (Liaw and Wiener, 2002). For each model, variable importance was estimated by the percent increase in mean squared error (MSE) after variable removal. Relevant variables were identified by progressively removing variables and estimating the reduction in cross-validated model performance (Genuer et al., 2016). A final reduced model was then constructed with only relevant variables included. Model goodness of fit was evaluated by comparing relative MSEs between response variables of similar classes. The influence of each predictor variable on the response variable of interest was visualized using partial dependence plots to illustrate the marginal effect of each variable on the modeled response while holding all other predictor variables constant (Liaw and Wiener, 2002). To further explore the influence of land use on individual compounds we repeated this procedure for compounds present at 10 or more sites (bifenthrin, permethrin, prometryn, diuron, pyrimethanil, trifloxystrobin, diethyltoluamide (DEET), and triclosan).

RESULTS

Catchment Demographics and Land Use

The median catchment size was 126 hectares, and the mean 480 hectares, indicating the distribution of catchment sizes was heavily skewed. The majority of catchments (as defined by the inter-quartile range) were between 37 and 467 hectares in size. Catchment land use was dominated by residential, parkland, and commercial use, with smaller proportions of institutional and industrial use. Population densities ranged from 0 to 48 persons per hectare, with a mean of 16.7 and a median of 17.4. Dwelling densities ranged from 0 to 19.6 dwellings per hectare, with a mean of 5.5 and a median of 6.0.

Spatial trends in land use and demographics were correlated with residential land use. Population density (tau = 0.47, $p < 0.001$) and dwelling density (tau = 0.43, $p < 0.001$) were positively correlated, although this trend was non-linear and reversed as the proportion of residential area exceeded 0.80. Temporal change in land use between 2006 and 2011 ranged from −100 to 100%, although most catchments had relatively small changes in land use. Only five catchments had changes in residential land use (d_Residential) greater than 10%, all of which were on the rapidly growing urban fringe. Temporal changes in population density ranged from +18.4 to −2.1 persons per hectare. Changes in dwelling density ranged from +6.4 to −1.1 dwellings per hectare. The mean change in population density was +1.98 persons per hectare, while the mean change in dwelling density was +0.63 dwellings per hectare. The five catchments with the greatest increase in population density were again all located on the urban fringe, but were not necessarily those with the maximum increase in residential land use.

Correlations between temporal trends were weaker than those between spatial trends. The strongest correlations were between changes in residential and parkland area (tau = −0.52, $p < 0.001$) and between changes in institutional and commercial area (tau = −0.24, $p = 0.003$).

Trace Organics Occurrence and Distribution

Of the 29 organic compounds determined, 17 were detected at least once. The most common organic compound was the insecticide bifenthrin, which was detected in more than three quarters of wetlands. The insect repellant diethyltoluamide (DEET) was found at two thirds, while the herbicide diuron was detected at almost half the sites visited (**Table 1**). Other compounds commonly detected were the insecticide permethrin (21.6%), the fungicides pyrimethanil (16.5%) and trifloxystrobin (10.3%), the personal care product triclosan (31%) and the herbicide prometryn (17.5%) (**Table 1**). At least one compound was detected at 98 of the 99 sites surveyed. The only site where no compounds were detected was site 961 (Kirkham Dv Wetland, Greenvale), a mostly residential catchment near the northern urban boundary. Multiple compounds were present at the majority of sites: two or more compounds were detected at 79 sites (81%) and five or more compounds detected at 20 (21%) sites. The highest number of detections (8) occurred at sites 964 (Ringwood Lake), 971 (The Esplanade, Narre Warren South), and 992 (St Muirs Dr, Warrandyte), all predominantly residential catchments.

Insecticides were the most commonly detected class of trace organic compounds. At least one insecticide was detected at 78 sites, two at 23 sites, and three at 4 sites. The most common class of insecticide detected was the synthetic pyrethroids, with bifenthrin frequently occurring at concentrations likely to cause toxicity (**Table 1**). The high risk threshold (HT) for benthic invertebrates was exceeded by bifenthrin at 68 sites, and by permethrin at two sites (**Table 1**).

Personal care products were also common, with at least one PCP detected at 77 sites and at least two at 19 sites. DEET was the most common PCP, although it was never measured above the low risk threshold (LT) concentration. Triclosan was detected less frequently, but occurred at one third of sites and was always above the LT concentration. Herbicides were rare in comparison to insecticides. At least one herbicide was detected at 56 sites, at least two at 12 sites, and three at 2 sites. Prometryn exceeded the LT at 16 of the 17 sites where it was detected, but all other herbicides were below the LT. Fungicides were detected at 28 sites, but never exceeded the LT. Pyrimethanil (16 sites) and trifloxystrobin (10 sites) were the most commonly detected fungicides.

Toxic Unit Associations with Catchment Demographics and Land Use

The best fit achieved by any model was a pR-squared of 0.24 (**Table 2**). The model with the highest pR-squared was bifenthrin, although the model for insecticide TUs and total TUs had only marginally lower pR-squared. The final bifenthrin TU model had an pR-squared of 0.243 (**Table 2**) which can be interpreted as explaining 24% of the variance in this response variable, with the models for insecticide TUs and total TUs achieving only marginally lower pR-squared.

The final model for total TUs included only two predictor variables, population density, and dwelling density (**Figure 2**). No land use or temporal variables were selected in the final model, indicating total TUs were best predicted by the spatial demographic variables housing and population density, and that no additional predictive power resulted from the addition of further variables. The modeled partial dependence of TUs on spatial trends in catchment population and dwelling density show an initial increase followed by a steep decline as dwelling density increased (**Figure 4**). The same trend was evident for population density, although the magnitude of both the initial increase and the subsequent decline was smaller. The final model for insecticide TUs was almost identical to the total TUs in both predictive performance, selected variables (**Table 2**), and partial dependence profiles (**Figure 4**), indicating the total TU model was dominated by the insecticide component.

The final model for personal care products TUs (PCP TU) was very weak, with pR-squared of 0.029 (**Table 2**). The most important variable selected in the final model was change in institutional area, with population density and change in residential area contributing to a smaller extent (**Figure 2**). The modeled PCP TU partial dependence showed a sharp decrease with any increase in catchment institutional area. Increases in residential area were also linked with increased PCP TUs, although this was the least important of the three variables included in the final model (**Figure 2**). A small increase in PCP TUs was also associated with population densities between 5 and 25 persons/hectare (**Figure 4**).

TABLE 1 | Occurrence of pesticides in wetland sediments.

Class	Compound	>LOR	>LT	>HT	Min (ug/kg)	Max (ug/kg)	Mean (ug/kg)	Median (ug/kg)
I	Bifenthrin*	77	9	68	<2	330	36.4	22.3
I	Permethrin*	21	12	2	<3	930.5	26.1	–
PCP	Triclosan*	31	31	0	<10	320	24.3	–
H	Prometryn	17	16	0	<2	34.7	15.4	–
I	Fenamiphos	4	2	0	<10	69.6	12.4	–
I	Carbaryl	1	1	0	<5	276	–	–
I	Dimethoate	1	1	0	<25	69.1	–	–
H	Diuron*	47	0	0	<2.5	5316	84.6	7
H	Metolachlor	3	0	0	<2	51.9	22.6	–
H	Simazine	3	0	0	<5	16	14	–
F	Trifloxystrobin	10	0	0	<2	68	10.8	–
PCP	DEET*	65	0	0	<2	42	7.9	6.4
F	Pyrimethanil*	16	0	0	<1	7.6	2.3	–
F	Boscalid	1	0	0	<2	13.6	–	–
I	Chlorpyrifos	1	0	0	<10	25.2	–	–
F	Iprodione	1	0	0	<20	84.5	–	–
F	Myclobutanil	1	0	0	<10	15.2	–	–
H	Atrazine	0	0	0	<5	<40	–	–
F	Azoxystrobin	0	0	0	<30	<150	–	–
I	Cypermethrin	0	0	0	<10	<400	–	–
F	Difenoconazole	0	0	0	<50	<150	–	–
F	Dimethomorph	0	0	0	<15	<150	–	–
I	Fipronil	0	0	0	<5	<30	–	–
I	Indoxacarb	0	0	0	<10	<125	–	–
H	Linuron	0	0	0	<20	<100	–	–
I	Malathion	0	0	0	<5	<20	–	–
F	Metalaxyl	0	0	0	<5	<20	–	–
F	Prochloraz	0	0	0	<50	<400	–	–
F	Pyraclostrobin	0	0	0	<10	<80	–	–

*Compounds are sorted in descending order by the count exceeding first the high threshold (HT), then the low threshold (LT), and finally the limit of reporting (LOR). *Random forest models were developed for compound classes and for selected compounds where the frequency of detection exceeded 20%.*

The models with herbicide TUs and fungicide TUs as the response variables were the weakest, with pR-squared of 0.018 and −0.009 respectively (**Table 2**). The final model for herbicide TUs included the spatial demographic variables population and dwelling density as well as residential land use. Also included were the temporal variables summarizing changes in population, dwelling density and institutional land use (**Figure 2**). The final model for fungicide TUs included only the spatial variables residential land use, population and dwelling density. Due to the low pR-squared of these two models, no partial dependence plots were produced.

Compound Associations with Catchment Demographics and Land Use

The model for bifenthrin TUs had the highest predictive power of any individual compound, and the highest pR-squared of any model (**Table 2**). The only important variables selected for the final model were dwelling and population density (**Figure 3**), the same variables as for insecticide TU and total TU models (**Figure 2**). As dwelling and population density increased, the modeled partial dependence profile of bifenthrin TUs was an initial rise followed by a steep decline (**Figure 5**), very similar to the insecticide TU and total TU response profile (**Figure 4**).

The model for pyrimethanil TUs was stronger than combined fungicide TUs with a pR-squared value of 0.123 (**Table 2**). However, the final model retained more variables than other models (**Figure 3**). The final pyrimethanil TU model retained seven variables, with changes in dwelling and population density the most important predictors. All other predictive variables had change in MSEs under 50% (**Figure 3**). The partial dependence profile of pyrimethanil TUs on changes in dwelling density first decreased slightly then increased steeply with change above +4 dwellings per hectare (**Figure 6**). A similar trend was apparent with change in population density above +12 persons per hectare, although the initial decrease was more pronounced (**Figure 6**). Although the pR-squared for the final pyrimethanil TU model was higher than triclosan TU or DEET TU models, the range of the modeled response was much smaller in magnitude (**Figure 6**).

TABLE 2 | Model performance summary by class and compound.

Response variable	MSE	pR-squared
TU total	5.983E+00	0.239
Insecticide TUs	6.004E+00	0.235
Herbicide TUs	2.213E−05	0.018
Fungicide TUs	1.086E−04	−0.009
PCP TUs	6.328E−10	0.029
Permethrin TUs	2.420E−02	−0.029
Bifenthrin TUs	5.916E+00	0.241
Prometryn TUs	2.221E−05	0.014
Diuron TUs	1.576E−11	−0.089
Pyrimethanil TUs	1.016E−13	0.123
Trifloxystrobin TUs	5.054E−11	−0.057
Triclosan TUs	1.400E−11	0.031
DEET TUs	6.070E−10	0.038

Model performance by class indicates the strength of associations with major contaminant classes, while performance by compound indicates the strength of associations with individual contaminants.

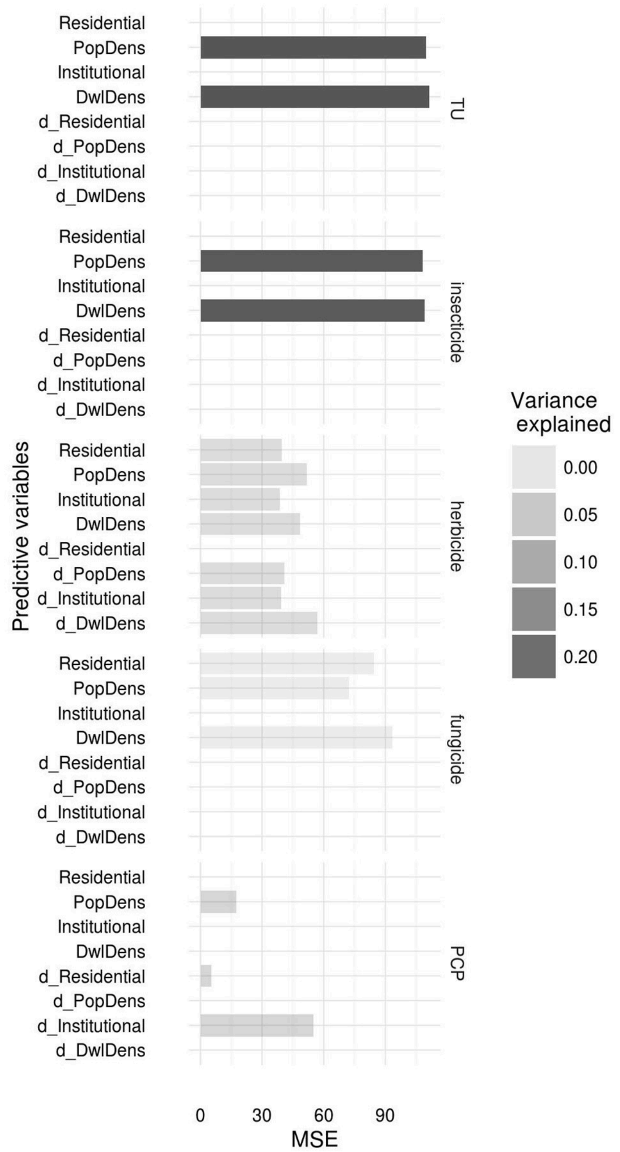

FIGURE 2 | Summary of selected predictor variables for contaminant classes and comparison of their relative influence in each model. The relative influence of each land use category is indicated on the x-axis, scaled to a percentage of the total for each model. Where a land use variable does not appear in a model, this indicates it did not contribute significantly to that model. Bars are shaded in proportion to relative goodness of fit for each model.

Final models for DEET TUs and triclosan TUs were only marginally predictive, with pR-squared values of 0.031 and 0.038 (**Table 2**) respectively, and included more variables than other models (**Figure 3**). Compared with just two variables in the final bifenthrin TU model, the final triclosan TU model retained nine variables (**Figure 2**). Of the selected variables, temporal change in population density (42% MSE) and industrial area (40% MSE) were the most important, followed by spatial trends in industrial (38% MSE) and agricultural area (37% MSE). The final model for DEET TUs included five variables, with temporal change in institutional area the most important (**Figure 3**). All other predictive variables had importance measures below 30% MSE. Although the pR-squared for the final DEET TU model was low, the modeled response spanned a greater magnitude than the final pyrimethanil model (**Figure 6**).

Final models for prometryn, diuron, permethrin and trifloxystrobin TUs had pR-squared values below 0.03. Due to the low pR-squared of these two models, no variable importance measures were estimated and no partial dependence plots were produced.

DISCUSSION

To establish the extent of trace organic contamination in urban runoff, we measured the concentrations of an indicative suite of trace organics in urban wetlands across Melbourne, Australia. We found insecticides and personal care products were common and widespread in urban wetland sediment. Preliminary ecological risk assessment found synthetic pyrethroid insecticides frequently occurred at concentrations exceeding ecological effect thresholds. Modeling suggested most common contaminants were linked with spatial trends in population and housing density, and to a lesser degree with temporal changes in land use and demographics. Bifenthrin frequently occurred at concentrations likely to present a high risk to the aquatic environment, and was associated with lower population and housing densities.

Catchment Demographics and Land Use

Wetland catchments were dominated by residential land use. This was expected as the focus of this survey was wetlands constructed for urban stormwater management, which are usually designed for catchments with predominately residential land use. Population densities were typical of suburban residential development internationally (Tu et al., 2007). The

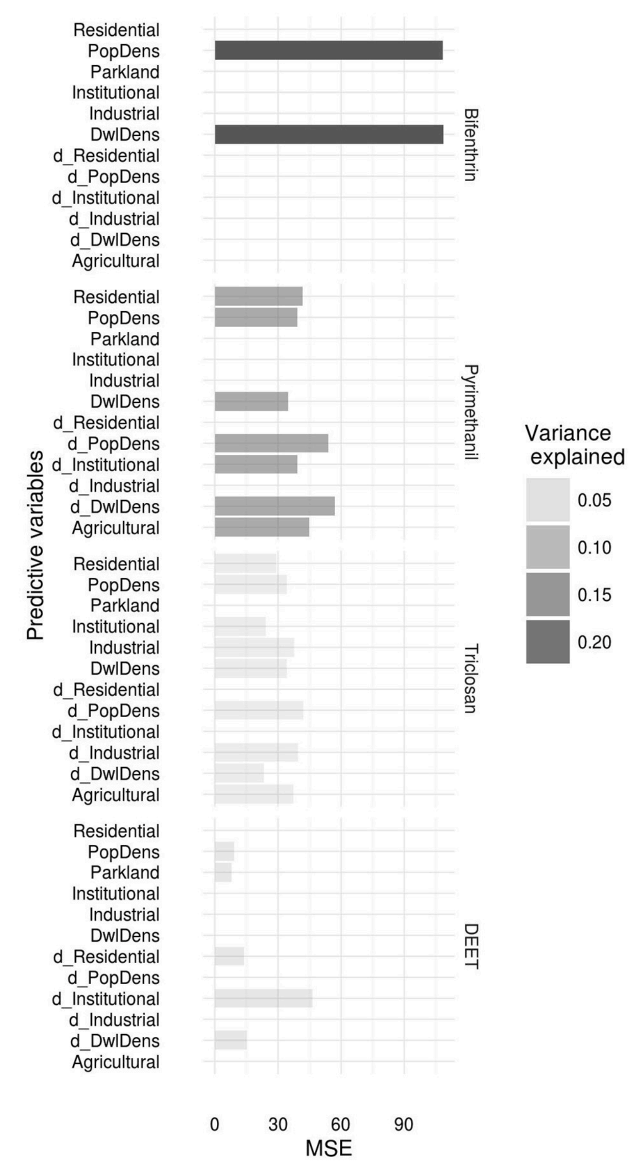

FIGURE 3 | Summary of selected predictor variables for frequently detected contaminants and comparison of their relative influence in each model. The relative influence of each land use category is indicated on the x-axis, scaled to a percentage of the total for each model. Where a land use variable does not appear in a model, this indicates it did not contribute significantly to that model. Bars are shaded in proportion to relative goodness of fit for each model.

positive but non-linear correlations between residential land use and population density reflect the fact that Melbourne is relatively low-density city with a wide urban sprawl (ABS, 2011), hence the highest population densities occur in commercial areas even though the majority of the population lives in low density suburbs. The negative correlation between temporal changes in land use observed in this study suggest recent growth in residential land has been primarily at the expense of parkland, while to a lesser extent there has been a transition from institutional to commercial land use. The weak correlation between temporal increases in residential land use and population density may reflect the delay between the time land is rezoned for residential use and the completion of housing construction. This may be one of the reasons demographic variables were effective predictors of contaminant trends, with all final models in this survey including either population or housing density as predictor variables. This effect has been previously observed when demographic variables were included as potential predictors of sediment (Horowitz and Stephens, 2008) or water pollution (Tu et al., 2007), suggesting they should be considered more widely as indicators.

Trace Organic Occurrence, Distribution, and Ecological Risk

At least one trace organic compound was detected in the sediment of almost every wetland surveyed. Most wetlands had multiple compounds detected, and bifenthrin was found at three quarters of wetlands, a substantial increase compared with a similar smaller survey conducted 5 years previously (Allinson et al., 2015). This suggests concentrations of trace organics—particularly insecticides—in urban runoff are increasing. Previous surveys of trace organics in urban areas in Australia (Birch et al., 2004) and worldwide (Dai et al., 2011) have often focused on legacy organochlorine compounds, with current use pesticides relatively under-represented. When current use pesticides have been included, they are often present at higher concentrations in urban than agricultural waterways (Amweg et al., 2005, 2006b; Hintzen et al., 2009). Although the present study was not designed to compare urban with agricultural catchments, the observed concentrations of synthetic pyrethroids—particularly bifenthrin—were comparable to urban areas of similar population density in the United States (Amweg et al., 2005, 2006a; Hintzen et al., 2009) and China (Sun et al., 2015).

Exploratory data analysis found insecticides dominated the summed TU, suggesting this class of trace organics presented the highest risk to aquatic life. Bifenthrin frequently exceeded ecological thresholds, echoing international trends in synthetic pyrethroids in urban areas (Amweg et al., 2005, 2006b; Hintzen et al., 2009). In contrast with recent surveys from China (Sun et al., 2015; Wang et al., 2016) and the US (Nowell et al., 2013), bifenthrin was not associated with increasing urbanization. With a spatial increase in housing density, bifenthrin first increased but then declined rapidly (**Figure 5**). The decline in bifenthrin with increased housing density was unexpected. Termite protection products have previously been implicated in bifenthrin contamination of urban waterways (Nowell et al., 2013). If termite-protection products were a major source of bifenthrin contamination, temporal changes in population, housing and residential area reflecting construction activity should have been important variables in the final bifenthrin TU model. In contrast, high bifenthrin TUs were associated with low-density urban housing and population, regardless of recent development. This concurs with a previous wetland survey which found bifenthrin concentrations were not related to catchment age (Allinson et al., 2015),

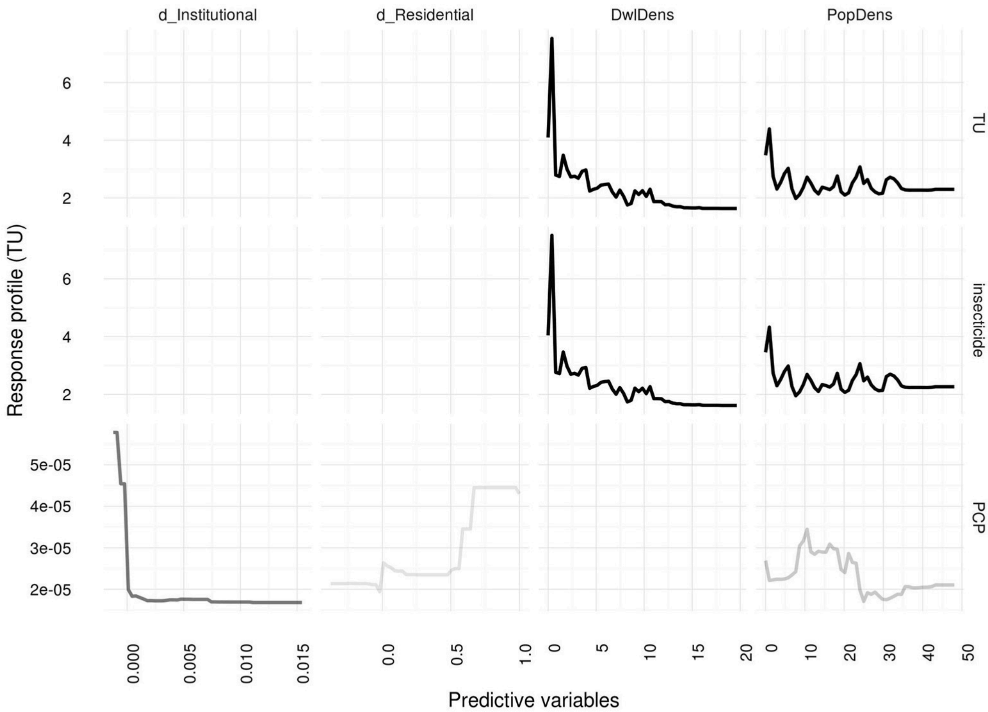

FIGURE 4 | Modeled partial dependence of all organic contaminants (TU total) insecticide and personal care products (PCP) in toxic units on important predictor variables. Marginal response is shaded in proportion to the change in MSE in the relevant model, hence darker shading indicates more important variables.

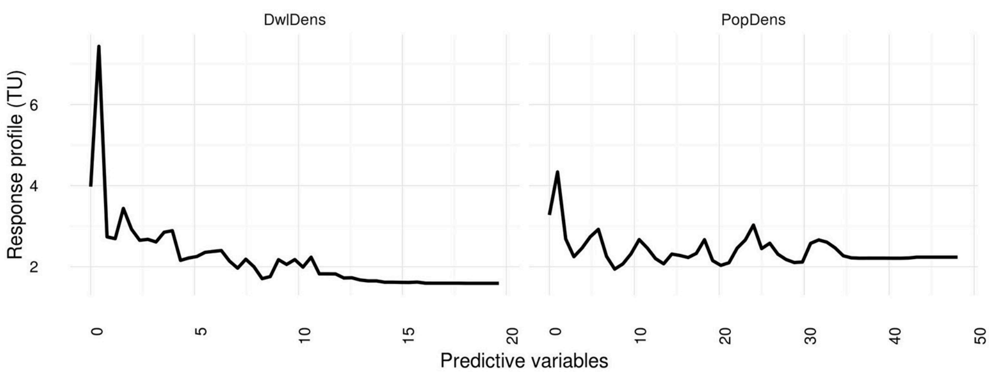

FIGURE 5 | Modeled partial dependence of bifenthrin toxic units (TU) on selected predictor variables. Marginal response is shaded in proportion to the change in MSE in the final bifenthrin model, hence darker shading indicates more important variables.

although this may also be due to the relatively short time period over which temporal change was measured in this study.

Bifenthrin pollution may be linked to the application of insecticides to impervious areas outdoors For example, bifenthrin is common in persistent insecticides registered for sale in the state of Victoria (APVMA, 2016). Bifenthrin is currently an active constituent of 256 products, the majority of which (174) are liquid formulations (APVMA, 2016). It is readily washed off impervious surfaces such as concrete (Jiang et al., 2010). Application of synthetic pyrethroids to impervious surfaces has been recognized as a key contributor to offsite transport in California (Davidson et al., 2014), and the present survey covers catchments with similar urban population and climate. The current study cannot definitively discriminate between these and other potential sources of bifenthrin to the urban aquatic environment. Identifying these sources is a high priority for further research.

To our knowledge, this is the first survey to highlight the specific association of low-density suburban housing on insecticide pollution of urban runoff. Demographic variables such population and housing density have usually been positively

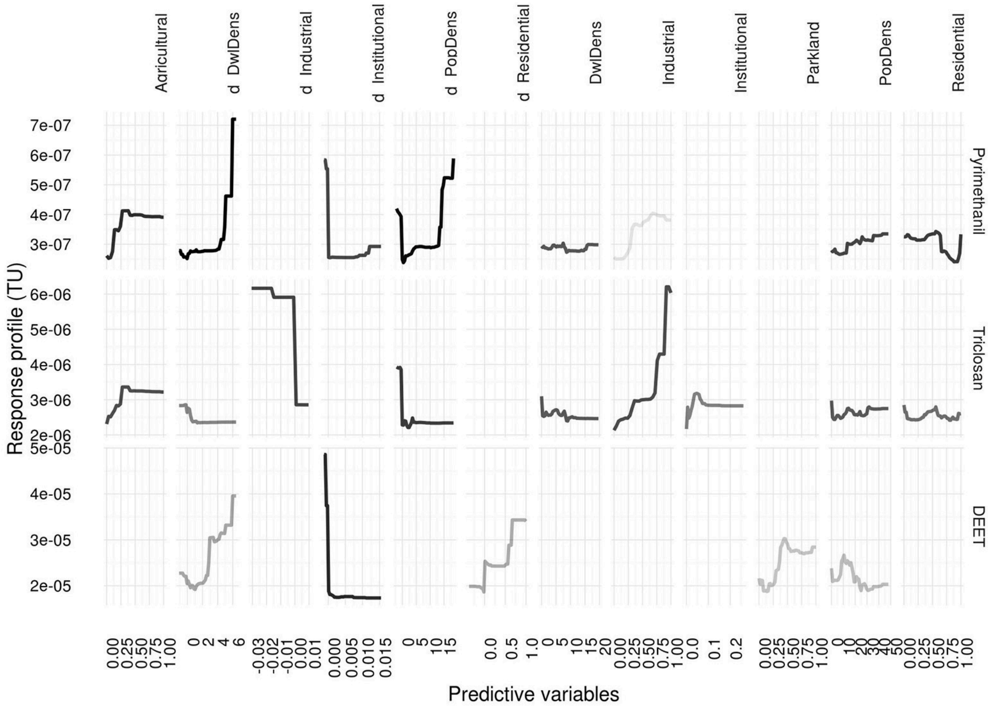

FIGURE 6 | Modeled partial dependence of pyrimethanil, triclosan, and DEET in toxic units (TU) on important predictor variables. Marginal response is shaded in proportion to the change in MSE in the final model, hence darker shading indicates more important variables. Note different response scales apply to each model.

associated with trace organics in urban runoff (Barber et al., 2006; Chen et al., 2014). Population density has previously been a more effective predictor of sediment chemistry than urban land use (Tu et al., 2007; Horowitz and Stephens, 2008), and the present study supports this. Attempts to link pesticide contamination with specific activities in urban landscapes have often been inconclusive. Despite hypothesizing that more expensive properties would use more lawn-care chemicals, Overmyer et al. (2005) found no correlation between property prices and pesticides in suburban Peachtree, Georgia. Similar surveys have often attempted to associate catchment variables with contaminants using rank correlations (Horowitz and Stephens, 2008; Nowell et al., 2013), which are best suited for detecting monotonic trends. The more complex trends observed in this study may be in part due to the larger sample size in this survey and more sensitive modeling approach.

Personal care products were frequently detected in urban wetlands, but presented less risk than insecticides to benthic invertebrates based on their summed TUs. The insect repellent DEET was the most commonly detected PCP in this survey, and is also common in urban waterways in the USA (Sandstrom et al., 2005), Europe (Quednow and Püttmann, 2009), and China (Liu et al., 2015). It is generally found in higher concentrations in urban than agricultural waterways (Sandstrom et al., 2005), suggesting personal use is a major contributing factor. The decline in DEET with temporal change in institutional area suggests a possible link with improved connection to the reticulated sewage system. Catchment urbanization may lead to reductions in wastewater input to local groundwater as sewage connections become available to properties which had previously used septic tanks. If domestic wastewater is an important source of PCPs, increased urbanization should be associated with reduced sources of PCPs to urban runoff as observed in this study. However, these associations were weak and further work is required to understand sources of PCPs to the urban environment.

Triclosan has been identified as an emerging chemical of concern due to its persistence and potential toxicity (Halden and Paull, 2005), and can serve as a useful surrogate for household waste water in urban areas (Chen et al., 2014). The mean concentration of triclosan observed in this survey was comparable to urbanized reaches of the Dongjiang (Chen et al., 2014) and Zhujiang Rivers (Zhao et al., 2010). Triclosan is widespread in the surface waters of the USA, associated with urban areas and waste-water treatment plants (Halden and Paull, 2005). Triclosan has been previously reported in Australian rivers, but generally downstream of waste-water treatment plants (Scott et al., 2014) and no link with urban land use was detected. Melbourne has separate sewer and stormwater systems, so the widespread occurrence of triclosan in wetlands with no connection to household wastewater was suprising. Triclosan in this context may represent a marker for contamination by sewage caused by illegal cross-connections or infiltration by contaminated groundwater. Triclosan associations with land use were complex. Although there was a trend for triclosan to increase with industrial catchment and decrease with changes in industrial catchment and population density, all associations with land use were relatively weak. This suggests that although on-site wastewater disposal may be a factor in triclosan contamination, to a large degree it is ubiquitous in the urban environment. More research is needed to understand the sources of personal care products to urban runoff.

Pyrimethanil was the most common fungicide detected. It was weakly associated with temporal increases in housing and population density, suggesting a link with newly developed urban area. At the time of writing there were 26 products containing pyrimethanil registered for use in Victoria (APVMA, 2016), the majority of which are for the control of gray mold (*Botrytis cinerea*). Viticulture is common on the urban fringe of Melbourne, and pyrimethanil has been detected in streams draining the wine-producing areas of the Yarra Valley (Schäfer et al., 2011b), so one possible source of pyrimethanil is airborne transport from neighboring agricultural regions (Hart et al., 2012), although further research would be needed to confirm this.

Diuron and prometryn were the most common herbicides detected in this survey. Although common, neither herbicide was associated with any temporal or spatial trends in catchment land use or demographics. Herbicides are common in urban runoff in the USA (Phillips and Bode, 2004) and Europe (Becouze-Lareure et al., 2016), and are probably under-represented in the present study due in part to the use of GC-MS as the sole analytical method in addition to higher solubilities and affinity for transport in surface-water. Future surveys should include a screen for small polar organics (Allinson et al., 2015) to provide better coverage of herbicides and fungicides.

Implications for Regulation

The weak regulation of insecticides globally has been identified as potentially inadequate to protect aquatic ecosystems (Stehle and Schulz, 2015). The frequent detection of insecticides in the present survey suggests Australia may be no exception. Pesticide regulation in Australia is complex, with roles and responsibilities shared between State and Federal government bodies. The registration of pesticides is controlled nationally by the Australian Pesticide and Veterinary Medicines Authority (APVMA), but the control and monitoring of pesticide use is the responsibility of different State and Territory government departments, depending on the intended purpose. For example, in the state of Victoria, responsibility is split between the Department of Environment, Land, Water, and Planning (DELWP) for pesticides intended for use in agriculture or for commercial weed control, and the Department of Health and Human Services for pesticides intended for commercial control of all other pests. Under the Public Health and Wellbeing Act 2008, all pest control operators must be licensed, although broad exemptions apply to pesticides used for: horticulture, agriculture, water treatment, weed control, and non-commercial use. Therefore, farmers and commercial pest control operators must keep records of application for possible compliance checks, but domestic use (i.e., not for commercial gain) is exempt. Even where application records are kept, there is no requirement to submit these records to a central database (Radcliffe, 2002). The lack of a central repository of pesticide application records is a serious impediment to the adaptive management of pesticide regulation. It is difficult to identify which aspects of the current complex regulation and licensing framework may be in need of reform without reliable temporal and spatial data on the amounts of pesticide applied.

The present survey is not the first to note the absence of a centralized pesticide reporting system in Australia (Radcliffe, 2002; Wightwick and Allinson, 2007). Similar systems have been operating successfully elsewhere for decades. For example, the State of California has required commercial pest controllers to submit application records to a central publically accessible database (CalPIP, 2016). Central reporting enables more accurate monitoring of changing trends in pesticide use (Amweg et al., 2005) and greater consideration of fate and transport. The contribution of specific activities to contamination can be isolated (Weston et al., 2008; Weston and Lydy, 2010), and the impact of improved regulation on pollution pathways can be more easily measured (Davidson et al., 2014). The adaptive management of pesticide regulation requires accurate and current data on application location and quantity, and a centralized reporting database should be considered an integral component of the regulation infrastructure in any jurisdiction. Further research is urgently required into the sources of bifenthrin entering urban runoff, both in Australia and globally. Centralized pesticide reporting databases would greatly facilitate this research.

CONCLUSIONS

Trace organic compounds are common in urban stormwater wetlands. A screening assessment suggests bifenthrin presents the greatest ecological risk, although pyrimethanil, diuron and the personal care products DEET and triclosan were also common. Associations between land use and demographics indicated bifenthrin was specifically associated with urban catchments of low housing and population density. Personal care products were weakly associated with industrial development, while pyrimethanil was weakly linked with new residential development. Further work is urgently required to understand sources of bifenthrin in urban runoff. To facilitate future research on pesticides in the environment, standardized central reporting of pesticide applications by commercial operators is recommended.

AUTHOR CONTRIBUTIONS

SM conducted the modeling and led the manuscript preparation, DS and KJ contributed to manuscript preparation, SS conducted the catchment spatial analysis and reviewed the manuscript, GR conducted chemical analysis, VP secured funding, designed the survey, and contributed to manuscript preparation.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: http://journal.frontiersin.org/article/10.3389/fenvs.2016.00075/full#supplementary-material

REFERENCES

ABS (2006). *Australian Bureau of Statistics - Census of Population and Housing: Mesh Blocks Digital Boundaries, Australia - 1209.0.55.002*. Available online at: http://www.abs.gov.au/AUSSTATS/abs@.nsf/DetailsPage/1209.0.55.0022006?OpenDocument [Accessed July 26, 2016].

ABS (2011). *Australian Bureau of Statistics - Census of Population and Housing: Mesh Block Counts*. 2074.0. Available online at: http://www.abs.gov.au/AUSSTATS/abs@.nsf/DetailsPage/2074.02011?OpenDocument [Accessed July 26, 2016].

Allinson, G., Zhang, P., Bui, A., Allinson, M., Rose, G., Marshall, S., et al. (2015). Pesticide and trace metal occurrence and aquatic benchmark exceedances in surface waters and sediments of urban wetlands and retention ponds in Melbourne, Australia. *Environ. Sci. Pollut. Res.* 22, 10214–10226. doi: 10.1007/s11356-015-4206-3

Amweg, E. L., Weston, D. P., Johnson, C. S., You, J., and Lydy, M. J. (2006a). Effect of piperonyl butoxide on permethrin toxicity in the amphipod Hyalella azteca. *Environ. Toxicol. Chem.* 25, 1817–1825. doi: 10.1897/05-440R.1

Amweg, E. L., Weston, D. P., and Ureda, N. M. (2005). Use and toxicity of pyrethroid pesticides in the Central Valley, California, USA. *Environ. Toxicol. Chem.* 24, 966–972. doi: 10.1897/04-146R1.1

Amweg, E. L., Weston, D. P., You, J., and Lydy, M. J. (2006b). Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. *Environ. Sci. Technol.* 40, 1700–1706. doi: 10.1021/es051407c

ANZECC/ARMCANZ (2000). *Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000*. Canberra: Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand.

APVMA (2016). Available online at: https://portal.apvma.gov.au/pubcris [Accessed August 21, 2015].

Barber, L. B., Murphy, S. F., Verplanck, P. L., Sandstrom, M. W., Taylor, H. E., Furlong, E. T., et al. (2006). Chemical loading into surface water along a hydrological, biogeochemical, and land use gradient: a holistic watershed approach. *Environ. Sci. Technol.* 40, 475–486. doi: 10.1021/es051270q

Becouze-Lareure, C., Dembélé, A., Coquery, M., Cren-Olivé, C., Barillon, B., and Bertrand-Krajewski, J.-L. (2016). Source characterisation and loads of metals and pesticides in urban wet weather discharges. *Urban Water J.* 13, 600–617. doi: 10.1080/1573062X.2015.1011670

Birch, G. F., Matthai, C., Fazeli, M. S., and Suh, J. (2004). Efficiency of a constructed wetland in removing contaminants from stormwater. *Wetlands* 24, 459–466. doi: 10.1672/0277-5212(2004)024[0459:EOACWI]2.0.CO;2

Breiman, L. (2001). Random forests. *Mach. Learn.* 45, 5–32. doi: 10.1023/A:1010933404324

CalPIP (2016). *California Pesticide Information Portal*. Available online at: http://calpip.cdpr.ca.gov/main.cfm [Accessed March 9, 2016].

Chen, Z.-F., Ying, G.-G., Liu, Y.-S., Zhang, Q.-Q., Zhao, J.-L., Liu, S.-S., et al. (2014). Triclosan as a surrogate for household biocides: an investigation into biocides in aquatic environments of a highly urbanized region. *Water Res.* 58, 269–279. doi: 10.1016/j.watres.2014.03.072

Dai, G., Liu, X., Liang, G., Han, X., Shi, L., Cheng, D., et al. (2011). Distribution of organochlorine pesticides (OCPs) and poly chlorinated biphenyls (PCBs) in surface water and sediments from Baiyangdian Lake in North China. *J. Environ. Sci.* 23, 1640–1649. doi: 10.1016/S1001-0742(10)60633-X

Davidson, P. C., Jones, R. L., Harbourt, C. M., Hendley, P., Goodwin, G. E., and Sliz, B. A. (2014). Major transport mechanisms of pyrethroids in residential settings and effects of mitigation measures. *Environ. Toxicol. Chem.* 33, 52–60. doi: 10.1002/etc.2411

Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Cowan, C. E., et al. (1991). Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* 10, 1541–1583. doi: 10.1002/etc.5620101203

Drury, B., Scott, J., Rosi-Marshall, E. J., and Kelly, J. J. (2013). Triclosan exposure increases triclosan resistance and influences taxonomic composition of benthic bacterial communities. *Environ. Sci. Technol.* 47, 8923–8930. doi: 10.1021/es401919k

Genuer, R., Poggi, J.-M., and Tuleau-Malot, C. (2016). *VSURF: Variable Selection Using Random Forests*. Available online at: https://CRAN.R-project.org/package=VSURF

Halden, R. U., and Paull, D. H. (2005). Co-Occurrence of Triclocarban and Triclosan in U.S. Water Resources. *Environ. Sci. Technol.* 39, 1420–1426. doi: 10.1021/es049071e

Hart, E., Coscollà, C., Pastor, A., and Yusà, V. (2012). GC-MS characterization of contemporary pesticides in PM10 of Valencia Region, Spain. *Atmos. Environ.* 62, 118–129. doi: 10.1016/j.atmosenv.2012.08.006

Heanes, D. L. (1984). Determination of total organic C in soils by an improved chromic acid digestion and spectrophotometric procedure. *Commun. Soil Sci. Plant Anal.* 15, 1191–1213. doi: 10.1080/00103628409367551

Hintzen, E. P., Lydy, M. J., and Belden, J. B. (2009). Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas. *Environ. Pollut.* 157, 110–116. doi: 10.1016/j.envpol.2008.07.023

Horowitz, A. J., and Stephens, V. C. (2008). The effects of land use on fluvial sediment chemistry for the conterminous US - results from the first cycle of the NAWQA Program: trace and major elements, phosphorus, carbon, and sulfur. *Sci. Total Environ.* 400, 290–314. doi: 10.1016/j.scitotenv.2008.04.027

Jiang, W., Lin, K., Haver, D., Qin, S., Ayre, G., Spurlock, F., et al. (2010). Wash-off potential of urban use insecticides on concrete surfaces. *Environ. Toxicol. Chem.* 29, 1203–1208. doi: 10.1002/etc.184

Kunapo, J., Chandra, S., and Peterson, J. (2009). Drainage network modelling for water-sensitive urban design. *Trans. GIS* 13, 167–178. doi: 10.1111/j.1467-9671.2009.01146.x

Lee, L. (2013). *NADA: Nondetects And Data Analysis for Environmental Data*. Available online at: http://CRAN.R-project.org/package=NADA

Lewis, K. A., Tzilivakis, J., Warner, D. J., and Green, A. (2016). An international database for pesticide risk assessments and management. *Hum. Ecol. Risk Assess.* 22, 1050–1064. doi: 10.1080/10807039.2015.1133242

Liaw, A., and Wiener, M. (2002). Classification and regression by randomForest. *R News* 2, 18–22.

Liu, W. R., Zhao, J. L., Liu, Y. S., Chen, Z. F., Yang, Y. Y., Zhang, Q. Q., et al. (2015). Biocides in the Yangtze River of China: spatiotemporal distribution, mass load and risk assessment. *Environ. Pollut.* 200, 53–63. doi: 10.1016/j.envpol.2015.02.013

Malaviya, P., and Singh, A. (2012). Constructed Wetlands for management of urban stormwater runoff. *Crit. Rev. Environ. Sci. Technol.* 42, 2153. doi: 10.1080/10643389.2011.574107

Nowell, L. H., Moran, P. W., Gilliom, R. J., Calhoun, D. L., Ingersoll, C. G., Kemble, N. E., et al. (2013). Contaminants in stream sediments from seven United States metropolitan areas: part I: distribution in relation to urbanization. *Arch. Environ. Contam. Toxicol.* 64, 32–51. doi: 10.1007/s00244-012-9813-0

Nowell, L. H., Norman, J. E., Moran, P. W., Martin, J. D., and Stone, W. W. (2014). Pesticide Toxicity Index—a tool for assessing potential toxicity of pesticide mixtures to freshwater aquatic organisms. *Sci. Total Environ.* 476–477, 144–157. doi: 10.1016/j.scitotenv.2013.12.088

Overmyer, J. P., Noblet, R., and Armbrust, K. L. (2005). Impacts of lawn-care pesticides on aquatic ecosystems in relation to property value. *Environ. Pollut.* 137, 263–272. doi: 10.1016/j.envpol.2005.02.006

Pettigrove, V., and Hoffmann, A. (2003). Impact of urbanisation on heavy metal contamination in urban stream sediments: influence of catchment geology. *Aust. J. Ecotoxicol.* 9, 119–218.

Phillips, P. J., and Bode, R. W. (2004). Pesticides in surface water runoff in south-eastern New York State, USA: seasonal and stormflow effects on concentrations. *Pest Manag. Sci.* 60, 531–543. doi: 10.1002/ps.879

Quednow, K., and Püttmann, W. (2009). Temporal concentration changes of DEET, TCEP, terbutryn, and nonylphenols in freshwater streams of Hesse, Germany: possible influence of mandatory regulations and voluntary environmental agreements. *Environ. Sci. Pollut. Res.* 16, 630–640. doi: 10.1007/s11356-009-0169-6

Radcliffe, D. J. C. (2002). *Pesticide Use in Australia*. Parkville, VIC: Australian Academy of Technological Sciences and Engineering, Ian McLennan House.

Sandstrom, M. W., Kolpin, D. W., Thurman, E. M., and Zaugg, S. D. (2005). Widespread detection of N,N-diethyl-m-toluamide in U.S. streams: comparison with concentrations of pesticides, personal care products, and other organic wastewater compounds. *Environ. Toxicol. Chem.* 24, 1029–1034. doi: 10.1897/04-297R.1

Schäfer, R. B., Pettigrove, V., Rose, G., Allinson, G., Wightwick, A., von der Ohe, P. C., et al. (2011b). Effects of pesticides monitored with three sampling methods in 24 sites on macroinvertebrates and microorganisms. *Environ. Sci. Technol.* 45, 1665–1672. doi: 10.1021/es103227q

Schäfer, R. B., Von Der Ohe, P. C., Kühne, R., Schüürmann, G., and Liess, M. (2011a). Occurrence and toxicity of 331 organic pollutants in large rivers of north Germany over a decade (1994 to 2004). *Environ. Sci. Technol.* 45, 6167–6174. doi: 10.1021/es2013006

Scott, P. D., Bartkow, M., Blockwell, S. J., Coleman, H. M., Khan, S. J., Lim, R., et al. (2014). A national survey of trace organic contaminants in australian rivers. *J. Environ. Qual.* 43, 1702–1712. doi: 10.2134/jeq2014.01.0012

Sen, P. K. (1968). Estimates of the regression coefficient based on Kendall's Tau. *J. Am. Stat. Assoc.* 63, 1379–1389. doi: 10.1080/01621459.1968.10480934

Simpson, S. L., Batley, G. E., and Chariton, A. A. (2013). *Revision of the ANZECC/ARMCANZ Sediment Quality Guidelines*. CSIRO Land and Water. Available online at: http://www.researchgate.net/profile/Stuart_Simpson/publication/269819076_Revision_of_the_ANZECCARMCANZ_Sediment_Quality_Guidelines/links/549792800cf2ec13375d3d9f.pdf [Accessed December 15, 2015].

Stehle, S., and Schulz, R. (2015). Agricultural insecticides threaten surface waters at the global scale. *Proc. Natl. Acad. Sci. U.S.A.* 112, 5750–5755. doi: 10.1073/pnas.1500232112

Sun, B.-Q., Wang, F., Li, H.-Z., and You, J. (2015). Occurrence and toxicity of sediment-associated contaminants in guangzhou college city and its adjacent areas: the relationship to urbanization. *Arch. Environ. Contam. Toxicol.* 68, 124–131. doi: 10.1007/s00244-014-0097-4

Tu, J., Xia, Z. G., Clarke, K. C., and Frei, A. (2007). Impact of urban sprawl on water quality in eastern Massachusetts, USA. *Environ. Manage.* 40, 183–200. doi: 10.1007/s00267-006-0097-x

Vyamzal, J. (2010). Constructed wetlands for wastewater treatment: a review. *Water* 2:530. doi: 10.3390/w2030530

Wang, J.-Z., Bai, Y.-S., Wu, Y., Zhang, S., Chen, T.-H., Peng, S.-C., et al. (2016). Occurrence, compositional distribution, and toxicity assessment of pyrethroid insecticides in sediments from the fluvial systems of Chaohu Lake, Eastern China. *Environ. Sci. Pollut. Res.* 23, 10406–10414. doi: 10.1007/s11356-015-5831-6

Weston, D. P., and Lydy, M. J. (2010). Urban and agricultural sources of pyrethroid insecticides to the Sacramento-San Joaquin Delta of California. *Environ. Sci. Technol.* 44, 1833–1840. doi: 10.1021/es9035573

Weston, D. P., Zhang, M., and Lydy, M. J. (2008). Identifying the cause and source of sediment toxicity in an agriculture-influenced creek. *Environ. Toxicol. Chem.* 27, 953–962. doi: 10.1897/07-449.1

Wightwick, A., and Allinson, G. (2007). Pesticide residues in Victorian waterways: a review. *Aust. J. Ecotoxicol.* 3, 91–112.

Zhao, J.-L., Ying, G.-G., Liu, Y.-S., Chen, F., Yang, J.-F., and Wang, L. (2010). Occurrence and risks of triclosan and triclocarban in the Pearl River system, South China: from source to the receiving environment. *J. Hazard. Mater.* 179, 215–222. doi: 10.1016/j.jhazmat.2010.02.082

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