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Predicting runoff induced mass loads in urban watersheds: Linking land use and pyrethroid contamination

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ABSTRACT

Pyrethroid pesticide mass loadings in the Ballona Creek Watershed were calculated using the volume-concentration method with a Geographic Information Systems (GIS) to explore potential relationships between urban land use, impervious surfaces, and pyrethroid runoff flowing into an urban stream. A calibration of the GIS volume-concentration model was performed using 2013 and 2014 wet-weather sampling data. Permethrin and lambda-cyhalothrin were detected as the highest concentrations; deltamethrin, lambda-cyhalothrin, permethrin and cyfluthrin were the most frequently detected synthetic pyrethroids. Eight neighborhoods within the watershed were highlighted as target areas based on a Weighted Overlay Analysis (WOA) in GIS. Water phase concentration of synthetic pyrethroids (SPs) were calculated from the reported usage. The need for stricter BMP and consumer product controls was identified as a possible way of reducing the detections of pyrethroids in Ballona Creek. This model has significant implications for determining mass loadings due to land use influence, and offers a flexible method to extrapolate data for a limited amount of samplings for a larger watershed, particularly for chemicals that are not subject to environmental monitoring. Offered as a simple approach to watershed management, the GIS-volume concentration model has the potential to be applied to other target pesticides and is useful for simulating different watershed scenarios. Further research is needed to compare results against other similar urban watersheds situated in mediterranean climates.

1. Introduction

Residential and urban areas are commonly sprayed for pest control, which includes the application of the insecticide, synthetic pyrethroids (SPs). In multiple studies, SPs have been detected in urban water ways (Ding et al., 2010; Hintzen et al., 2009; Kuivila et al., 2012; Li et al., 2013; Liu et al., 2004; Mehler et al., 2011; Wang et al., 2012; Weston et al., 2011) with evidence of toxicity exceeding threshold levels for sensitive, benthic invertebrates (Amweg et al., 2006; Bay et al., 2010; Delgado-Moreno et al. 2010, 2011; Lao et al., 2010). Moreover, urban (Domagalski et al., 2010; Ensminger et al., 2013; Jorgenson and Young, 2010; Weston and Lydy, 2010) and residential areas (Bay et al., 2010; TDC Environmental, 2005; Weston et al., 2009; Wilen et al., 2005) have been implicated as the source of SP contamination. In climates often considered mediterranean, usage of pyrethroids and pesticides have increasingly polluted regional river and freshwater bodies through urbanized settlements and crop production (López-Doval et al., 2013). For instance, SPs enter surface waters primarily during storm-water discharge (Jorgenson et al., 2013; Weston et al., 2005; Weston and Lydy, 2010) in such climates characterized by alternating rainy seasons and droughts (Lee et al., 2004). SPs are transported mainly adsorbed to suspended solids, and secondarily, in association with dissolved organic carbon (DOC) (Weston and Lydy, 2012), which contributes to SP transport in urban waterways to downstream water bodies during storm events (Amweg et al., 2006). Because these recent studies reveal that SPs transfer from impervious surfaces, and impair urban water bodies that are

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Abbreviations

BC	Ballona Creek
BCW	Ballona Creek Watershed
CDPR	California Department of Pesticide Regulation
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EMC	Event mean concentration
GIS	Geographic Information Systems
PUR	Pesticide Use Database (CDPR)
RC	Runoff coefficient
SCAG	Southern California Association of Governments
SMB	Santa Monica Bay
SP	Synthetic pyrethroid
TOC	Total organic carbon
UBC	Upper Ballona Creek
UBCW	Upper Ballona Creek Watershed
USGS	United States Geological Survey
WOA	Weighted Overlay Analysis

particularly susceptible to SP runoff during rainy seasons such as in mediterranean climates, there is an urgent need for simple stormwater modeling to estimate stormwater pollution for SPs and avert the potential environmental costs associated with SP contamination.

Research has linked the transport of synthetic pyrethroids from residential areas in urban systems (Hintzen et al., 2009; Jiang et al., 2012) with storm events where SPs can sorb to soils, sediment, and DOM and potentially cause downstream contamination. It is widely suspected that DOM likely increases the distribution of non-polar SPs from the sediment to facilitate transport within Ballona Creek (Delgado-Moreno et al., 2010). DOM has the ability to associate with hydrophobic molecules such as SPs in natural water systems, thereby reducing their uptake by sediment (Suffet et al., 1982). This finding is in agreement with DOM-bound chemicals becoming mobile, which may subsequently equilibrate and become partially solubilized as free pesticides at downstream locations where they can become bioavailable.

Several studies have used stormwater watershed modeling to predict pyrethroid contamination in waterways and sediment from storm events, linking SP contamination to land use. To observe the multiple processes that include pesticide buildup and the contributing effects that influence wash off, Luo et al. (2013) developed a four-pool conceptual model that could be used to predict pyrethroid wash off potentials from concrete surfaces. Jorgenson et al. (2013) developed a screening-level exposure model to predict that toxic unit exposure was related to the synthetic pyrethroids from urban stormwater discharge. Luo and Zhang's (2011) hybrid PRZM-GIS watershed model correlated sediment toxicity to SP contamination using Geographic Information Systems (GIS) map layers to simulate agricultural landscape characteristics. GIS modeling has also used to isolate high pyrethroid runoff specific areas within an agricultural watershed (Zhang et al., 2008), and identified potential pyrethroid emission hot spots to analyze for water and soil contamination in the European continent using Eurostat database on pesticides and land cover classes from the Corine Land Cover 2000 map (CLC2000) (Pistocchi et al., 2009). While these valuable studies predicted SP contamination on a watershed-scale based on agricultural and urban land use to estimate SP pollutant loads in streams, they do not differentiate between the specific areas within an urban watershed that produce the most mass loadings within an urban environment, nor do they offer a simple GIS-based model that can evaluate multiple SP mass input scenarios. Because urban systems have been increasingly associated with SP contamination in urban creeks and sediments, this study concentrates on the different land uses within an urban watershed.

The goal of this project is to predict SP mass loadings into watershed runoff using a customized GIS modeling and the volume-concentration method of Park et al. (2009). Specifically, this study focuses on whether impervious surfaces in Upper Ballona Creek Watershed (UBCW) show higher SP mass loadings from SP applications and if the water-phase concentration of synthetic pyrethroids (SPs) can be calculated from the reported usage. As a secondary interest in this study, SPs from residential, commercial, industrial, or public land uses or residential/commercial land uses are evaluated to see if severely limiting SP land use emissions can result in a significant (80%) reduction in SP mass loadings into Upper Ballona Creek (UBC). To validate the results, a comparison of predicted mass loading was made to the total measured SP mass from field sampling during two storm events in 2013–2014. The results were also compared to sales records and usage reports of the target SPs in the study area.

2. Materials and methods

2.1. Study area

This study was conducted in the Ballona Creek Watershed, in Los Angeles, California, which initially had not been sampled for synthetic pyrethroid water concentrations. The State Water Resources Board Surface Water Monitoring Program (Phillips et al., 2014) has, however, periodically monitored SP sediment contamination, and the California Department of Pesticide Regulations (CDPR) recently established a monitoring site at Centinela Avenue for Ballona Creek in their Study 270 (2014–2015) (Budd, 2014). Ballona Creek has already been identified as a major source of pollutants for Santa Monica Bay as a result of untreated stormwater runoff being received into estuary and bay, and the concrete channelization of Upper Ballona Creek (Curren et al., 2011; Wong et al., 1997).

Ballona Creek emerges from a series of underground drains and continues for 16 km as an open channel from south of Hancock Park in Los Angeles through Culver City, where it merges with Sepulveda Channel and Centinela Creek, eventually discharging all watershed runoff into Santa Monica Bay at Playa del Rey (Fig. 1). The Upper Ballona Creek Watershed (UBCW) is a concrete lined ephemeral creek and storm drain that covers approximately 255 km^2 of mostly residential and vacant land spaces in the western portion of the Los Angeles Basin (Curren et al., 2011; Wong et al., 1997). Ballona Creek (BC) itself is a flood-control channel (Bay et al., 2010), and was designed to reduce flooding in the Los Angeles urban environment. UBCW is 65% impervious for the entire watershed (Curren et al., 2011; Lao et al., 2010; Park et al., 2009), however, for the land uses that were considered for this study, UBCW is considered 51% impervious. The City of Los Angeles' storm water collection station is located downstream of Ballona Creek and demarcates the bottom of the Upper Ballona Creek Watershed, which is above tidal influence. In previous studies, research groups at UCLA have conducted research on UBCW (Curren et al., 2011; Park et al., 2009; Wong et al., 1997). In comparison, Bay et al. (2010) and Lao et al. (2010) conducted research on pyrethroids in Ballona Creek Estuary (BCE), however, UBC was excluded from the analysis.

The mean annual rainfall in Los Angeles is between 300 and 380 mm (McPherson et al., 2005; SMBRC, 2010). Having a mediterranean climate, the local area is characterized by limited rainfall with the wet-season occurring primarily between the months of

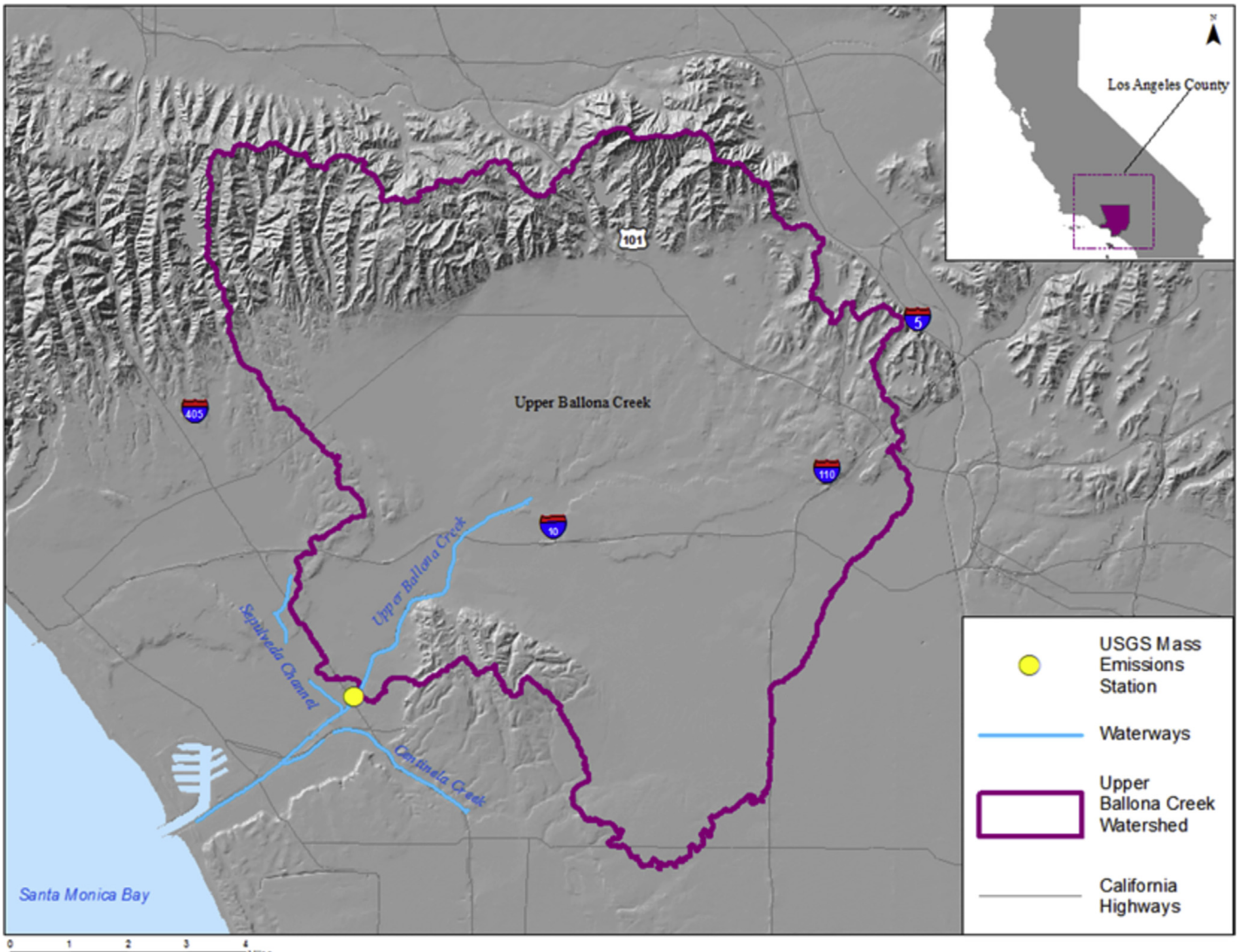

Fig. 1. UBCW and associated tributaries.

October to March (McPherson et al., 2002). Pest control application in Los Angeles is non-seasonal, and is either performed on a contractual basis or by homeowners (Weston and Lydy, 2012). Since the use of pyrethroids in Los Angeles County is for structural pest control (CDPR, 2013) and Ballona Creek Watershed is drained primarily by concrete surfaces from the surrounding residential land, it can inferred that structural pest control is primarily responsible for pyrethroid transport into Ballona Creek. While data on homeowner use is currently unavailable (Amweg et al., 2006; Bay et al., 2010), it is strongly speculated that residential use may still be a significant contributor to the pyrethroid load into Ballona Creek. SPs have been shown to be one of the commonly used conventional pesticide active ingredients for the home and garden market sector (USEPA, 2011).

2.2. Sampling program

The three sampling sites (X, 1 and 5) were chosen for measurement of water and suspended solids concentrations in Upper Ballona Creek (Fig. 2). The USGS gage station at Sawtelle Boulevard (Site X) marks the upper portion of the watershed of interest to this study. In contrast, the Centinela site (Site 1) is downstream and the suspended solids at this site can form sediments during low-flow and wash-out during high storm-water flow. Because the site is under tidal influence, results from Site 1 were not used for model calibration. Sepulveda channel (Site 5) is a drainage channel above Centinela Boulevard that drains freshwater directly into Ballona Creek. This site is fed almost entirely by residential runoff; the channel hydraulics prevent tidal influence therefore the channel runoff is considered freshwater. Both Sepulveda Channel and Centinela sites are downstream of the United States Geological Survey (USGS) gauge, which means their pyrethroid measurements cannot be included in the mass emission model.

Grab samples were collected by aluminum buckets and poured into 4-L amber bottles with Teflon lined caps. Extended grab samples were collected over five to ten minutes (Ma et al., 2009). Amber glass bottles were rinsed three times with sample water before collection. Samples were stored in coolers for transportation to the storage facility and stored at 4 °C.

Samples were taken from October 2013 until February 2014 during the wet season. Total number of the samples depended upon the intensity and duration of the storm. Storm events took place on October 9th, 2013 and on February 28th, 2014; suspended solids sampling took place over the duration of both storms.

Ten water samples were collected at the Sawtelle location during the October 2013 storm event. Eleven water samples were collected at the Sawtelle location during the storm event in February 2014 (see Supplementary Material). Because seasonal first

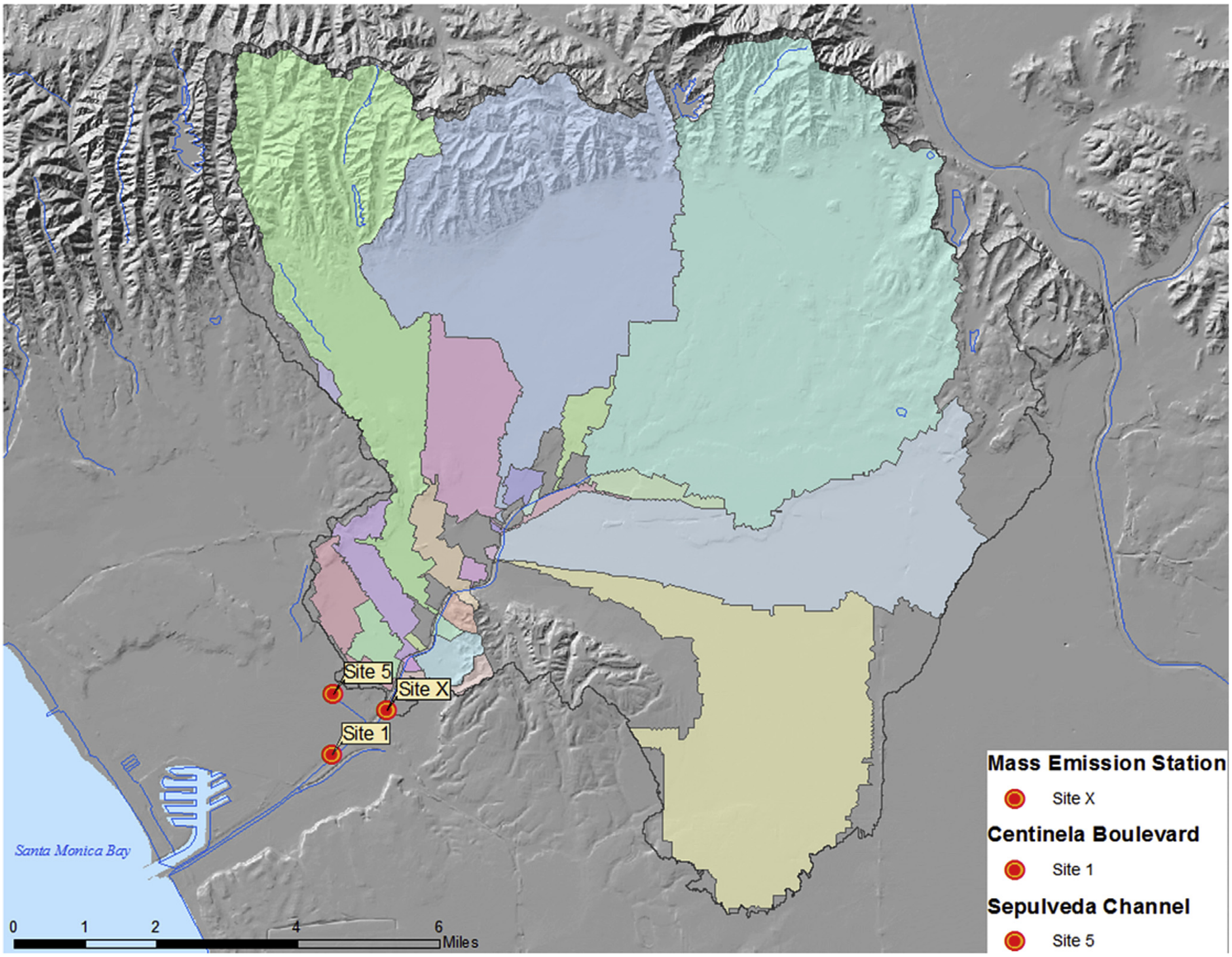

Fig. 2. Sampling locations: Mass Emission Station (Site X), Centinela (Site 1), and Sepulveda Channel (Site 5).

flush has a significant influence on SP runoff into Upper Ballona Creek (Lee et al., 2004) samples were collected every half hour for the first two-hour period and every hour thereafter for a total of eight hours for the October 2013 storm. During the February 2014 storm, samples were collected every hour for the first two hours, then every half hour for the next two hours, and finally every hour until the end of the storm during the more intense rainfall (see Supplementary Material for hydrographs for these two storm events). In this study, differences in sampling frequencies reflected the intensity and duration of the storm. The sampling frequency was adjusted in anticipation of the storm magnitude to cover the storm with a reasonable number of samples.

Pyrethroids were measured in the liquid phase and on suspended solids. Water samples were filtered with 0.7-micron glass fiber filters (Whatman GF/F) and the residue was extracted using the Microwave Digestion System MARS X, (CEM, Matthews, NC) following the USGS Techniques and Method 5-C2 (Hladik et al., 2009). Results were reported as a solid phase concentration (mass of pyrethroid per dry weight of suspended solids, ng/g see Supplementary Material). Pyrethroids in the filtrate were measured using an SPE extraction and the same GC/Dual ECD procedure and were always below detection limits (0.1–0.025 ng/L). To convert to a total water phase concentration, the solid phase concentration was multiplied by the suspended solids concentration; the liquid phase pyrethroids were always below detection limits and ignored. The detection limits on the Dual ^{63}Ni ECD for the water samples were between 0.025 and 0.100 ng/L for the target pyrethroids (Table 1).

2.3. Modeling variables

The GIS volume-concentration model was applied to the Upper Ballona Creek Watershed area. With the exception of the Ballona Creek Watershed shapefile, the geographical features of the study area were downloaded from the 2013 U.S. Census Bureau: Geography, TIGER/Line® Shapefiles and TIGER/Line® Files (U.S. Census Bureau). Population estimates came from American FactFinder 2009–2013 data for Los Angeles County (U.S. Census Bureau). Southern California Association of Governments (SCAG) GIS and Data Services provided the shapefile for the UBCW geographic area (USGS) as well as the elevation levels (USGS). To analyze the land use variables, ArcMap10.2 GIS program (ESRI ™) was used. A detailed shapefile of land use categories of the Upper Ballona Creek Watershed was obtained from earlier work on Ballona Creek Watershed (Ha and Stenstrom, 2008; Park et al., 2009). The reclassification of land uses was based on Park et al. (2009). The pyrethroid mass loading and distance variables from Upper Ballona Creek-shape areas, runoff volume, event mean concentration

Table 1
Target pyrethroids with their physicochemical properties, detection limit, and half-life data.

Compound	Molecular weight (g/mol)[a]	Water solubility (mg/L)[a]	Vapor pressure (mm Hg)[a]	Photolysis in water	Detection limit
				Half-life value (day)[b]	Method (1 L) (ng L^{-1})[c]
Bifenthrin	422.9	$1.4 \cdot 10^{-5}$	$1.8 \cdot 10^{-7}$	408 (stable)	0.050
Cyfluthrin	434.3	$2.3 \cdot 10^{-3}$	$1.5 \cdot 10^{-8}$	0.673–4.5	0.050
Cypermethrin	416.3	$4.0 \cdot 10^{-3}$	$2.5 \cdot 10^{-9}$	30.1–36.2	0.050
Deltamethrin[e]	505.2	$2.0 \cdot 10^{-4}$	$9.3 \cdot 10^{-11}$	55.5 (stable)	0.050
Esfenvalerate	419.9	$6.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-9}$	6–17.2	0.025
λ-Cyhalothrin	449.9	$5.0 \cdot 10^{-3}$	$1.6 \cdot 10^{-9}$	24.5–25	0.025
Fenpropathrin	349.4	$1.0 \cdot 10^{-2}$	$1.4 \cdot 10^{-8}$	603 (stable)	0.050
Fenvalerate[d]	419.9	$2.4 \cdot 10^{-2}$	$1.5 \cdot 10^{-9}$	6	0.050
Permethrin	391.3	$5.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-8}$	80–110	0.100
Tralomethrin[e]	665.0	$8.4 \cdot 10^{-2}$	$1.8 \cdot 10^{-11}$	<0.5–2.47	0.050

[a] With the exception of fenvalerate, all molecular weight, water solubility and vapor pressure information were provided by Laskowski (2002).
[b] All half life values were provided by Laskowski (2002) and Shamim et al. (2008) except for fenvalerate, for which only Shamim et al. provided the information.
[c] Detection limits were provided by our study's GC-ECD analysis.
[d] Fenvalerate chemical property information was provided Hazardous Substances Databank (HSDB) (2015).
[e] Deltamethrin and tralomethrin eluted simultaneously, thus, their detection limits cannot be differentiated.

(EMC), and pyrethroid mass loading-were calculated using GIS and Excel.

Land use, distance and pyrethroid mass loading variables were rasterized using ArcGIS Feature to Raster in Conversion Tools. The distance variable was rasterized using the Euclidean Distance tool. In order to set a maximum distance from the creek, the maximum distance in the Euclidean distance tool created distance rasters of 100 m, 200 m, 500 m, 1000 m and the maximum distance from the creek (12,068 m). To avoid repeatedly summing the same distance for distance rasters greater than 100 m, the lower distance was subtracted from the next higher distance to create null values. A Python command in the raster calculator subtracted the null values from the original values.

$$SetNull(\ \sim(IsNull(\text{“}200newrstr\text{”})),\ \text{“}200rstr\text{”})\ =\ 200finalrst \tag{1}$$

Each raster was prioritized with the Reclassify tool in Spatial Analyst Tools using quantile classification method for 10 groups. Reclassifications assigned priority to the distance closest to Upper Ballona Creek, the highest pyrethroid mass loading, and land uses with the highest impervious surfaces. A raster analysis was performed using the Weighted Overlay Analysis tool. To assign importance to each of these rasters, a percent weight of importance was assigned to each variable relative to one another. Trial values of [60%] pyrethroid mass loading, [25%] land use, and [15%] distance were selected but other values are possible based upon the user's confidence in the various datasets. Raster cells were assigned a scale of 1–10 with 1 being the most important (see Supplementary Material for the threshold of each class).

2.4. Prediction

SP mass loading is predicted for Upper Ballona Creek using a GIS volume-concentration model based on land use, rainfall, slope, and runoff volume. Calculating mass loadings can involve multiple calculations that link storm water runoff volume to important spatial variables, and determine runoff quantities that relate to different land uses. The volume-concentration method by Park et al. (2009) is a two-equation relation used to calculate the pollutant loads when given a runoff volume and an event mean concentration (EMC). The equations for a storm runoff volume and pollutant loading are:

$$RV = RC \times A \times CF \times RF \tag{2}$$

$$PL_i = RV \times EMC_i \tag{3}$$

where RC is the runoff coefficient calculated according to the predictive modeling of Ha and Stenstrom (2008), A is the drainage area (m^2) and was calculated based on the reclassification of land uses by Park et al. (2009), CF is the conversion factor, and RF is the rainfall depth (mm). The pollutant loading is calculated by multiplying the runoff volume by the event mean concentration (EMC) or the average pollutant concentration during a storm event. EMC_i (Eq. (4)) reflects an initial estimate for a synthetic pyrethroid EMC, and is the ratio of reported pesticide use for 2003 Non-Ag diazinon (CDPR, 2015a) and 2013 Non-Ag pyrethroid data (CDPR, 2013).

$$EMC_i = \frac{2013\ Total\ Reported\ non-ag\ Pyrethroid\ Use}{2003\ Total\ Reported\ non-ag\ Diazinon\ Use} \tag{4}$$

The experimental EMC or EMC_{SP} (Eq. (5)), which reflects the final estimate, can then be calculated, where the geometric mean concentration of diazinon (0.02 μg/L) (Ackerman and Schiff, 2003) is compared to the ratio of 2003 Non-Ag diazinon (CDPR, 2015a) and 2013 Non-Ag pyrethroid data, and an EMC of 0.13 μg/L for synthetic pyrethroids is obtained:

$$EMC_{SP} = \frac{0.02\ \mu g}{L} \times \frac{186,839\ kg\ Pyrethroid}{28,580\ kg\ Diazinon} = 0.13\ \frac{\mu g}{L} \tag{5}$$

An averaged EMC of 0.27 μg/L (Eq. (6)) for total SP emissions for the two monitored storm events was also calculated from the measured concentrations and measured runoff volumes for Sawtelle Boulevard. The average annual SP pollutant load was estimated by averaging the two storm event EMCs and then multiplied by the total annual runoff volume.

$$EMC_{ave} = \bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i = \frac{0.520\ \frac{\mu g}{L} + 0.029\ \frac{\mu g}{L}}{2} = 0.27\ \frac{\mu g}{L} \tag{6}$$

$$\sum x_1 = 0.520\frac{\mu g}{L},\ Storm\ Event\ 1\ (Sept.\ 9,\ 2013),\ Sawtelle\ Blvd.$$

$$\sum x_2 = 0.029\frac{\mu g}{L},\ Storm\ Event\ 2\ (Feb.\ 28,\ 2014),\ Sawtelle\ Blvd.$$

The EMC_{SP} of 0.13 μg/L was applied to residential (MR, MFR, and SFR or Mixed Residential, Multi-Family Residential and Single-Family Residential, respectively) commercial, public facilities, and industrial UCLA land use codes within the volume-concentration method equation because SPs can be applied to impervious surfaces. For example, SPs can be applied to building exteriors and pavement in addition to perimeter settings around domiciles and lawn/gardens. This takes into consideration several assumptions: 1) anticipated SP usage, 2) these four land uses comprise the most impervious surfaces while also receiving the most pyrethroid applications, 3) commercial and industrial land uses possess the most restaurants, grocery stores, and 4) factories, which process food products, are sprayed with pesticides by professional pest control applicators. All other land use codes were assigned 0 μg/L. An experimental pollutant mass loading was then calculated by multiplying the runoff volumes by the EMC for each land use to predict SP contribution per land use, which reflected a hierarchy in land uses with the most runoff.

Assuming a yearly average surface velocity of 0.3048 m/day where N_0 is the initial mass, t is the half-life, and λ based on an upper bound half-life of $T_{1/2} = 300$ days and a lower bound half-life of $T_{1/2} = 10$ days (see Table 1 and Supplementary Material), a final SP mass amount or N(t) was also calculated to take into account exponential decay. This calculation showed the influence of distance from the creek to predict how much SP runoff makes it to the creek.

$$N(t) = N_0 e^{-\lambda t} \tag{7}$$

Based on the pyrethroid detection list (Table 1), the initial mass N_0 in UBCW, or the amount of SPs in runoff prior to the effects of decay, was calculated as a proportion of the total urban SP use [kg] (see Supplementary Material) in California urban areas (CDPR, 2015b) by using the ratio of population in UBCW and California (U.S. Census, 2009–2013) and UBCW's total runoff volume from storm event 2 and UBCW's annual runoff volume (Eqs. (8) and (9)).

$$N_0 = \text{Total urban SP use} \times \left(\frac{Population\ UBCW}{Population\ California}\right) \tag{8}$$

$$N_0 = 275,700\ \text{kg} \times \left(\frac{1,292,038\ UBCW}{38,431,393\ California}\right) = 20,729\ lbs. \tag{9}$$

2.5. Model validation

To determine whether the model functioned within a range of two-fold of the predicted total mass emission, comparisons were made between the total calculated mass and the average of the total sampled mass of pyrethroids for the two storm events (October 9, 2013 and February 28, 2014). Water-phase concentrations were calculated by multiplying the solid phase concentration (ng/g) by the TSS (g/L) while excluding the soluble pyrethroids concentrations, which were always below detection limits.

3. Results

3.1. Pyrethroid measurements

During the first storm in October 2013, ten samples were collected at the Sawtelle Boulevard/Ballona Creek sampling location and almost all samples had detectable amounts of pyrethroids. The concentration of detected pyrethroids ranged from 5.1 ng/g to 1408 ng/g. Permethrin was detected in the highest concentration at 1408 ng/g (Table 2). Deltamethrin was detected in three of the samples (Fig. 4). Permethrin and cyfluthrin were also frequently detected and were each detected in three samples.

For the February 2014 storm event, 11 samples were collected at the Sawtelle. Boulevard/Ballona Creek location. The February 2014 storm flow was much smaller than the October 2013 storm event. All samples had detectable amounts of pyrethroids ranging in concentration from 11 ng/g to 1210 ng/g (Table 3). Out of 11 samples, lambda-cyhalothrin was detected as the highest concentration at 1210 ng/g and was also the most frequently detected pyrethroid (Fig. 4). Other pyrethroids detected in high concentrations included permethrin (877 ng/g), cyfluthrin (280 ng/g), deltamethrin (158 ng/g), bifenthrin (133 ng/g), and fenvalerate (64 ng/g). Of the ten pyrethroids targeted for analysis, esfenvalerate was not detected in any of the samples.

3.2. Validation of the GIS volume-concentration model

For the synthetic pyrethroids under investigation in the suspended solids phase, the GIS-volume concentration model predicted total mass emissions of 9736 g/year and 4655 g/year when using an averaged EMC of 0.27 μg/L (see Supplementary Material) an experimental EMC of 0.13 μg/L, respectively, and a yearly rainfall of 361 mm (14.8 inches). In both cases, the two EMC estimates are ±35% of the mean, which is an acceptable estimate of method accuracy. Park et al. (2009) found differences in results from several investigators of ±25% in runoff volumes and factors of two to three in pollutant mass emissions based on assumptions for land uses. A difference of only two-fold is more accurate than this previous work.

Correspondingly, the total SP mass emissions measured in the experimental program were 48.9 g and 24.2 g during the two rainfall events on September 9, 2013 and February 28, 2014, with a total rainfall of 0.3 mm and 5.6 mm. If these two events are averaged and the results extrapolated to the yearly rainfall of 361 mm, the total mass emission of pyrethroids would be 4466 g/year. From these results, the likely emissions of total pyrethroids from the UBCW are within the bounds of 4000 to 10,000 g/year. This level of agreement among the different calculation methods, which is essentially within a factor of 2.0, is considered within an acceptable range of accuracy (Park et al., 2009; Wong et al., 1997).

3.3. Land use and distance from the creek

Fig. 3 shows the raster analysis using these weightings. The darker areas have the highest weighting, which can be interpreted as the greatest potential to discharge pyrethroids to Upper Ballona Creek, as well as the most promising areas for source control. The highest ranked areas do not correspond precisely with political boundaries but are generally located in Hollywood, West Hollywood, Beverly Hills, Culver City, Baldwin Hills, University of Southern California (USC), Downtown Los Angeles, and Silver Lake.

In the exponential decay scenarios, when considering pyrethroids with $T_{1/2} = 300$ days and $T_{1/2} = 10$ days, less than 1% of the mass actually reached the creek. With a very short half-life of $T_{1/2} = 10$ days, almost no pyrethroids reach Upper Ballona Creek (0.24 g/year), which is much lower than the best estimate of the observed land use emission amounts of 4655 to 9736 g/year. With a much longer half-life of $T_{1/2} = 300$ days, a larger mass (127 g/yr) reaches the creek, but it is still less than the observed mass.

4. Discussion

4.1. Storm runoff and pyrethroid contamination in Ballona Creek

Both the high concentration and frequent detection of pyrethroids in storm water suspended solids taken at the Sawtelle Boulevard site clearly indicates that pyrethroids are being flushed

Table 2
Concentrations of pyrethroids detected in suspended solids samples taken at Sawtelle Boulevard during the stormwater runoff conditions in Ballona Creek (October 2013).

Compound	Concentration of suspended solids (ng/g)[a]									
	2:05 AM	2:35 AM	3:05 AM	3:35 AM	4:35 AM	5:35 AM	6:35 AM	7:35 AM	8:35 AM	9:35 AM
Bifenthrin	0	76.96	0	0	0	113.49	0	0	0	0
Cyfluthrin	0	195.17	273.66	0	0	0	0	0	0	75.75
Cypermethrin	0	74.29	0	0	0	92.67	0	0	0	0
Deltamethrin[b]	0	0	0	0	0	34.68	0	10.36	14.87	0
Esfenvalerate	0	0	0	0	27.15	0	0	0	0	0
λ-Cyhalothrin	0	0	0	0	0	0	0	0	0	0
Fenpropathrin	0	0	0	0	0	0	0	0	0	0
Fenvalerate	0	0	54.92	0	0	0	0	0	0	0
Permethrin	0	0	0	1407.63	1254.29	0	0	0	0	160.84
Tralomethrin[b]	0	0	0	0	0	34.68	0	10.36	14.87	0

[a] Collected at Sawtelle Boulevard sampling site for Storm Event 1 (October 9, 2013).
[b] Deltamethrin and tralomethrin co-eluted, thus, their detection limits cannot be differentiated.

Table 3
Concentrations of pyrethroids detected in suspended solids samples taken at Sawtelle Boulevard during the stormwater runoff conditions in Ballona Creek (February 2014).

Compound	Concentration of suspended solids (ng/g)[a]										
	12:00 AM	1:00 AM	2:00 AM	2:30 AM	3:00 AM	3:30 AM	4:00 AM	5:00 AM	6:00 AM	7:00 AM	8:00 AM
Bifenthrin	0	0	0	0	59.65	0	0	132.58	0	0	0
Cyfluthrin	0	0	0	280.33	0	242.72	263.40	0	0	0	0
Cypermethrin	0	0	0	0	0	0	0	0	0	0	0
Deltamethrin	0	0	157.56	0	50.27	65.29	20.95	76.46	0	0	0
Esfenvalerate	0	0	0	0	0	0	0	0	0	0	0
λ-Cyhalothrin	1210.24	10.92	52.69	0	0	0	20.95	0	21.52	31.41	17.90
Fenpropathrin	0	0	0	0	0	0	0	0	0	0	0
Fenvalerate	0	15.03	0	0	0	63.93	0	0	0	0	0
Permethrin	0	0	876.93	0	0	0	0	333.69	0	0	0
Tralomethrin[b]	0	0	157.56	0	50.27	65.29	20.95	76.46	0	0	0

[a] Collected at Sawtelle Boulevard sampling site for Storm Event 2 (February 28, 2014).
[b] Deltamethrin and tralomethrin co-eluted, thus, their detection limits cannot be differentiated.

into the system either from the surrounding residential and commercial land uses, which have been sprayed for pest control purposes, or, via soils and sediment being washed into the watershed from upstream urban landscapes. Since pyrethroids are readily mobilized during storm events, this indicates that the greatest mobilization of pollutants by runoff generally occurred after the start of each storm event. Having high pollutant concentrations including organics in the beginning of the wet season is consistent with the phenomenon known as the "seasonal first flush" effect where the first storm of the wet season has high pollutant concentrations (Lee et al., 2004).

Pyrethroid contamination in Ballona Creek can be partly explained by seasonal first flush and differences in total organic carbon (TOC) values. During the first storm event of the season, the TOC was high. The October 2013 storm averaged a maximum of 158 mg/L of TOC during the first flush of the season. The February 2014 storm averaged 20 mg/L of TOC after the initial first flush of the season. High TOC values during storm events may play a direct role in the mobilization and subsequent detection of pyrethroids in sediment and suspended solids samples. SPs bound to dissolved organic matter (DOM) were continually flushed into Ballona Creek during the storm events, even towards the end of the events. Following storm events when flow rates return to pre-storm conditions, DOM, which can more readily equilibrate with SPs in sediments, flowed downstream bound to hydrophobic organic pollutants (HOPs), which includes SPs. It is strongly speculated that upon reaching the Bay, SPs, which can remain associated with the DOM or desorb from the DOM as freely dissolved SPs, then sorb to suspended solids and settle to the sediments due to the increase of salinity (Turner, 2003; Zhou and Rowland, 1997). Sediments that remained in UBC after the storm are dissimilar to the TSS observed during the storm; the sediments are largely inorganic with large particle size and adsorbed SPs were below detection limits. Since a majority of pyrethroids and other pesticides are entering Ballona Creek at the beginning of the storm, this indicates that there is typically a large flush of pollutants into the estuary and into Santa Monica Bay occurring during storm events (Lao et al., 2010).

4.2. Validation of GIS-volume concentration watershed model

The averaged EMC value of 0.27 μg/L is approximately twice as large as the 0.13 μg/L EMC calculated from the ratio of reported usage of pyrethroids to the reported usage of diazinon (Ackerman and Schiff, 2003) in the Upper Ballona Creek Watershed. Prior uses of the volume-concentration method have shown various degrees of accuracy when compared to urban storm-water data. Wong et al. (1997) found accuracies that sometimes differed by an order of magnitude from storm-water data. In a study of six investigators modeling the Upper Ballona Creek Watershed, Park et al. (2009) found differences in load predictions of ±14% in TSS load predictions based upon land use definitions and up to −68 to 118% in TSS loads from all causes. This indicates that a two-fold difference is still well within an acceptable estimate of storm-water pollution (Park et al., 2009). Therefore, this model predicts the measured discharge within a two-fold difference of the predicated discharge, 9736 g/year and 4655 g/year, respectively.

Predicting pyrethroid contamination from runoff from an urban watershed using a simple GIS-volume concentration model has not been performed to date. Furthermore, an EMC for SPs has not been previously measured or estimated, and an initial estimate for a synthetic pyrethroid EMC was created by using a ratio of pesticide usage. While our results show that the ratio of the population was a

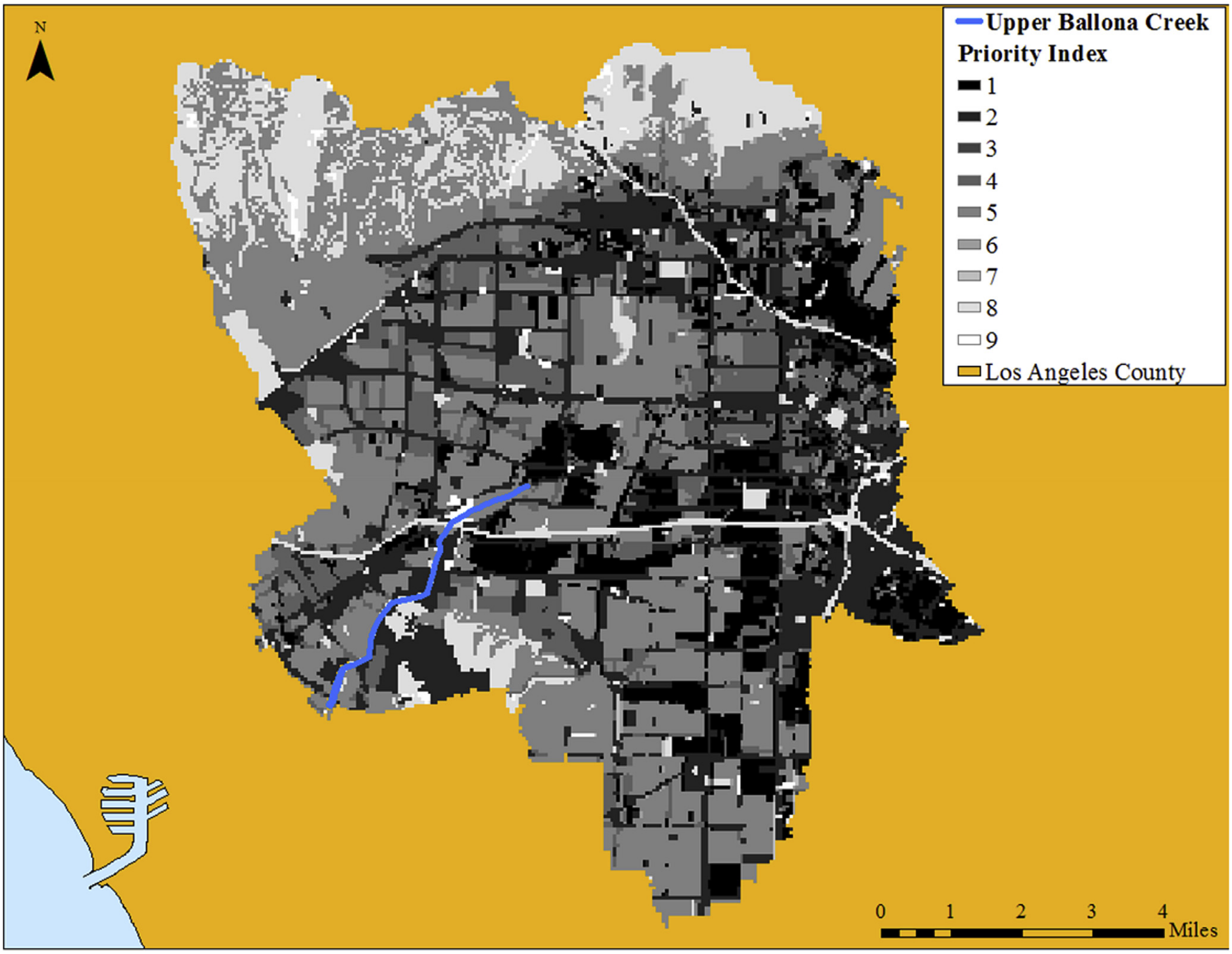

Fig. 3. Analysis of potentially contributing areas to SP emissions with priority index values based on mass loading, land use type, and distance to Ballona Creek. Darker areas have the highest priority and the greatest potential for SP emissions.

better indicator of pyrethroid usage, a land use ratio could also have been used. Although past studies possessed the predictive modeling components, none combined a validated GIS model based on the simple mathematical two-equation volume concentration method, which requires fewer input variables that can be obtained through available databases. Such modeling efforts have a wide range of application for predicting emissions for next generation pesticides such as fipronil (Thuyet et al., 2012; Weston and Lydy, 2014).

It is also useful that the GIS-volume concentration model, validated through field sampling, is able to indicate which urban areas produce the most pyrethroid stormwater runoff as well as how distance to the creek can affect the amount of pyrethroid that actually reaches the creek. Specifically, the weighted overlay analysis reveals the areas where a regulatory agency could give priority, based on land use category, SP mass loads, and distance from the creek. The high-priority areas appear to conform to residential/commercial areas. Accounting for the half-life of the chemicals may also allow watershed protection efforts to concentrate on specific types of pyrethroids that affect the water quality of the Upper Ballona Creek. In a simple analysis, SPs used in parcels farther from the creek had less of an impact since it takes more time for those SPs to travel to the creek, in part, because the time of travel gives pyrethroids more time to decay.

While assumptions behind our half-life calculations indicate that SPs should be completely decayed by the time they reach the USBG mass emissions station, this study's measurements indicate the opposite. Permethrin, which has an approximate half-life of $T_{1/2}$ = 80–110 days, had the highest concentrations (334 ng/g to 1407 ng/g). These results could be attributed to the fact that permethrin has been reported to be relatively stable under alkaline conditions (Shamim et al., 2008). Half-life or decay rates in the creek therefore may be different than those predicted in laboratory studies. In a matrix of the creek environment, SPs with a lengthy half-life may in fact degrade more slowly. Furthermore, bifenthrin, which has an approximate half-life of 408 days, and had relatively high concentrations (60–133 ng/g) has been reported to have consistent persistence across different sediments ($T_{1/2}$ = 428–483 d) (Gan et al., 2008). More importantly, this could mean that the relatively low amounts of bifenthrin and permethrin that reach BCE could have a higher persistence depending on the direction of the degradation mechanism and estuarial conditions. Using the approach of SP half-lives to estimate downstream pollutant loads could be valuable in the selection of interventions by government agencies to mitigate SP contamination in downstream waterbodies. This would save valuable time and resources

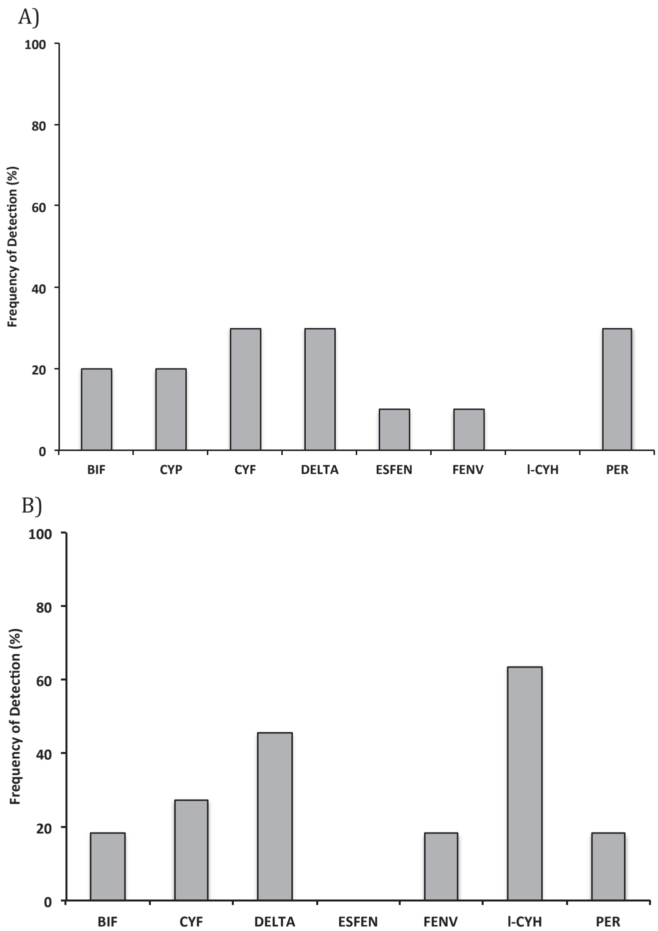

Fig. 4. Frequency of detection of water and suspended solid samples collected at Sawtelle Boulevard site at Ballona Creek, Los Angeles, CA during October 2013 and February 2014 storm events. *A*) BIF, bifenthrin; CYF, cyfluthrin; DELTA, deltamethrin; ESFEN, esfenvalerate; FENV, fenvalerate; l-CYH, lambda-cyhalothrin; PER, permethrin *B*) BIF, bifenthrin; CYF, cyfluthrin; DELTA, deltamethrin; ESFEN, esfenvalerate; FENV, fenvalerate; l-CYH, lambda-cyhalothrin; PER, permethrin.

that might otherwise be spent on targeting SPs with less potential to contaminate.

Implications of this model's simple and flexible approach could be beneficial to regulatory agencies because it can generate different pyrethroid management scenarios, which requires fewer input variables, and provide a potentially cost-effective watershed management strategy. A hypothetical control strategy that can reduce the mass of pyrethroid emissions by 80% was assumed and applied to each individual land use. It was found that application to a single land use could not reduce emissions by 80% alone. In this scenario, percent reduction was simulated by setting the EMC of the land use of interest to zero. While individual land uses could not independently generate an 80% reduction, when residential and commercial land uses were combined, an 83.2% reduction was predicted (Fig. 5).

A general limitation of this model was that its validation only included data from Upper Ballona Creek and from two storms, one of which was the first storm of the season. In mediterranean climates the first storm of the season may overestimate the overall annual flux (Lee et al., 2004). Future studies should include other similar urban watersheds in mediterranean climates, and should attempt to analyze storm events that normalize for first flush events. In addition, Euclidean distance was used in the model. While this approach aims to streamline the GIS-volume concentration model, the use of a storm sewer layer could improve the calculation of the distance because Los Angeles employs separate sewer systems.

For the Weighted Overlay Analysis, the distance raster cell size was based on the smallest cell size of the input field-the Upper Ballona Creek line shapefile. Manually inputting smaller cell sizes did not create rasters. Thus, with a finer resolution for different watersheds, results could vary with an increase in detailed information. It is also important to note that the first storm event occurred during a drought year in California. Thus, a much higher than average amount of pesticides and DOM (measured TOC) had accumulated in the runoff. These higher than average amounts of TOC detected in the storm water samples (particularly in the October 2013 samples) contributed to a greater mobility of pyrethroids during the storm event (independently of suspended solids), as pyrethroids readily sorb soluble TOC allowing for greater mobility downstream to Santa Monica Estuary and Bay. Considering the concentrations of pyrethroids found on suspended solids samples as well as expected to be associated with soluble TOC during storm events, this is of great concern for the protection of sensitive, benthic and estuarine/marine organisms.

Land use and mass loading variables in the GIS-volume concentration method both demonstrate that densely populated areas in urban watersheds with a high factor of impervious surfaces produce the highest amount of SP runoff. We assigned an EMC of 0.13 μg/L to land use categories of commercial, residential, industrial and public facilities and zero EMCs to other land use categories based on anticipated SP usage. Assigning unique EMCs to each land use could be valuable in intervention measures in urban watersheds. However, this approach would require data that could distinguish the pervious areas from overall land area for residential and other properties in UBCW. In the future, as more remote sensing information becomes available, such weightings might be possible (Park et al., 2007).

While theoretical calculations that incorporate distance from the creek indicate that only a small fraction of the pyrethroids applied to these areas actually make it to the creek, analysis of Ballona Creek water and suspended solids samples indicate detectable amounts of pyrethroids. Impervious surfaces as reflected in the runoff coefficient of the mathematical component of the model have been shown to have a significant influence on runoff but changes in pyrethroid product formulation may also reduce the degree of washoff from concrete (Jorgenson et al., 2012).

Reducing homeowner use, which is not reported to CDPR and captured in their databases, could also have an impact on pyrethroid contamination in urban creeks. Unreported urban use has been estimated to be approximately 33% of the total pyrethroid usage (see Supplementary Material). Due to the high concentrations of certain pyrethroids in the suspended solids samples during storm events, this is especially concerning. Labels on products that contain synthetic pyrethoids and are sold commercially, may help educate the public and increase precautionary awareness of the dangers of applying pyrethroid products on impervious surfaces where untreated runoff could drain into a public waterway. Utilization of stormwater BMP practices such as infiltration devices or other controls could limit SP runoff from impervious surfaces (Birch et al., 2005; Tsihrintzis and Hamid, 1997; Weston and Lydy, 2012). While Ballona Creek Watershed lacks BMP controls therefore consumers need to reduce their usage of products that contain SPs. The generation of different scenarios for decentralized BMPs for each target compound as well as large BMPs to treat runoff from the entire UBCW merits further consideration and study. Although the GIS-volume concentration model is not meant to predict exact values for individual pyrethroids, the validated model can be used to predict pyrethroid emissions for specific management scenarios.

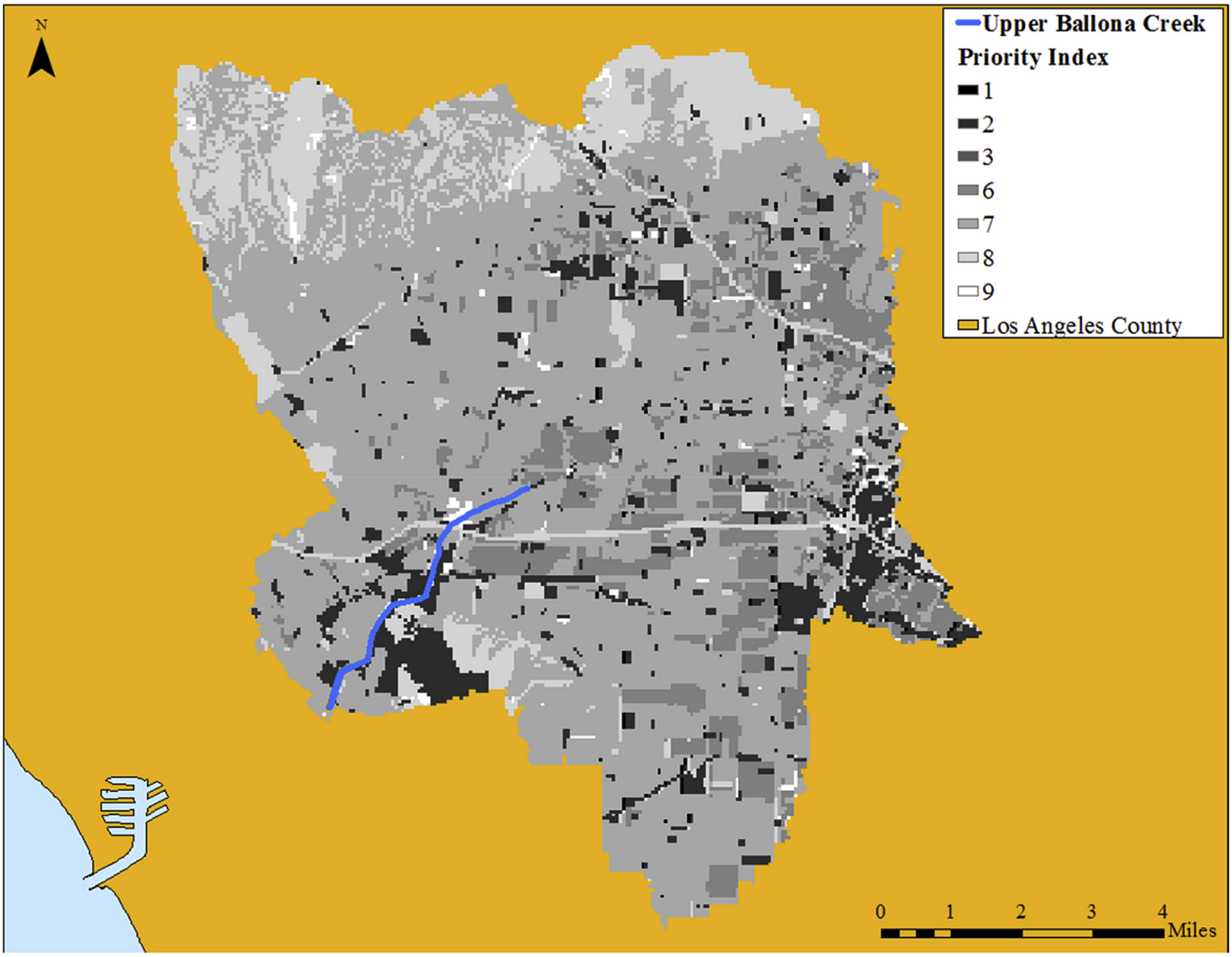

Fig. 5. Hypothetical control strategy scenario relative to Fig. 3. Impact of simulating controls on each type of residential (MFR, SFR, MR) and commercial land use.

Such models are valuable for exploring management alternatives as opposed to precise estimates. While there are too few data to perform a statistical analysis on specific pyrethroids, as more data become available.

5. Conclusions

This project evaluated the discharge of synthetic pyrethroids to the Ballona Creek Estuary from upstream sources. The study was motivated in part by the detection of toxicity to benthic organisms, with the causes tentatively identified as SPs. A field-sampling program at two locations for two storm events detected 10 different pyrethroids. Estimates of the total mass emission of synthetic pyrethroids from UBCW (255 km^2, 1.3 million population) ranged from approximately five to 10 kg/year, which is less than 0.1% of the estimated total residential usage of pyrethroids (see Supplementary Material).

A geographic information system was used to model pyrethroid usage and discharges and found the following:

- A GIS-based volume-concentration model predicted pyrethroid discharge within 50% of the measured discharge.
- Such models are valuable for exploring management alternatives as opposed to predictive modeling that aims at generating precise estimates. For example, the model showed that it would be necessary to eliminate emissions for the two largest land uses-residential and commercial, to affect an 80% overall mass reduction.
- The seasonal nature of the rainfall creates a long dry period, which may allow pyrethroids to degrade. An evaluation of the typical half-life of the various pyrethroids may reveal opportunities to reduce emissions to the receiving water by managing application times. A time-of-travel calculation was included in the GIS model to facilitate this type of analysis.
- Agencies responsible for managing pyrethroid emissions should focus on residential and commercial land uses which were identified as the highest dischargers, and minimizing pyrethroid usage, especially those with the longest half-lives. Best management practices that reduce suspended solids emissions will also reduce pyrethroid emissions.
- Pyrethroid pesticide mass loadings in Ballona Creek Watershed were calculated using the volume-concentration method with GIS to explore potential relationships between urban land use and impervious surfaces, and pyrethroid runoff flowing into Upper Ballona Creek. Weighted overlay analysis and exponential decay were used to show the effects of pyrethroid mass, distance from the creek, and land use. The GIS volume-concentration model was validated using 2013 and 2014 wet-

weather sampling data, and this model validation showed that suspended solids phase flux of synthetic pyrethroids (SPs) could be calculated from the reported usage.

- Results from this study will be useful to regulatory agencies managing urban areas in mediterranean climates, such as the European Union, which have not yet set regulations for pyrethroid emissions. Synthetic pyrethroids can cause toxicity in receiving waters and the proposed model and its findings related to fraction of applied pyrethroids released to waterways could be useful in establishing regulatory limits.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.06.040.

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