Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011

Michael P. Ensminger · Robert Budd · Kevin C. Kelley · Kean S. Goh

Abstract Urban pesticide use has a direct impact on surface water quality. To determine the extent of pesticide contamination, the California Department of Pesticide Regulation initiated a multi-area urban monitoring program in 2008. Water and sediment samples were collected at sites unaffected by agricultural inputs in three areas: Sacramento (SAC), San Francisco Bay (SFB), and Orange County (OC). Samples were analyzed for up to 64 pesticides or degradates. Multiple detections were common; 50 % of the water samples contained five or more pesticides. Statewide, the most frequently detected insecticides in water were bifenthrin, imidacloprid, fipronil, fipronil sulfone, fipronil desulfinyl, carbaryl, and malathion. Bifenthrin was the most common contaminant in sediment samples. Key differences by area: OC had more pesticides detected than SAC or SFB with higher concentrations of fipronil, whereas SAC had higher concentrations of bifenthrin. The most frequently detected herbicides were 2,4-D, triclopyr, dicamba, diuron, and pendimethalin. Key differences by area: OC and SFB had higher concentrations of triclopyr, whereas SAC had higher concentrations of 2,4-D and dicamba. Detection frequency, number of pesticides per sample, and pesticide concentration increased during rainstorm events. In water samples, all of the bifenthrin, malathion, fipronil, permethrin, and λ-cyhalothrin detections, and most of the fipronil sulfone and cyfluthrin detections were above their lowest US EPA aquatic benchmark. Diuron was the only herbicide that was detected above its lowest benchmark. Based on the number of pesticides and exceedances of aquatic benchmarks or the high number of sediment toxicity units, pesticides are abundant in California surface waters.

Keywords Urban runoff · Bifenthrin · Fipronil · Imidacloprid · Aquatic benchmark · Sediment TU

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Introduction

High urban pesticide use may account for pesticide loading into urban creeks and streams. In California, annual urban pesticide use is on the order of millions of kilogram of active ingredient (ai). Homeowner use is not reported to the California Department of Pesticide Regulation (CDPR), but professional pest managers (PMPs) annually apply over 4.5 million kg ai of pesticides for urban (non-agriculture) pest control (CDPR 2011). Non-agricultural (mostly urban) pesticide use may account for approximately 20 % of all total pesticide use in the United States (Kiely et al. 2004). In 2010,

excluding adjuvants, the total reported pesticide use in California was over 72 millionkgai (CDPR 2011). Total urban use in California is arguably much greater than the amount applied by PMPs due to unreported home and garden and other uses, although the exact amounts cannot be determined. High levels of urban pesticide use may adversely affect the environmental health of urban surface waters. Urban pesticide runoff may exceed agricultural runoff due to high use and lack of consumer awareness (Wittmer et al. 2011). Pesticide runoff into urban creeks and rivers can occur during the dry season (in California, usually from May to September) or with stormwater runoff, leading to concentrations that may be toxic to aquatic organisms (Budd et al. 2007; Sprague and Nowell 2008; Weston et al. 2009; Gan et al. 2012). Many urban use pesticides have been detected at concentrations that are sufficient to cause toxicity in laboratory bioassays (Hunt et al. 2003; Holmes et al. 2008; Lao et al. 2010; Weston and Lydy 2010). In addition, numerous urban creeks are listed as impaired water bodies on the Clean Water Act Section 303(d) list due to the presence of organophosphorus (OP) and pyrethroid insecticides (Cal/EPA 2011).

Pesticides in urban surface water are common. In a 10-year review of US Geological Survey data, 97 % of US urban streams had one or more pesticide detected. Diazinon, chlorpyrifos, carbaryl, and malathion were the most commonly detected insecticides; prometon, simazine, tebuthiuron, dacthal, and diuron were the most commonly detected herbicides (Gilliom et al. 2006). Urban structures and areas are a source for pesticide runoff (Jiang et al. 2010; Thuyet et al. 2012; Gan et al. 2012). Recent monitoring in California shows that urban waterways are frequently contaminated with pyrethroids, fipronil, and chlorpyrifos (Weston et al. 2009; Weston and Lydy 2010; Lao et al. 2010; Gan et al. 2012). Few peer-reviewed journal articles have focused on monitoring data for many other urban use pesticides in California, especially herbicides. Herbicides are often acutely toxic to algae, although their environmental impacts on aquatic systems are not well understood (Jassby et al. 2003; Sommer et al. 2007). In addition, there are synergistic interactions between different pesticides to aquatic organisms (Lydy and Belden 2006). Additional monitoring of urban waterways is therefore needed in order to assess the potential impacts of urban pesticide use on urban surface waters.

In 2008, CDPR initiated a statewide urban monitoring project to address the lack of pesticide information in urban waterways. The primary objective of this study was to determine the detection frequency and concentrations of pesticides in urban runoff from residential areas in northern and southern California. Additionally, the effect of seasonality (dry season vs. rainstorm) was investigated. Detected pesticide concentrations were compared to aquatic toxicity benchmarks. A consistent statewide monitoring program provides useful data on the environmental fate of urban use pesticides and aid in the development and implementation of management measures. The results from this study provide a baseline for future pesticide runoff studies with changes in pesticide regulations (CDPR 2010a; US EPA 2011a).

Materials and methods

Field sampling

Monitoring was conducted between April, 2008 and June, 2011 in three main urban areas of California: Sacramento area (SAC, 12 sites), San Francisco Bay area (SFB, 7 sites), and in Orange County (OC; 11 sites) (Fig. 1; detailed information, Online Resource Figures 1–3). In OC, sampling sites were located in the Wood Creek and Salt Creek watersheds; in SFB, Grayson Creek and Alamo Creek watersheds; and in SAC, Pleasant Grove Creek and Alder Creek watersheds (Online Resource Table 1). Samples were not collected at all the monitoring sites in all years; site locations were modified over the course of the 3-year study to more fully characterize the urban areas. Sampling sites were located at storm drain outfalls from residential neighborhoods or small streams connecting storm drain outfalls to the urban creeks, as well as at sites further downstream within the urban streams (receiving waters). None of the monitoring areas had agricultural inputs during the monitoring period (CDPR 2011).

Monitoring occurred during California's dry season when surface waters receive no input from rain (typically from May to September) and during or within 24 h after a rainfall (between October and April). During the 3 years of the study, water samples were collected from 15 dry season events and 13 rain events. Sediments were collected during nine events, mostly during the dry season. Water samples were collected by hand or with an extendable pole directly

Fig. 1 The three monitoring areas in California, USA
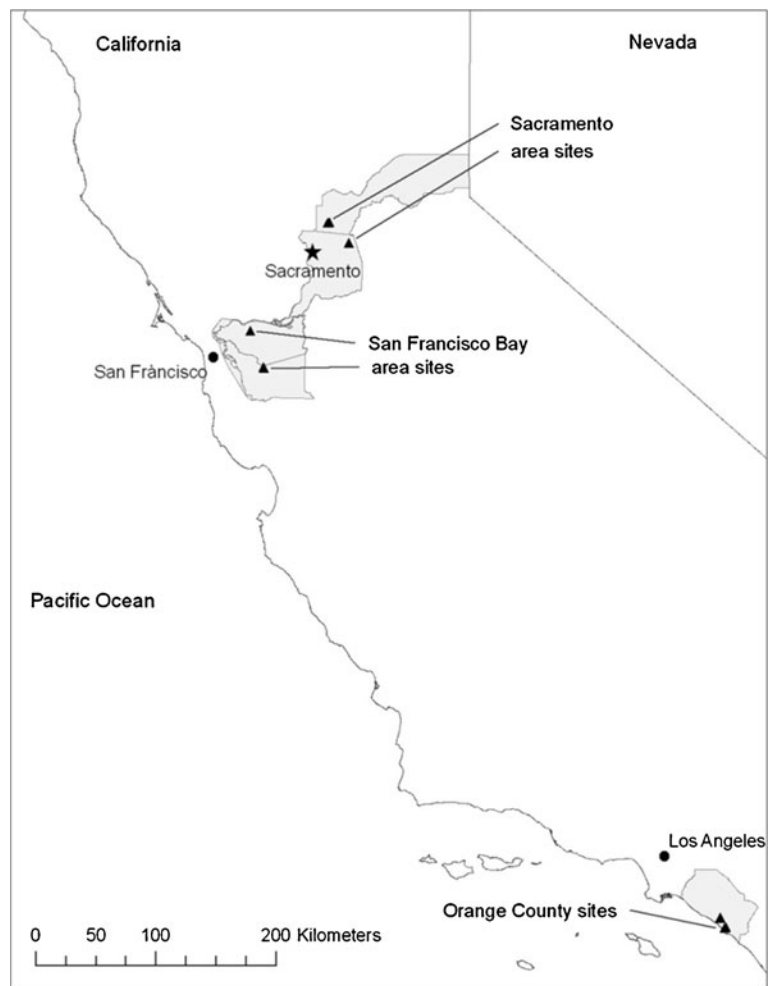
into 1-L glass amber bottles and sealed with Teflon®-lined lids. In shallower waters, samples were collected with a stainless steel container and aliquots were poured into 1-L glass bottles. Some rainstorm samples were collected as a composite sample with a Hach-Sigma 900 Max automated sampler (Hach Company, Loveland CO, USA) and split into 1-L amber bottles for transport. Sediments (up to a 2 cm depth) were collected with a stainless steel trowel into glass Ball® Mason jars. Sediments could not be collected at all sites due to lack of sediment accumulation. In the field, water and sediment samples were stored on wet ice for transport. Upon arrival at the laboratory, water samples were refrigerated (4 °C) and sediments samples were frozen (−20 °C) until chemical analysis. Ten percent of the field samples were field duplicates or field blanks. Water physiochemical properties (dissolved oxygen, electrical conductivity, pH, turbidity,

and temperature; Online Resource Table 2) were measured in situ during all sampling events with a calibrated YSI 6920 V2 meter (YSI Incorporated, Yellow Springs, OH, USA) (Doo and He 2008).

Analysis

The California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry conducted the chemical analysis. Analysis included up to 64 different pesticides, or associated degradates, from the following pesticide classes: pyrethroids, carbamates, neonicotinoids, organophosphorus insecticides, fipronil, synthetic auxin herbicides, photosynthesis inhibitor herbicides, and dinitroaniline herbicides (method information and pesticide properties, Online Resource Table 3). Although some of the pesticides included in the chemical analysis are not registered for

urban use, they were analyzed and reported by the laboratory from the same analytical method.

Quality control for this study followed CDPR SOP guidelines (Segawa 1995). Laboratory quality control consisted of reagent blanks, laboratory matrix spikes, blind spikes, and surrogate spikes. Laboratory blanks and matrix spikes were analyzed in each extraction set. There were no detections in any of the reagent blanks (water, 1,301; sediment, 70). Recoveries of the 1,290 water matrix spikes ranged from 50 % to 149 %; 2 % were outside the control limits (two cypermethrin and fipronil amide detections were flagged as questionable; Online Resource Table 4). Recoveries of the 70 sediment matrix spikes ranged from 58 % to 101 % (all within QC control levels). Propazine was added as a surrogate spike in the photosynthetic inhibitor herbicide analyses; recovery of the 372 surrogates ranged from 62 % to 110 % (all within QC control levels). Sixty-seven blind spikes recoveries ranged from 57 % to 128 % (all within QC control levels).

CDPR analyzed total suspended solids (TSS) and total organic carbon (TOC). TSS samples were analyzed following US EPA method 160.2 (US EPA 1971). Briefly, water samples were filtered under vacuum through a Buchner funnel lined with Whatman^{TM} GF/F glass fiber filters (0.7 μm), dried overnight at 103–105 °C, and weighed. TOC in water and sediment was analyzed using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan). Prior to sediment TOC analysis, sediments were dried, ground, and sieved through a 2.0-mm sieve to remove gravel. Plant material was removed prior to grinding.

Comparison to benchmarks and sediment toxicity

Analytical results were compared to the US EPA Office of Pesticide Programs' Aquatic Life Benchmarks for pesticides with available benchmarks. For this analysis, we used the lowest benchmark reported by the US EPA. Benchmark values are based on the most sensitive aquatic toxicity data for each pesticide. They are estimates of the concentrations below which pesticides are not expected to harm aquatic life and assist in identifying pesticides, and monitoring sites, that may warrant further research (US EPA 2011b). Specifically for sediment samples, toxicity units (TUs) were calculated, using pyrethroid sediment concentrations and commonly accepted and LC_{50} values, both normalized to organic carbon

(Amweg et al. 2006; Maund et al. 2002; Weston and Jackson 2009). TUs for different pyrethroids are assumed to be additive due to a similar mode of action.

Statistics

Statistical analyses were conducted using the nonparametric Mann–Whitney (Wilcoxon rank-sum) test, significance at the 0.05 level, with Minitab® Statistical Software (Release 15; non-detections were given the value of one-half the reporting limit to allow for ranking). Nonparametric methods do not require an assumption that data follow a specific distribution and allow censored (non-detect) data to be ranked and compared with uncensored data (Helsel 2012).

Results and discussion

Pesticides detected in surface waters

Pesticide detections in water samples were common. Of the 64 pesticides in the chemical analyses, 32 different pesticides or degradates were detected above their analytical reporting limit (20 insecticides and 12 herbicides). Many pesticides in the analyses were not registered for use in urban areas and detections were not expected. More than 90 % of the water samples contained at least one pesticide, three-fourths of the samples contained at least two pesticides, and half of the water samples contained five or more pesticides. The insecticides bifenthrin, imidacloprid, fipronil, and three synthetic auxin herbicides (2,4-D, triclopyr, dicamba) were the most frequently detected pesticides in the study, being detected more than 40 % of the time. Diuron, pendimethalin, MCPA, carbaryl, malathion, and two fipronil degradates (fipronil sulfone, fipronil desulfinyl) were also detected more than 15 % of the time (Online Resource Tables 5 and 6).

Bifenthrin was the most frequently detected pesticide. It was more frequently detected in SAC (84 % detection frequency [DF]), than in OC (68 % DF) or in the SFB (56 % DF; Fig. 2). In addition, bifenthrin was detected at significantly higher concentrations (median, 0.02 μg L^{-1}) in SAC than either in OC or SFB (median, 0.008 and 0.006 μg L^{-1}, respectively; $p <$ 0.0002) (Fig. 3). Except for bifenthrin, other pyrethroids were detected at low frequencies and not in all areas of the state. Permethrin was the second most
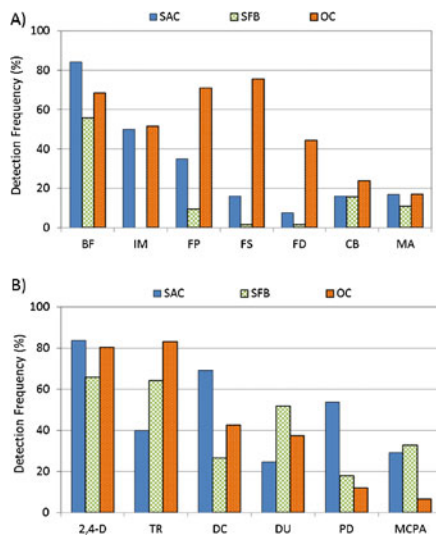
Fig. 2 Pesticide detection frequency of water samples collected at three areas of California, USA (SAC, Sacramento area; SFB, San Francisco Bay area; OC, Orange County), between April 2008 and June 2011. *A*, insecticides; *B*, herbicides; *BF*, bifenthrin; *IM*, imidacloprid (no data from SFB); *FP*, fipronil; *FS*, FP sulfone; *FD*, FP desulfinyl; *CB*, carbaryl; *MA*, malathion; *TR*, triclopyr; *DC*, dicamba; *DU*, diuron; *PD*, pendimethalin

commonly detected pyrethroid, with detection frequencies of 18 %, 6 %, and 5 % for OC, SAC, and SFB, respectively. Cyfluthrin and cypermethrin had moderate detection frequencies in SAC (16 % and 13 %, respectively) but not in SFB or OC. All other pyrethroids were detected infrequently (Online Resource Table 5). Pest management professionals (PMPs) routinely apply bifenthrin for structural pest control; in OC, it also has sizeable use in nurseries and in landscape maintenance applications. Bifenthrin is also sold in numerous homeowner products (Osienski et al. 2010). PMP use is reported by county to CDPR, but homeowner use is not. Thus, it is difficult to ascertain how much bifenthrin is being applied near the monitoring sites. Nevertheless, reported use may partially explain the observed detections in surface water. In the counties of the monitoring sites, the highest reported use of bifenthrin was associated with highest detection frequencies in this study. Except for permethrin, bifenthrin also has the highest reported use of the pyrethroids in the counties of the sampling areas (CDPR 2011). This, along with its high number of homeowner products, may account for bifenthrin's high detection frequency.

Imidacloprid was the second most frequently detected insecticide, but we did not monitor for it in SFB and in SAC only eight water samples were analyzed for this

pesticide (in June 2011, with four detections). In OC, monitoring for imidacloprid began in October 2010, and in 37 samples, it was detected 19 times (51 % DF; Fig. 2). There were no significant differences between the imidacloprid concentrations between OC and SAC (Fig. 3). Urban use of imidacloprid includes structural pest control (termites) and landscape maintenance (to control sucking insects and beetles). San Diego and Los Angeles counties have by far the largest reported non-agricultural use of imidacloprid in California, but OC and SAC had over 500 kg active ingredient applied in 2010 (CDPR 2011). Imidacloprid is also found in numerous homeowner products in these areas (Osienski et al. 2010). The environmental fate characteristics (non-volatile, low affinity for soil, high water solubility, lengthy persistence)(Fossen 2006) coupled with use in urban areas give imidacloprid the potential to move into surface waters, although infrequently reported in the literature. Data presented here supports previous work showing that imidacloprid can be a frequent contaminant of surface waters in urban or agricultural areas (Phillips and Bode 2004; Starner and Goh 2012).

Fipronil was the third most commonly detected insecticide throughout the study with the highest detection frequency in OC than in the other areas of the state (Fig. 2). Fipronil was detected in 71 % of the samples from OC, but in only 34 % of the samples from SAC and in 9 % of the samples from SFB. Significantly higher concentrations of fipronil were detected in OC than in northern California (with SAC higher than SFB; $p < 0.0004$; Fig. 3). The sulfone, desulfinyl, and amide degradates are major fipronil degradates. Like parent fipronil, these degradates were also detected more frequently and at higher concentrations in OC than in northern California ($p < 0.006$). SAC had higher detection frequencies of these degradates than did SFB, but like the parent compound, these were detected at a much lower frequency than that observed in OC (Fig. 2 and Online Resource Table 5). In California, fipronil is not registered for agricultural use nor is it registered for any homeowner products. It is strictly applied by PMPs to control insects common in urban areas, as termites, ants, and cockroaches (Gunasekara et al. 2007). OC had second largest reported use of fipronil in California (second to Los Angeles County), mainly for structural pest control. Following the detection trends, SAC had higher reported use than the counties of the sampling sites in SFB (CDPR 2011). Although we cannot determine
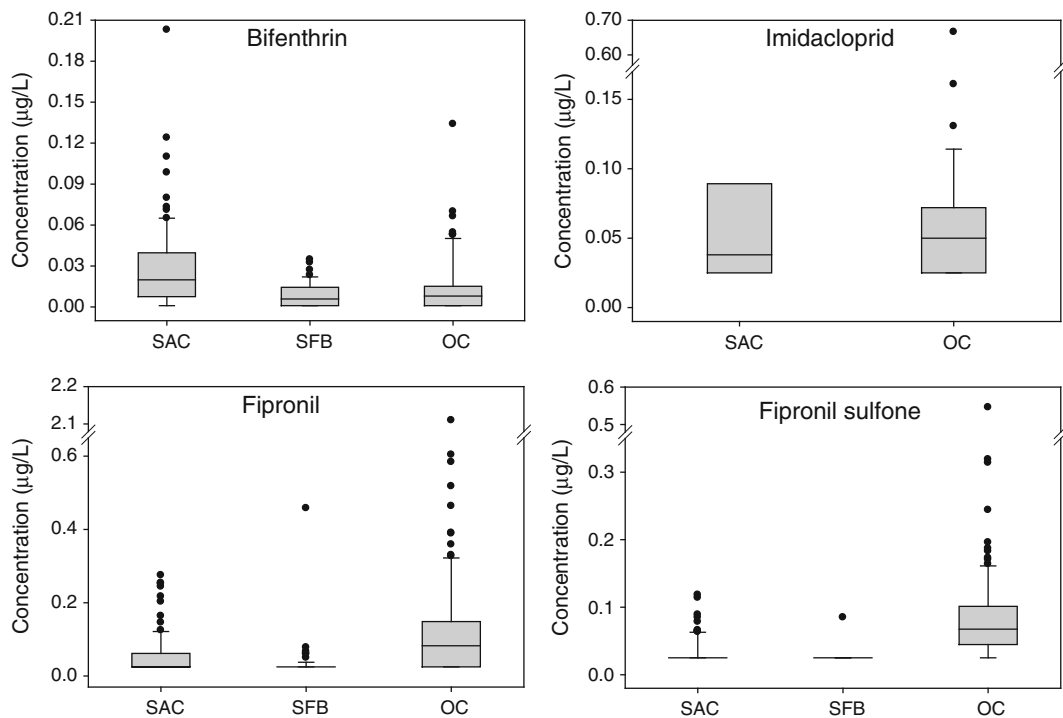
Fig. 3 Boxplots of the insecticide concentrations in surface waters of bifenthrin, imidacloprid, fipronil, and fipronil sulfone from the three sampling area in California, USA (SAC, Sacramento area; SFB, San Francisco Bay area; OC, Orange Count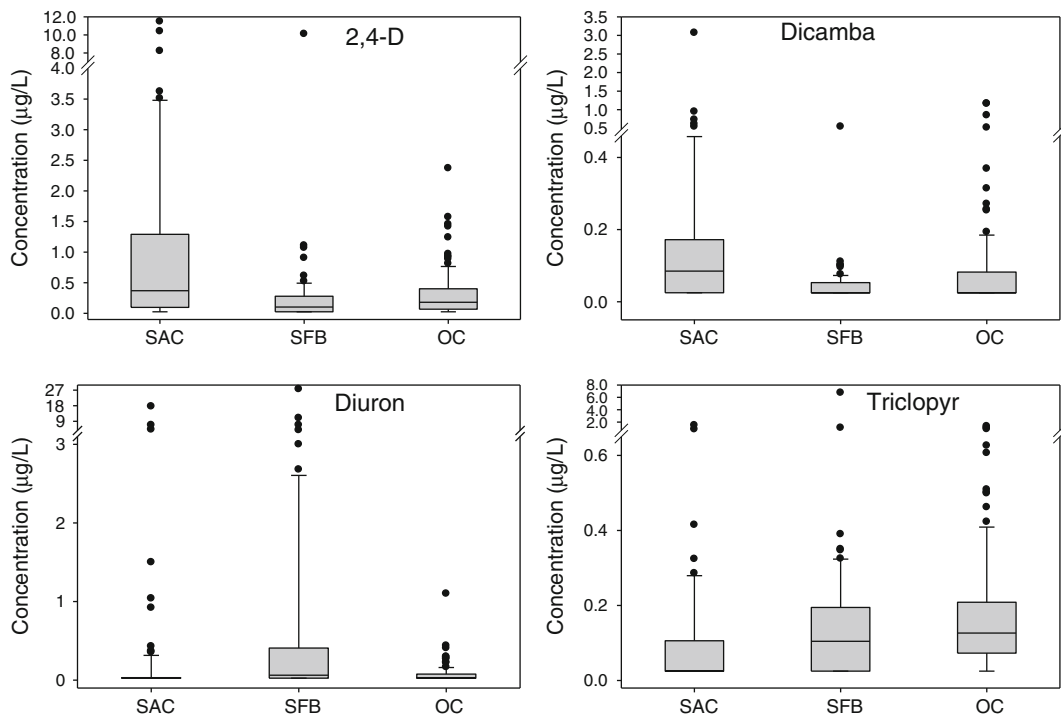y). The bottom and the top of each box are the 25th and 75th quartiles, respectively. The median is the middle line in the box (if no middle line, the line at the bottom of the box). *Whiskers* extend to the lowest or highest data point within 1.5 times the interquartile range. Outliers (*dots*) are an unusually large observation

proximity of PMP applications to sampling sites, the overall higher fipronil use in OC likely accounts for the high percentage of detections in OC. Gan et al. (2012) has recently shown that OC has higher amounts of fipronil in surface waters than SAC, likely due to differing pest management and gardening practices, growing season length, and pest pressures.

Carbaryl (carbamate insecticide) and malathion (OP) were detected consistently throughout the state, with similar frequencies in the three areas. Carbaryl was detected in 16–24 % of the samples and malathion was detected in 11–17 % of the samples from the three areas (Fig. 2). Two other OPs, chlorpyrifos and diazinon, were routinely detected in urban runoff studies prior to being banned for most urban uses (Gilliom et al. 2006; CDPR 2010b). Chlorpyrifos and diazinon phaseout for residential use began in 2000 but still have minimal use in urban areas (US EPA 2012a, b); for example, 142 kg of chlorpyrifos was applied by professional applicators in the counties of this study in 2010 (CDPR 2011).

Either due to this minimal use, to homeowner use of remaining stocks of these chemicals, persistence, or atmospheric deposition from agricultural applications, both diazinon and chlorpyrifos show up in a few waters samples from urban creeks (Online Resource Table 5). Most of the diazinon and all of the chlorpyrifos detections occurred during the rainstorm sampling.

Notably, three of the five most commonly detected pesticides in the study were synthetic auxin herbicides (2,4-D, triclopyr, dicamba). These herbicides are frequently applied to control post-emergent broadleaf weeds in turf (Vencill 2002). 2,4-D was most frequently detected, although there were also high detections of triclopyr and dicamba. 2,4-D was detected about equally in SAC and OC (80–84 % DF) but had a lower detection frequency (66 %) in the SFB (Fig. 2). Even though SAC and OC had similar detection frequencies, SAC had significantly higher concentrations of 2,4-D than did OC (and OC was greater than SFB, $p < 0.02$; Fig. 4). Triclopyr was detected more frequently

Fig. 4 Boxplots of the herbicide concentrations of 2,4-D, triclopyr, dicamba, and diuron in surface waters from the three sampling area in California, USA (*SAC*, Sacramento area; *SFB*, San Francisco Bay area; *OC*, Orange County). The bottom and the top of each box are the 25th and 75th quartiles, respectively.

The median is the middle line in the box (if no middle line, the line at the bottom of the box). *Whiskers* extend to the lowest or highest data point within 1.5 times the interquartile range. Outliers (*dots*) are an unusually large observation

in OC than in northern California (SAC or SFB); it was also detected more frequently in SFB than SAC (Fig. 2). Triclopyr was detected at higher concentrations in OC and SFB than in SAC ($p < 0.015$). Dicamba detections were more in line with what was observed for 2,4-D. SAC had a higher detection frequency and higher concentrations of dicamba than did either OC or SFB ($p < 0.001$; Figs. 2 and 4). Dicamba concentrations were also significantly higher in OC than in SFB ($p = 0.008$). A fourth synthetic auxin herbicide, MCPA, had higher detections (>30 % DF) and concentrations in SAC and SFB than in OC (Online Resource Table 5). All four of these synthetic auxin herbicides are applied by PMPs and are in numerous homeowner products (CDPR 2011; Osienski et al. 2010). Their high detection frequency in surface waters may be due to their frequent urban use, availability at retail stores, water solubility, and mobility or persistence (triclopyr). Besides these factors, detection frequencies may differ due to differences in watershed characteristics (soil types,

extent of impervious surfaces, etc.; Phillips and Bode 2004). The detection frequency differences between areas of the state could not be explained by reported use (CDPR 2011).

In at least one area of the state, several other herbicides were detected 10 % of the time, or more: diuron, pendimethalin, prodiamine, oryzalin, and prometon (Online Resource Table 5). Diuron was detected statewide 36 % of the time, making it the most frequently detected herbicide that was not a synthetic auxin (thus different application timings and use). Diuron was more commonly detected in SFB than in OC or SAC, with higher concentrations ($p < 0.002$; Figs. 2 and 4). Detections of pendimethalin mostly occurred in SAC, which had three to four times more detections than the either OC or SFB, with corresponding significantly higher concentrations ($p < 0.005$). Prodiamine, oryzalin, and prometon were only detected in northern California with comparable detection frequencies in both SAC and SFB.

Rainstorm runoff

Detection frequencies, the number of detected pesticides per sample, and concentrations were greater in samples collected during rainstorm events than in dry season sampling (Fig. 5). The median number of pesticides in northern California waters (SFB, SAC) significantly increased from 1 to 2 pesticides per sample to 5 to 6 pesticides per sample ($p < 0.001$). In OC, the increase was not as dramatic, due to the high number of pesticides detected per sample during dry season sampling. Nevertheless, in OC, the median number of pesticides significantly increased from six to eight pesticides per sample. The overall higher number of detections in OC may be due to higher use in this area. OC residents tend to have slightly more pest problems than residents in northern California which may warrant more pesticide applications (Flint 2003). Coinciding with the increase in the number of pesticide detections, the detection frequency of almost all pesticides increased (Fig. 6). Bifenthrin, diuron, all the synthetic auxin herbicides, the dinitroaniline herbicides (pendimethalin, oryzalin, prodiamine), and malathion had the biggest difference between dry season and rainstorm sampling. Some of the FP degradates had more detections in the dry season, as did imidacloprid. The persistence of the FP degradates (Gunasekara et al. 2007) and the low number of imidacloprid samples (Online Resource Table 5) may have accounted for higher detection frequency during dry

season (nonstorm) sampling. The concentrations of most of the pesticides also significantly increased during rainstorm sampling (of those that had statewide detection frequencies greater than 15 %). Concentrations of 2,4-D, triclopyr, dicamba, diuron, pendimethalin, MCPA, bifenthrin, fipronil, carbaryl, and malathion had significantly higher concentrations in surface waters during rainstorms (Table 1). For a few pesticides (imidacloprid, FP sulfone, FP desulfinyl), there were no significant differences between dry season and rainstorm sampling concentrations.

With fipronil, the relative distribution of parent and degradates was different for dry season and rain runoff samples. During dry season (nonstorm) sampling, fipronil and FP sulfone accounted for most of the total fipronil concentrations, about 40 % apiece (Fig. 7). FP desulfinyl and FP amide were lesser degradation products, accounting for about 10 % each. During rainstorm sampling, however, more parent fipronil was detected and concentrations of all degradates decreased. A higher parent to degradate ratio between the dry season and rainstorm events indicate less time for photolysis and oxidative transformation processes to occur before offsite transport. This may indicate that fipronil has been recently applied (perhaps immediately before or during raining). If so, fipronil runoff could be mitigated by preventing applications for a time immediately before predicted rain, or when it is raining.
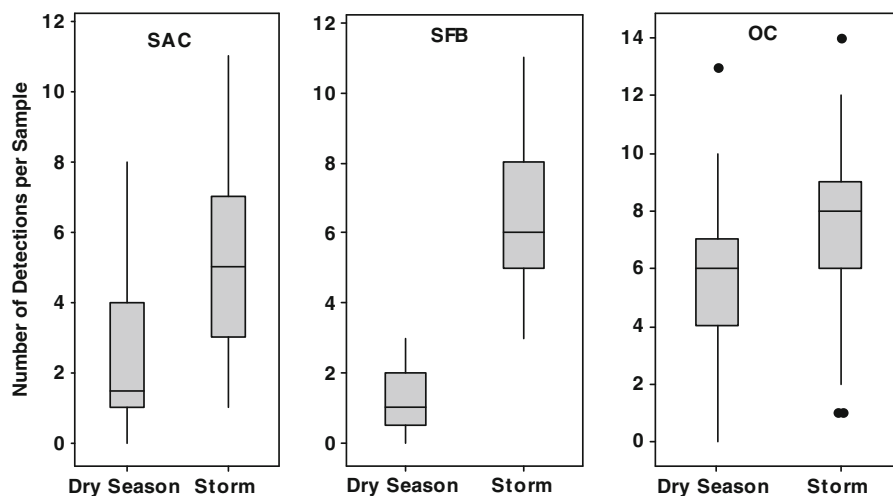

Fig. 5 Number of detections per sample collected between April 2008 and June 2011 in three areas of California, USA (SAC, Sacramento area; SFB, San Francisco Bay area; OC, Orange County) during storm and dry season sampling. The bottom and the top of each box are the 25th and 75th quartiles, respectively. The median is the middle line in the box. *Whiskers* extend to the lowest or highest data point within 1.5 times the interquartile range. Outliers (*dots*) are an unusually large or small observation

Fig. 6 Influence of storm sampling on pesticide detections. Data is state-wide; *BF*, bifenthrin; *DU*, diuron; *DC*, dicamba; *MC*, MCPA; *TC*, triclopyr; *MA*, malathion; *OR*, oryzalin; *PD*, pendimethalin; *PR*, prodiamine; *FP*, fipronil; *CA*, carbaryl; *CF*, cyfluthrin; *DZ*, diazinon; *PM*, permethrin; *FD*, FP desulfinyl; *FS*, FP sulfone; *IM*, imidacloprid; *FA*, FP amine
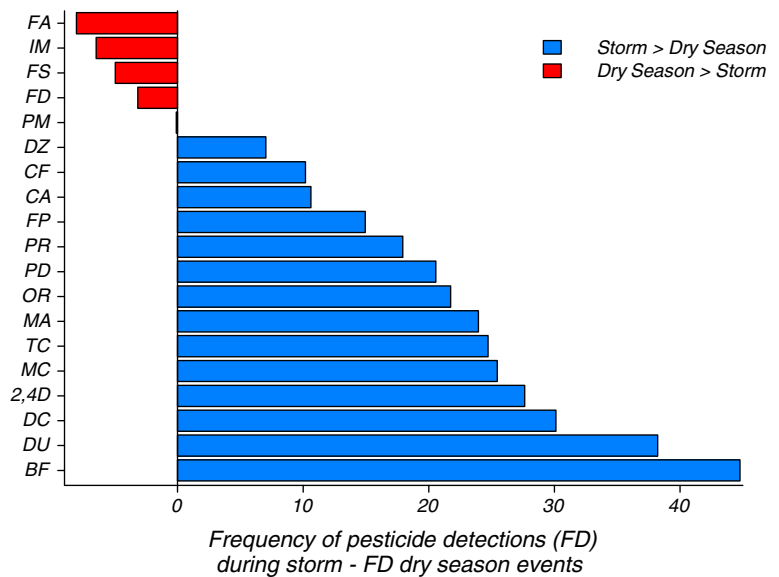
Aquatic toxicity benchmarks

All monitoring sites had at least one aquatic benchmark exceedance during the study. For the entire study, 72 % of the water samples had had at least one pesticide above its benchmark, and 50 % of the samples had two. This value is only slightly less than that reported by Gilliom et al. (2006) in urban streams during a 10-year review of NAWQA data. Differences are likely due to changes in urban insecticide use that has occurred (decreased chlorpyrifos and diazinon use with concomitant increased pyrethroid use), as well as different watershed characteristics, sampling sites and monitoring regimes. We detected 12 pesticides in water samples above their lowest US EPA aquatic benchmarks (Table 2). Bifenthrin, fipronil, fipronil sulfone, and malathion accounted for nearly 85 % of all exceedances over the US EPA aquatic benchmarks in this study. In the study, all bifenthrin, malathion, and fipronil detections and all but one fipronil sulfone detection were above their respective lowest US EPA benchmarks. Because the reporting limits for these chemicals are higher than the US EPA benchmarks, the number of exceedances is likely higher than we are reporting here. Bifenthrin, fipronil, and malathion have been

Table 1 Median, minimum, and maximum concentrations of water samples collected during dry season (nonstorm) sampling and during rainstorm sampling events (pesticides listed below had greater than 15 % detection frequencies statewide)

Sampling event		Concentration (μgL^{-1})					
		2,4-D	Triclopyr	Dicamba	Diuron	Bifenthrin	Imidacloprid
Dry season	Median	0.08	0.06	<RL	<RL	<RL	0.05
	Min	<RL	<RL	<RL	<RL	<RL	<RL
	Max	11.5	1.5	3.1	0.05	0.05	0.16
Storm	Median	0.28	0.13	0.06	0.02	0.02	<RL
	Min	<RL	<RL	<RL	<RL	<RL	<RL
	max	10.4	6.8	1.2	0.20	0.2	0.67
Significant *p* value		0.0000	0.0003	0.0004	0.0000	0.0000	ns
N Dry season		119	119	119	134	91	26
N Storm		106	106	106	130	113	19

Pendimethalin, MCPA, fipronil, carbaryl, and malathion had significantly higher concentrations during rainstorm sampling than during dry season sampling ($p=0.0000–0.04$), but median concentrations were less than the reporting limit (<RL). There were no significant differences in concentrations (median concentrations <RL) for fipronil sulfone and fipronil desulfinyl
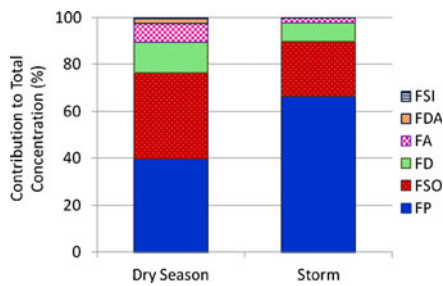
Fig. 7 Differences in percentages of fipronil (FP) and each degradate of total FP concentration during dry season (nonstorm) and storm (rain) sampling. Data is statewide; *FP* degradates: *FSO*, sulfone; *FD*, desulfinyl; *FA*, amide; *FDA*, desulfinyl amide; *FSI*, sulfide

classified by the US EPA as very highly toxic to aquatic invertebrate organisms or fish; their detections in surface waters are a concern (US EPA 1996, 2010, 2012c).

Like bifenthrin, most of the cyfluthrin and all of the λ-cyhalothrin, deltamethrin, and permethrin detections were above their lowest US EPA benchmark. Pyrethroids are highly hydrophobic and have a strong tendency to bind to sediment and organic carbon. Initial surface water monitoring characterized pyrethroid sediment toxicity (Amweg et al. 2006; Gan et al. 2005; Weston et al. 2005; Budd et al. 2007; Holmes et al. 2008). More recently, pyrethroids have been characterized in the water phase (Hladik and Kuivila 2009; Weston et al. 2009;

Table 2 Frequency of detected pesticides greater than the minimum aquatic benchmark (BM) listed by the U.S. EPA within three areas of California (units, μL^{-1})

Analyte	RL[a]	Min BM[b]	Area	N	#>RL	Max Result	#>BM (%)
Bifenthrin	0.002, 0.005	0.0013	SAC	82	69	0.20	69 (84)
			SFB	43	24	0.04	24 (56)
			OC	79	54	0.13	54 (68)
Carbaryl	0.05	0.5	OC	101	25	0.70	2 (2)
Chlorpyrifos	0.01	0.04	SFB	64	6	0.05	2 (3)
			OC	106	1	0.06	1 (1)
Cyfluthrin	0.005, 0.015	0.007	SAC	82	13	0.04	9 (11)
			OC	79	3	0.03	3 (4)
Deltamethrin/tralomethrin	0.005, 0.015	0.004	OC	79	5	0.04	5 (6)
Diazinon	0.01	0.11	SAC	94	4	0.13	1 (1)
			OC	106	9	0.12	1 (1)
Diuron	0.05	2.4	SAC	94	23	18.0	3 (3)
			SFB	64	33	28.0	8 (13)
Fipronil	0.05	0.011	SAC	94	32	0.28	32 (34)
			SFB	64	6	0.46	6 (9)
			OC	106	75	2.11	75 (71)
Fipronil sulfone	0.05	0.037	SAC	94	14	0.12	14 (15)
			SFB	64	1	0.09	1 (2)
			OC	106	80	0.55	80 (75)
λ-Cyhalothrin	0.005, 0.015	0.002	SAC	82	1	0.02	1 (1)
			OC	79	2	0.02	2 (3)
Malathion	0.04	0.035	SAC	94	16	0.36	16 (17)
			SFB	64	7	0.19	7 (11)
			OC	106	18	4.10	18 (17)
Permethrin	0.005, 0.015	0.0014	SAC	82	5	0.03	5 (6)
			SFB	43	2	0.02	2 (5)
			OC	79	14	0.35	14 (18)

[a] *RL* reporting limit; for pyrethroids, fipronil, and malathion the RL was higher than the benchmark so exceedances may be greater than we report here

[b] All invertebrates are chronic, except for diazinon (invertebrate acute) and diuron (nonvascular plant)

Weston and Lydy 2010). Pyrethroids in the water are associated with suspended sediment and organic matter, but water column toxicity is possible (Spurlock et al. 2005; Yang et al. 2006, 2007; Hladik and Kuivila 2009). Likely a portion of the pyrethroids detected in this study were bioavailable to aquatic organisms (Ensminger and Kelley 2011).

A few of the carbaryl, diazinon, chlorpyrifos, and diuron detections were also detected above their respective US EPA aquatic benchmarks (Table 2). Diuron was the only herbicide detected over its benchmark, with 11 detections solely in northern California. In the past work, the potential importance of diuron toxicity to the overall food chain has been overshadowed by pesticides that cause toxicity to aquatic invertebrates (Munn et al. 2006; Sprague and Nowell 2008). The ecological importance of diuron toxicity to phytoplankton is not well understood (Jassby et al. 2003; Sommer et al. 2007). Imidacloprid was detected at high frequency in this study. Imidacloprid is classified by the US EPA as very highly toxic to aquatic organisms so detections in surface waters are a concern (US EPA 2008). Of the 23 imidacloprid detections, none were detected above its lowest US EPA benchmark of 1.05 μL^{-1}. However, imidacloprid has been detected at potentially toxic concentrations in California surface waters (Starner and Goh 2012).

Water quality criteria (WQC) have recently been developed for five pyrethroids, three OPs, and the herbicide diuron (Fojut et al. 2012a, b; Palumbo et al. 2012). In all cases, the WQC are lower than the US EPA benchmarks. Comparing our results to WQC instead of the US EPA benchmarks increases the number of detections of concern for chlorpyrifos, cyfluthrin, cypermethrin (not detected above its US EPA benchmark) diazinon, and diuron (Online Resource Table 7).

In pesticide risk assessment, toxicity is usually based on exposure to one stressor or contaminate. However, the results from this study confirm that multiple pesticides in an urban water body are the norm. Although many pesticides were detected below their aquatic benchmarks, little is known about toxicological interactions among multiple pesticides as it is impossible from a practical point of view to investigate all chemical combinations (Lydy and Belden 2006). Multiple stressors other than pesticides (e.g., metals, salts, low dissolved oxygen, habitat degradation) may also exhibit toxicological interactions with pesticides.

Pesticides detected in sediments

Sediments contained numerous pyrethroids. All of the sediment samples contained at least one pyrethroid, 75 % of the samples contained four or more pyrethroids, and 25 % of the sediments contained seven or more pyrethroids. Pyrethroids had higher detection frequencies in sediments than in water samples, implying the importance of offsite transport of particle bound hydrophobic chemicals. Bifenthrin, permethrin, cyfluthrin, deltamethrin, and λ-cyhalothrin were commonly detected; each was in more than half of the sediments. SAC and OC contained significantly more pyrethroids per sample than did SFB ($p < 0.01$). More detailed sediment data is available (Online Resource Table 5).

Calculated TUs suggest that the potential toxicity of the sediments in the three areas differ (statewide median,
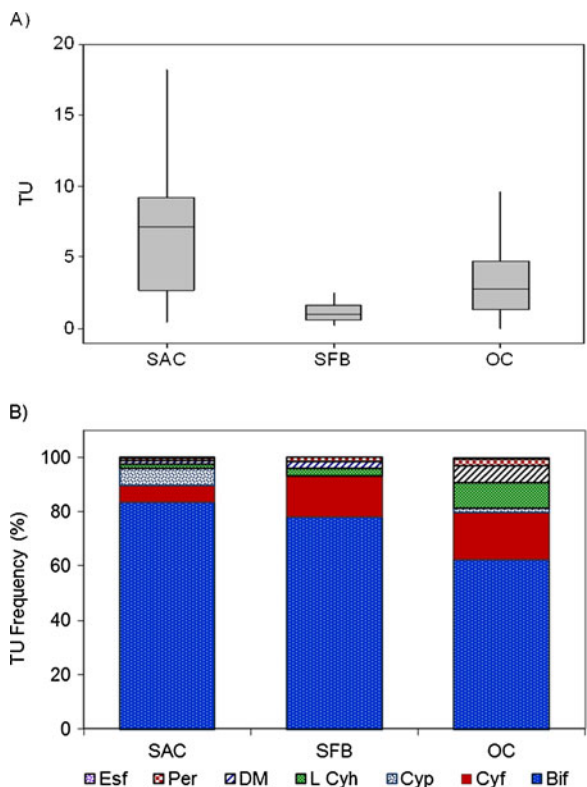
Fig. 8 Toxicity units (TUs) of sediment samples collected between April 2008 and June 2011 in the three sampling areas of California, USA (SAC, Sacramento area; SFB, San Francisco Bay area; OC, Orange County). **a** Boxplots of the number of TUs; **b** percentage of TUs accounted for by each pyrethroid. For boxplots, the *bottom* and the *top* of each box are the 25th and 75th quartiles, respectively. The median is the middle line in the box. Whiskers extend to the lowest or highest data point within 1.5 times the interquartile range

2.6 TUs). Sediment from the SAC had the highest level of TUs, containing a median concentration of 7.2 TUs. This was significantly higher than sediment from OC and SFB (medians 2.8 and 1.1 TUs, respectively; $p <$ 0.01; Fig. 8a). OC had significantly more TUs than did the SFB ($p = 0.004$). High TUs in SAC was attributed to sediment accumulation in the storm drain outfalls. Due to stream depth and configuration, there were no sediment depositions at the receiving water sampling site at Pleasant Grove Creek, thus sediments were not collected for pyrethroid analysis. Lower TUs in SFB may be due to lack of pyrethroid runoff into the urban creeks or due to lack of fine-grained sediment deposition at several of the sediment sampling sites (especially in Alamo Creek watershed). Amweg et al. (2006) and Holmes et al. (2008) also showed that SFB has lower toxicity than many other areas of the state.

Bifenthrin accounts for most of the potential sediment toxicity. For the entire study, bifenthrin accounted for 77 % of the TUs, with another 10 % due to cyfluthrin. Bifenthrin has been shown to be stable in sediments which partially account for its high prevalence (Budd et al. 2011). Cypermethrin, λ-cyhalothrin, deltamethrin, permethrin, and esfenvalerate accounted for the remaining TUs (Fig. 8b). The three areas of the state differed slightly in the percentage of TUs. In SAC, bifenthrin accounted for 83 % of the TUs. Cyfluthrin had the next largest percentage, but only accounted for 6 % of the TUs; all other pyrethroids individually were less than 5 %. Except for the lack of cypermethrin detections, the SFB most closely resembled the state totals; bifenthrin accounted for 78 % of the TUs followed by 15 % by cyfluthrin. No other pyrethroid accounted for more than 3 % of the TUs. In OC, cyfluthrin, λ-cyhalothrin, and deltamethrin accounted for a larger percentage of TUs than the sampling areas in northern California (17 %, 9 %, and 6 %, respectively). However, bifenthrin still accounted for the majority of TUs (63 %). Consistently, bifenthrin has been the biggest contributor to aquatic invertebrate toxicity (Weston et al. 2005; Amweg et al. 2006; Budd et al. 2007; Holmes et al. 2008; Hintzen et al. 2009; Ding et al. 2010; Delgado-Moreno et al. 2011).

Conclusion

Surface urban waters in the areas of this study frequently contain numerous different pesticide combinations at any given time. Many of these pesticides are at concentrations that are of concern, especially due to their frequent occurrence and the unknown effect of multi-pesticide combinations. The watersheds selected in this study had no reported agriculture pesticide use, thus pesticides detected were solely from urban applications. Many of the detected pesticides have high use by PMPs, appear in numerous homeowner products (with unknown amount of use), and move to surface waters via rain runoff (major transport mechanism) as well as less-defined transport during the dry season. Several pesticides detected in this study stand out above others and warrant more comprehensive study: bifenthrin, fipronil, 2,4-D, triclopyr, dicamba, and diuron. Imidacloprid might also be included on this list due to its high use and prevalence in surface waters. Continued monitoring of these pesticides in urban streams is warranted to clearly understand both spatial and temporal trends in pesticide concentrations that will allow effective mitigation measures to be put in place.

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