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PREDICTED TRANSPORT OF PYRETHROID INSECTICIDES FROM AN URBAN LANDSCAPE TO SURFACE WATER

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Abstract: The authors developed a simple screening-level model of exposure of aquatic species to pyrethroid insecticides for the lower American River watershed (California, USA). The model incorporated both empirically derived washoff functions based on existing, small-scale precipitation simulations and empirical data on pyrethroid insecticide use and watershed properties for Sacramento County, California, USA. The authors calibrated the model to in-stream monitoring data and used it to predict daily river pyrethroid concentration from 1995 through 2010. The model predicted a marked increase in pyrethroid toxic units starting in 2000, coincident with an observed watershed-wide increase in pyrethroid use. After 2000, approximately 70% of the predicted total toxic unit exposure in the watershed was associated with the pyrethroids bifenthrin and cyfluthrin. Pyrethroid applications for aboveground structural pest control on the basis of suspension concentrate categorized product formulations accounted for greater than 97% of the predicted total toxic unit exposure. Projected application of mitigation strategies, such as curtailment of structural perimeter band and barrier treatments as recently adopted by the California Department of Pesticide Regulation, reduced predicted total toxic unit exposure by 84%. The model also predicted that similar reductions in surface-water concentrations of pyrethroids could be achieved through a switch from suspension concentrate–categorized products to emulsifiable concentrate–categorized products without restrictions on current-use practice. Even with these mitigation actions, the predicted concentration of some pyrethroids would continue to exceed chronic aquatic life criteria. *Environ Toxicol Chem* 2013;32:2469–2477. © 2013 SETAC

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INTRODUCTION

Recent efforts to monitor pyrethroid insecticides in surface waters tributary to the Sacramento–San Joaquin Delta have targeted both agricultural and urban sources, including the effluent discharges of publicly owned treatment works [1]. Although pyrethroid insecticides are present in a wide variety of discharge types, storm-water discharges from urban landscapes are a major source in terms of both concentration and frequency of pyrethroid-related toxicity [1,2].

Monitoring studies focused on the point of discharge or relatively small waterways near pesticide sources tend to underestimate concentrations. Dilution and other dissipation pathways such as sedimentation and biotic and abiotic degradation may result in substantial attenuation in both concentration and bioavailability. Efforts to monitor pyrethroids and pyrethroid-related toxicity throughout the Sacramento–San Joaquin Delta have yielded sporadic evidence of pyrethroid activity [3] at environmentally detrimental concentrations. Toxicity thresholds were often below analytical chemistry detection limits.

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Pyrethroid use in urban settings affects the ultimate fate and environmental relevance of pyrethroids in receiving surface waters. Important contributing factors include application surface type and product formulation [4,5]. In the present study, we develop a simple screening-level model that incorporates these contributing factors, empirically derived washoff functions, and observed watershed conditions for the lower American River (California, USA) for a use and exposure period of 1995 through 2010. We aimed to make broad comparative predictions of pyrethroid exposure to investigate the relative proportion of predicted toxic exposure across pyrethroid active ingredients, product formulations, and sites of application (i.e., turf vs structural perimeter).

We focused on the lower American River below the Lake Natoma and Folsom Reservoirs because it is close to the Sacramento–San Joaquin Delta and within the Sacramento metropolitan area. Moreover, the tail-water hydrology of the lower American River is comparatively simple to model. In the present study, we document the development of the model and use its predictions of pyrethroid washoff to evaluate how patterns of pesticide use may influence the exposure of aquatic organisms in the river. We compared the baseline results of the model with alternative mitigation scenarios, including regulations for protection of surface waters recently adopted by the California Department of Pesticide Regulation. These regulations targeted pyrethroid use for structural pest control and landscape maintenance.

METHODS

The lower American River below Lake Natoma Reservoir flows through Sacramento County and the Sacramento metropolitan area. Surface runoff over much of Sacramento County is ultimately discharged to the lower American River through a system of storm drains and urban creeks. Given their dense population and urbanization, the lower American River and tributary watersheds and storm drain catchments are useful for studying how the patterns of pyrethroid use within an urbanized watershed may affect water quality in a river system of regional significance.

To assess source effects on pyrethroid concentration in the waters of the lower American River, we developed a simple screening-level exposure model in FORTRAN 77. The computation scheme to which FORTRAN 77 was applied is depicted in Supplemental Data, Figure S1. Within this model, we used reported historic landscape and structural pyrethroid use in Sacramento County, measured lower American River flow, measured Sacramento County precipitation amounts, and experimentally derived insecticide washoff coefficients to predict daily pyrethroid concentration at the river's lowest reach prior to its discharge to the Sacramento River from 1 January 1995 through 31 December 2010. The model uses these elements to predict the daily mass of available pyrethroid washed off from surfaces in the watershed during a precipitation event divided by the river flow plus precipitation runoff volume. For simplicity, the model does not account for 1) equilibrium partitioning processes, 2) settling and resuspension processes, 3) degradative losses within the river, 4) sorption to bed sediments, 5) atmospheric deposition, or 6) application of pyrethroid products obtained by consumers through retail sales. As such, the model is largely limited to evaluating how pyrethroid use may contribute to exposure of aquatic organisms by focusing on the basic mechanics of pyrethroid transport from their points of application to the river. In doing so, the model provides a snapshot of the relative proportions of the various urban pyrethroid active ingredients and sources and how these patterns change over time. Although we calibrated the model with the limited available in-river concentration data during this period, accurate prediction of concentrations in the river was not the primary purpose for which it was constructed.

Washoff functions

Pyrethroid washoff functions were obtained from previously published small-scale rainfall simulation experiments [4,5]. In these experiments, commercially available pyrethroid products were applied at label-specified rates to 0.64 m^2 concrete, turf, and bare soil test plots. Drop-forming rainfall simulators were used to simulate 1-h precipitation events with storm intensities of 25 mm/h and 50 mm/h. The elapsed time between application and rainfall simulation (i.e., set time) of products ranged from 1.5 h to 49 d. In total, 49 experiments were conducted with a range of product formulations, including emulsifiable concentrate, suspension concentrate, and granular formulations.

We compiled the data from these experiments and the functional form of each washoff profile analyzed. In all cases except the suspension concentrate on concrete, a linear function best approximated the observed washoff profile. A logarithmic function best fit the experimental treatments of suspension concentrate on concrete. However, we used a linear function (Equation 1) to standardize the washoff calculation

$$\frac{M_w}{M_{avail}} = \beta_1 P + \beta_0 \quad (1)$$

where M_w/M_{avail} is the fraction of mass washed off divided by the mass available, P is precipitation (centimeters), and β_1 and β_0 are the slope and intercept, respectively. To account for the effect of increased set time (Supplemental Data, Figure S2), Equation 1 was modified as in Equation 2 to arrive at the final functional form expressed in Equation 3.

$$\beta_1 = \beta_2 e^{-k_{deg} t} \quad (2)$$

$$\frac{M_w}{M_{avail}} = \beta_2 e^{-k_{deg} t} P + \beta_0 \quad (3)$$

where t was elapsed time from application in days and k_{deg}, β_0, and β_2 were the empirical parameters obtained from the simulated-rainfall experiments. Equation 3 was assumed to give a reasonable estimate of the true regression function of the washoff of differently formulated pyrethroid insecticides on variable surface types and different set times.

Final selected coefficients derived in the model-building and data-fitting processes are provided in Table 1. In deriving these coefficients, the data set was randomly divided to provide a model-building set and a model-validation set. We evaluated the predictive capability of the washoff function and the potential for predictive bias by comparing the mean square error of the building set and the mean squared prediction error of the validation set.

Flow and precipitation

We obtained daily average American River flow from the California Data Exchange Center for Lake Natoma Reservoir (http://cdec.water.ca.gov). We obtained daily accumulated precipitation depth from the California Irrigation Management Information System for Fair Oaks and Davis, California (http://cdec.water.ca.gov/queryTools.html).

Pesticide use report database

We downloaded raw pesticide user report data for 1995 through 2009 from the Pesticide Use Reporting (PUR) database maintained by Department of Pesticide Regulation (http://calpip.cdpr.ca.gov/main.cfm). We obtained provisional data for 2010 via direct communication with the Department of Pesticide Regulation. To prepare the pesticide-use data for model input, we applied 4 criteria to filter and cull records in the PUR database.

First, we filtered data for Sacramento County to obtain only structural pest control and landscape maintenance entries for

Table 1. Washoff function coefficients for formulations on various surfaces.

Treatment combination	β_2	β_0	$-k_{deg}$	r^2	N_{obs}
Concrete					
Emulsifiable concentrate	4.33E-4	4.78E-3	2.30E-3	0.466	143
Suspension concentrate	1.52E-3	1.13E-1	3.30E-3	0.782	86
Soil					
Emulsifiable concentrate	3.48E-4	7.91E-6	5.98E-3	0.617	42
Granule	2.37E-5	1.45E-4	5.02E-3	0.252	76
Suspension concentrate	4.15E-4	–1.99E-3	5.54E-3	0.917	41
Turf					
Emulsifiable concentrate	1.76E-5	–3.51E-5	9.95E-3	0.963	27
Granule	6.24E-6	–1.02E-4	5.49E-3	0.566	48
Suspension concentrate	4.99E-4	–6.08E-4	9.32E-3	0.967	27

pyrethroid active ingredients (Supplemental Data, Table S1). In the PUR database, entries for structural and landscape applications are usually dated as the first of the month. We manually converted dates other than the first of the month to the first of the month shown in the original entry.

Second, we used product names from the Department of Pesticide Regulation label finder (http://www.cdpr.ca.gov/docs/label/labelque.htm) to categorize each entry in the filtered database as a suspension concentrate, emulsifiable concentrate, granular, or other formulation type (Supplemental Data, Table S2). When a label finder query did not yield a clear means of categorization, we categorized the formulation type by inspecting the product label and material safety data sheet.

We removed all entries categorized as "other" under the assumption that these formulated products had little effect on surface-water quality. We then removed all entries for products with labels that specified indoor use only. At the same time, products labeled as permitting the treatment of subterranean termites were flagged and subjected to a belowground application screening procedure, discussed in greater detail in the Supplemental Data.

Watershed characteristics

We obtained regional land-use and land-cover data for the lower American River watershed from existing land-use and parcel data developed for a Sacramento regional air-quality study [6]. Land-use classes followed a US Geological Survey level II classification scheme [7]. The land-cover classes were tree and shrub, irrigated grass and ground cover, water, roof, other impervious, and pervious covers such as bare soil and nonirrigated grass [8]. The rational method was applied to proportions of the watershed with pervious and impervious cover to calculate an overall runoff coefficient of 0.35843. We used this coefficient to determine the storm-water discharge to the American River during precipitation events; the total flow at the modeling point (Discovery Park, Sacramento, CA, USA) was determined by adding this flow to the daily discharge at the upstream boundary of the domain (Nimbus Dam, Sacramento County, CA, USA, 38.63 N 121.21 W).

Pyrethroid apportionment

We coded the exposure model to apportion the monthly sum total of pyrethroid applications evenly over each day of the month and evenly over the developed portion of the watershed. Monthly total pyrethroid applications for landscape-maintenance purposes were assumed to have been applied entirely to turf. Monthly total aboveground pyrethroid applications for structural pest control were assumed to have been applied outdoors as a perimeter barrier spray. No assumption was made as to structural pest-control applications indoors other than the previously described culling of indoor use–only products from the PUR database.

Application of pyrethroids to building perimeters occurs over both pervious (e.g., soil) and impervious (e.g., concrete) surfaces. To estimate the relative fraction of perimeter landscape with pervious and impervious covers, we overlaid a high-resolution aerial image from 2006 with regional land-cover data [8]. We used the Urban Forest Effects random plot selection tool [9] to select 104 sample parcels stratified among 4 major urban land-use types on the basis of their proportional cover within the watershed. We selected 77 low-density residential parcels, 4 high-density residential parcels, 7 institutional parcels, and 16 commercial and industrial parcels. We obtained an average pervious perimeter fraction of 0.2638 and an average impervious perimeter fraction of 0.7362 for Sacramento County; we distributed aboveground structural pyrethroid applications to the PUR data accordingly.

RESULTS AND DISCUSSION

Model calibration

Because the exposure model did not account for partitioning or other attenuating processes between washoff and transport to the river, we introduced an attenuation coefficient to scale the predicted river concentration to an observed concentration. We obtained the attenuation coefficient by regressing observed pyrethroid concentration for the precipitation seasons of 2009 and 2010 [2] against model-predicted concentration. We only used data from the American River within 1 km of its confluence with the Sacramento River and for days of precipitation that yielded a pyrethroid detection in river water (>1 ng/L). Of the resulting 12 data records, 5 had detectable concentrations of pyrethroids. All of the 5 contained bifenthrin at concentrations from 1.1 ng/L to 5.6 ng/L, and 2 of the samples had detectable concentrations of permethrin (Table 2). Although the exposure model could only be calibrated to bifenthrin, model predictions fit these data reasonably well (Table 2). In addition, model predictions for the other pyrethroids were near or below the reported analytical quantification limit of 1 ng/L, consistent with the nondetections in the published monitoring data [2].

Table 2. Comparison of observed and predicted pyrethroid concentrations

	Measured concentration[a] (ng/L)		Model predicted concentration (ng/L)						
Monitoring Date	Bif	Perm	Bif	Cyf	Cyhal	Cyper	Delta	Fenv	Perm
2/18/2009	5.6	5.0	6.7	0.9	0.4	1.3	0.6	0	0.7
2/23/2009	ND	ND	5.3	0.7	0.4	1.1	0.5	0	0.8
3/3/2009	ND	ND	4.6	0.6	0.6	1.1	0.5	0	0.9
10/13/2009	ND	ND	4.8	2.9	0.3	1.1	0.6	0	0.9
10/14/2009	ND	ND	5.1	3.0	0.3	0.9	0.6	0	0.4
1/18/2010	ND	ND	1.4	1.1	0.1	0.5	0.3	0	0.2
1/19/2010	1.8	ND	1.3	1.0	0.1	0.5	0.3	0	0.1
1/20/2010	2.1	ND	1.1	0.9	0.1	0.5	0.3	0	0.2
1/22/2010	ND	ND	1.2	1.0	0.1	0.4	0.3	0	0.1
12/18/2010	1.1	ND	0.2	0.1	0	0	0.3	0	0
12/19/2010	1.6	7.0	0.2	0.1	0	0	0.3	0	0

[a]Measured concentration data from Weston and Lydy [2].
Bif = bifenthrin; Cyf = cyfluthrin/beta cyfluthrin; Cyhal = cyhalothrin/lambda cyhalothrin; Cyper = cypermethrin; Delta = deltamethrin; Fenv = fenvalerate/esfenvalerate; Perm = permethrin; ND = not detected at or above 1 ng/L, predicted concentrations less than 1 ng/L can be considered non-detections.

Pyrethroid use in Sacramento County

For each calendar year, we excluded between 62% and 84% of the total pyrethroid mass listed in the PUR database from the model input data file (Figure 1). The screening of belowground structural pest-control applications was responsible for the majority of this mass difference.

The belowground screening procedure was rational in its formulation because pyrethroids have high organic carbon partition coefficient (K_{OC}) values and are not mobile in soil, but we aimed to obtain independent evidence whether omission of application data was supported. We based our screening method on an approximation of a preconstruction whole-house termite treatment. Such treatments are required for all Federal Housing Administration–conforming home loans in designated termite-affected areas, including California. We modeled an exposure period of 1995 through 2010, straddling a boom and crash in housing construction statewide. Assuming that a relatively fixed percentage of homes under construction would receive a preconstruction termite treatment, as would be required by a Federal Housing Administration–insured loan, we expected to observe a strong correlation between housing starts (i.e., permits for new single-family home construction) and mass of below-grade pyrethroid screened from the PUR database.

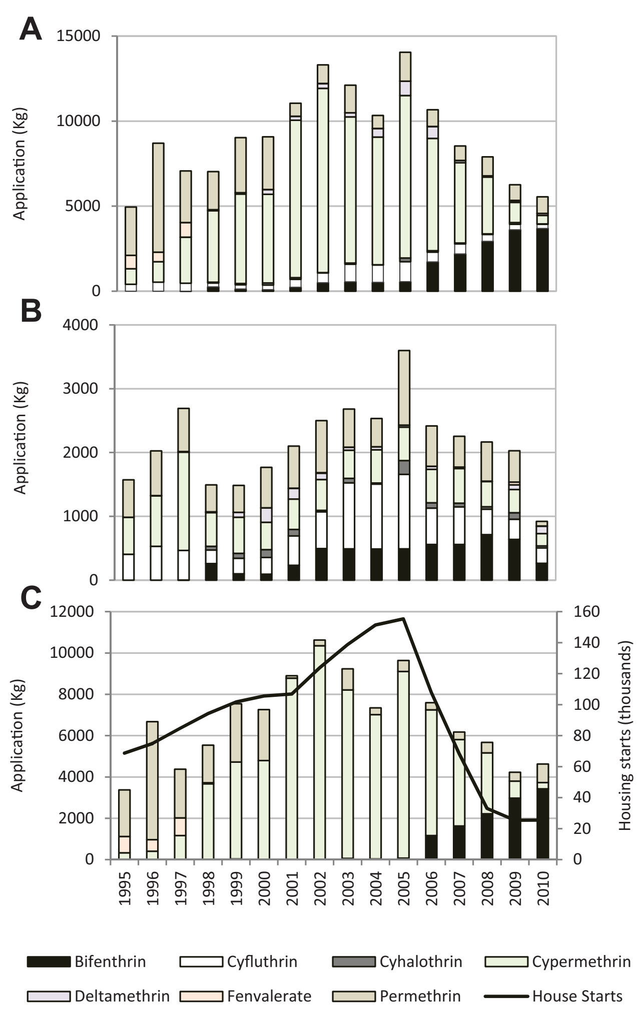

Figure 1. (A) Unadjusted pyrethroid totals for structural pest control and landscape maintenance applications. (B) Adjusted pyrethroid totals for structural pest control and landscape maintenance applications, including only exterior and aboveground applications. (C) California housing starts compared to whole-house preconstruction termite application totals removed from the pesticide use data.

Total annual pyrethroid mass removed and total annual housing starts were highly correlated (Pearson's $r = 0.768$, 2-sided $p < 0.001$; Figure 1c). Although the screening procedure resulted in a substantial removal of applied mass, this removal appeared to be well supported. Details regarding the below-ground screening procedure and associated error estimates are provided in Supplemental Data.

Observations regarding the mass amounts applied and the mass amounts removed from the database also revealed a trend in pyrethroid use in Sacramento County. Total structural and landscape pyrethroid use was fairly consistent until 2000, at which point pyrethroid use increased steadily. This steady increase was most likely related to the US Environmental Protection Agency (USEPA)–negotiated phase-out of 2 organophosphate insecticides, diazinon and chlorpyrifos, from most urban uses. As a result, there was also a shift in the specific pyrethroid active ingredient used. In the late 1990 s, use of subterranean termite-control products containing permethrin and fenvalerate steadily declined, while cypermethrin steadily increased, followed by a steady decline of cypermethrin and a steady increase of bifenthrin from approximately 2005 to the present (Figure 1c). The change in active ingredient could be because of their respective efficacies toward termites; emulsions of 0.5% are required for permethrin and fenvalerate, 0.25% for cypermethrin, and 0.06% for bifenthrin. Bifenthrin is the only pyrethroid that has grown consistently in the nonagricultural Sacramento County market despite the decline in total pyrethroid use since 2005. Without screening of the database, such trends in use are obscured in the unadjusted PUR database totals.

Exposure-model predictions

Patterns in concentration trends generated by the calibrated exposure model generally were consistent with the observed pattern of pyrethroid use (Figure 2). The concentration profiles for cyhalothrin, cypermethrin, deltamethrin, fenvalerate, and permethrin were relatively static over the model period. Modeled concentrations of bifenthrin and cyfluthrin peaked in about 2007, coincident with the increase in their use. However, maximum and upper-quartile predictions were highly sensitive to individual entries in the PUR database. For example, the predicted peak cypermethrin concentration of 20.9 ng/L on 18 April 1997 reflected a single PUR database entry of 232 kg recorded for the same month; this entry is a statistical outlier (Grubb's test, $Z = 35.5$), with 99.9% of all cypermethrin entries below 32 kg ($n = 9733$). Similarly, the 2 predicted cyfluthrin concentrations above 20 ng/L on 7 and 8 February 2007 reflected a single PUR database entry of 364 kg in January 2007. This single cyfluthrin entry is a statistical outlier (Grubb's test, $Z = 71.1$), with 99.9% of all cyfluthrin entries below 63 kg ($n = 15\,882$). There was no justification for removal of these statistical outliers; we assumed that amounts reported in the PUR database were accurate. Nevertheless, such values demonstrate the sensitivity of the exposure model to individual entries in the PUR database. For this reason, our discussion focuses on averages.

Average predicted concentrations of pyrethroids during periods of precipitation, when washoff and river exposure would be expected, ranged from 0.0 ng/L to 7.1 ng/L (Table 3), with the greatest average concentration routinely occurring in October and November (data not shown). Reasons for high concentrations during these months included the accumulation of available insecticide through the dry summer coupled with low river flows and correspondingly low dilution capacity.

The USEPA has not yet developed water-quality criteria for pyrethroids. Fojut et al. [10] developed pyrethroid water-quality

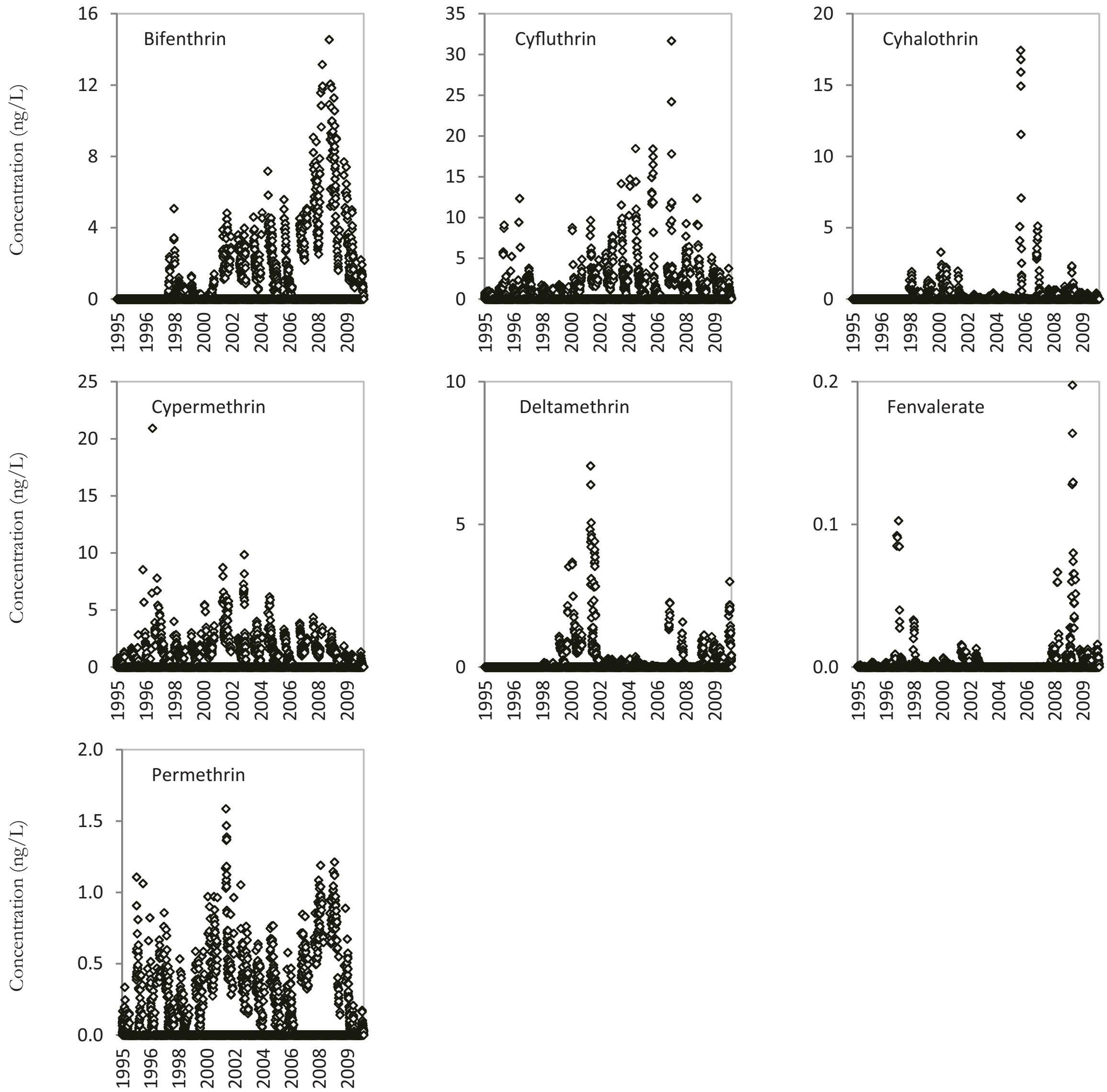

Figure 2. Baseline predictions of chemical concentrations generated by an exposure model for 1995 to 2010. Symbols represent predicted daily concentration in the lower American River.

criteria by modifying the USEPA's method of criteria derivation. Consistent with the USEPA method, Fojut et al. created a species sensitivity distribution on the basis of data for all aquatic species with suitable median effective and lethal concentration data, and established the acute criterion at one-half the 5th percentile of that distribution. For 2 pyrethroids (cyfluthrin and cypermethrin), Fojut et al. [10] made an a posteriori adjustment to the criteria by using the first percentile of the distribution, believing the fifth percentile to not be adequately protective of the amphipod *Hyalella azteca*. We did not make this adjustment in the American River analysis because *H. azteca* was not a focus of the present study and it was necessary to retain consistency with established use of the fifth percentile. Fojut et al. derived both acute (1-h average concentration) and chronic (4-d average concentration) water-quality criteria on the basis of whether the criterion was exceeded more than once every 3 yr on average. Runoff flowing to the American River has shown no appreciable decline in pyrethroid concentrations after several days of rain, and elevated pyrethroid concentrations in the river persist for up to 3 d [2]. Thus, although we do not have sufficient data to support use of the chronic criteria, exposure is likely to be well over 1 h and use of the acute criteria is well justified (Table 4).

We used the acute water-quality criteria to express model-predicted pyrethroid concentrations as toxic units, that is, the ratio of the predicted concentration to the criteria. Toxic units for deltamethrin and fenvalerate/esfenvalerate could not be determined because of the absence of similarly derived criteria for these pyrethroids; but the model predicted no fenvalerate/esfenvalerate in the river, and deltamethrin concentrations were among the lowest of the pyrethroids. Because pyrethroids share the same mode of action, effects of pyrethroid insecticides often are assumed to be additive [1,11], and summing pyrethroid toxicities has been recommended in applying the water-quality criteria [10]. Therefore, the model-predicted sum of toxic units is a reasonable means of estimating the aggregate toxic effect of pyrethroids discharged to the lower American River during precipitation events.

The predicted sum of toxic units indicated that pyrethroid concentrations in the American River far exceeded the water-quality criteria (Figure 3). The potential for acute toxicity to sensitive aquatic species, as predicted by the model, is supported by the frequent observation of mortality or paralysis of *H. azteca* when exposed to river water collected during precipitation events [2]. Again, as with the individual pyrethroid

Table 3. Daily average river concentration in ng/L (standard deviation)[a] predicted by the model of exposure from 1995 to 2010.

Year	Bif	Cyf	Cyhal	Cyper	Delta	Fenv	Perm
1995	–	0.5 (0.3)	–	0.5 (0.4)	–	0.0 (0.0)	0.2 (0.2)
1996	–	1.1 (1.8)	–	0.9 (1.3)	–	0.0 (0.0)	0.3 (0.2)
1997	0.0 (0.0)	1.7 (2.1)	–	2.4 (3.0)	0.0 (0.0)	0.0 (0.0)	0.4 (0.2)
1998	0.4 (0.9)	0.6 (0.4)	0.8 (0.5)	0.9 (0.8)	0.0 (0.0)	0.0 (0.0)	0.2 (0.1)
1999	0.4 (0.3)	0.8 (0.5)	0.4 (0.4)	0.9 (0.6)	0.2 (0.3)	0.0 (0.0)	0.2 (0.1)
2000	0.1 (0.1)	1.1 (1.5)	0.6 (0.6)	1.2 (1.1)	0.7 (0.8)	0.0 (0.0)	0.3 (0.2)
2001	1.1 (0.9)	2.7 (1.9)	0.7 (0.5)	2.9 (1.7)	1.6 (1.6)	0.0 (0.0)	0.7 (0.3)
2002	2.6 (0.9)	2.8 (0.9)	0.2 (0.1)	2.8 (1.4)	1.1 (1.3)	0.0 (0.0)	0.5 (0.2)
2003	2.3 (0.9)	4.8 (2.7)	0.1 (0.1)	2.3 (2.1)	0.1 (0.1)	0.0 (0.0)	0.4 (0.1)
2004	2.6 (1.4)	4.1 (4.0)	0.1 (0.1)	2.4 (1.4)	0.1 (0.1)	0.0 (0.0)	0.4 (0.2)
2005	1.9 (1.3)	3.4 (4.5)	1.4 (3.9)	1.3 (0.8)	0.1 (0.0)	0.0 (0.0)	0.2 (0.1)
2006	1.5 (1.4)	1.1 (1.1)	0.5 (1.2)	1.0 (1.0)	0.2 (0.6)	0.0 (0.0)	0.3 (0.2)
2007	5.0 (1.7)	4.0 (5.9)	0.5 (0.9)	2.0 (0.7)	0.3 (0.5)	0.0 (0.0)	0.6 (0.1)
2008	7.1 (3.2)	4.1 (2.4)	0.4 (0.1)	1.7 (0.7)	0.0 (0.0)	0.0 (0.0)	0.9 (0.1)
2009	5.3 (2.3)	1.9 (1.1)	0.6 (0.4)	1.0 (0.4)	0.5 (0.3)	0.0 (0.0)	0.6 (0.3)
2010	1.6 (1.1)	1.3 (0.9)	0.2 (0.1)	0.4 (0.3)	0.6 (0.6)	0.0 (0.0)	0.1 (0.1)

[a]Calendar year average of predicted pyrethroid concentrations for days of measured precipitation.
Bif = bifenthrin, Cyf = bcyfluthrin/beta cyfluthrin, Cyhal = bcyhalothrin/lambda cyhalothrin, Cyper = bcypermethrin, Delta = bdeltamethrin, Fenv = bfenvalerate/esfenvalerate, Perm = bpermethrin.

concentrations, the sum of the toxic unit metric reflects the sensitivity of the exposure model to individual data points. Nevertheless, the watershed exposure model predicted water quality frequently exceeding 5 toxic units after 2000. The calendar year 2000 is a logical division for comparing water quality in the lower American River before and after phase-out of many organophosphates. On days when the exposure model predicted pyrethroid discharge to the river (i.e., during precipitation events), concentrations exceeded 5 toxic units from 1995 through 1999 on 1% of days, whereas concentrations exceeded 5 toxic units on 12% of days from 2000 through 2010. Moreover, when total toxic unit exposure was predicted to be its greatest, between 2003 and 2008, bifenthrin and cyfluthrin/β-cyfluthrin were responsible for approximately 75% of the total exposure.

In addition to predictions of accumulated toxic exposure, the model allows an investigation into the role of application site (e.g., landscape vs structure) and product formulation (e.g., suspension concentrate, emulsifiable concentrate, granular). The percentage of distribution of toxic units across surface type and formulation type varied little among modeled years. Accordingly, we summarized the distribution as an average of all years modeled. Application of suspension concentrate–categorized products for exterior, aboveground structures accounted for an average of 97.1% of the accumulated toxic exposure (Figure 4) despite the fact that suspension concentrate–categorized products comprised 26.7% of the total average mass of pyrethroid applied in the watershed. This model prediction is a product of 3 factors. First, toxic unit is a weighted metric. Permethrin comprised approximately 25% of the total pyrethroid mass applied in most years, but permethrin is approximately 2 to 10 times less toxic than the other pyrethroids and, thus, contributes comparatively less toxic exposure in the river. Second, more than 99% of the permethrin applications were with emulsifiable concentrate–categorized products. Third, the prediction in part reflects that in our washoff functions suspension concentrate–categorized products applied to impervious surfaces yield the greatest fractional washoff. The dominance of suspension concentrate structural applications in the model-predicted effects on water quality in the American River fundamentally limits mitigation options.

Mitigation options

In July 2012, the Department of Pesticide Regulation announced new regulations restricting pyrethroid applications in a nonagricultural setting to the exterior of buildings and structures and to landscapes. The regulations significantly curtailed the application of pyrethroids as a perimeter barrier spray, limiting applications to the vertical surface of a structure and eliminating all but localized applications to horizontal impervious surfaces, such as concrete patios, walkways, and driveways (Supplemental Data, Table S3). The Department of Pesticide Regulation placed additional limitations on bifenthrin use given its prevalence in monitoring data and estimated fractional contribution to toxicity.

Table 4. Published fifth percentile acute criteria values (ng/L)[a]

Bif	Cyf	Cyhal	Cyper	Delta[b]	Fenv[b]	Perm
4	2	1	6	–	–	10

[a]Acute criteria values from Fojut et al. [10].
[b]Acute criteria values for deltamethrin and fenvalerate/esfenvalerate were not derived.
Bif = bifenthrin; Cyf = cyfluthrin/beta cyfluthrin; Cyhal = cyhalothrin/lambda cyhalothrin; Cyper = cypermethrin; Delta = deltamethrin; Fenv = fenvalerate/esfenvalerate; Perm = permethrin.

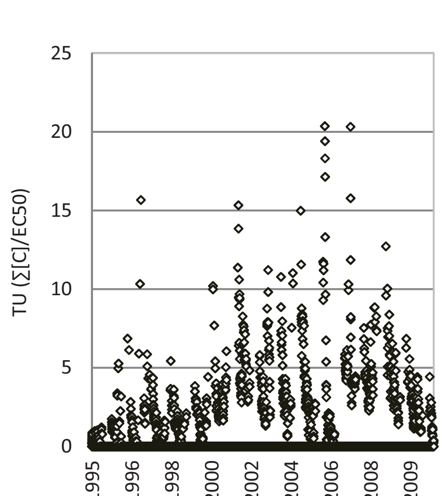

Figure 3. Exposure model-predicted daily sum of toxic units (TUs).

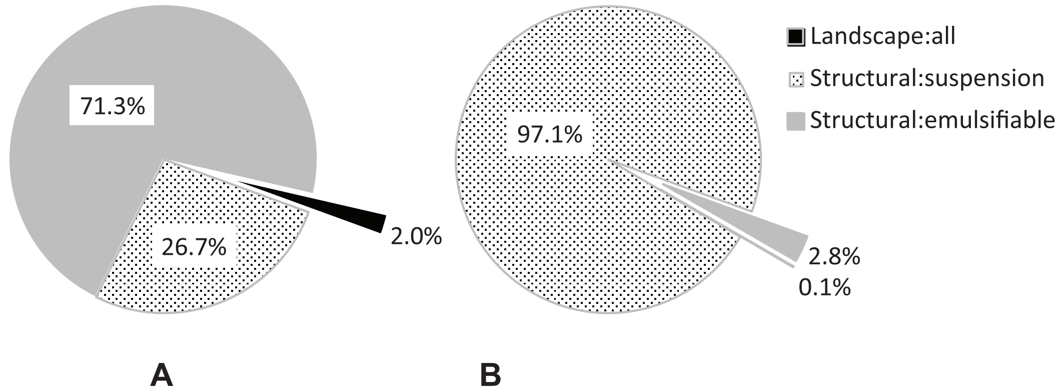

Figure 4. Comparison of mass applied versus accumulated toxic units as a function of dominant surface and formulation type (surface:formulation). (**A**) Distributed mass applied aboveground (average of all years modeled). (**B**) Distributed total toxic units (average of all years modeled).

A key assumption of the model is that all aboveground applications in the structural pest-control category are to the exterior perimeter of buildings. The model further distributes these applications to both pervious and impervious surfaces. Per these assumptions, the Department of Pesticide Regulation–adopted surface water–protection rules would reduce mass applied to the pervious and impervious perimeter fraction of structural pest control by approximately 50% and 80%, respectively. The model predicted that these regulations would have resulted in a reduction in total annual toxic unit exposure of nearly 84% (Figure 5). Because of the model's assumption that structural pest control is only a perimeter treatment, these estimated reductions in toxic unit exposure likely represent an upper bound.

To obtain these reductions in total annual toxic unit exposure requires a substantial change in current pest-control practices. Aboveground pyrethroid applications in Sacramento County are overwhelmingly for structural pest-control purposes and use suspension concentrate–categorized products. The new surface-water protection rules drastically curtail the permitted use of these products for the postconstruction treatment of building perimeters. Such a substantial limitation could possibly promote a change in active ingredients applied for postconstruction structural pest control. Products already available for pest control include imidacloprid and fipronil. Given the recent controversy over the potential effects of neonicotinoids on honey bees (*Apis mellifera*) [12] or the nontarget toxicity of fipronil [13], it is not clear if such a substitution from pyrethroids would result in a net environmental or water-quality benefit. Some degradation products of fipronil have equal or greater toxicity than fipronil itself [14,15].

An alternative to the rules adopted by the Department of Pesticide Regulation would be a shift to the use of emulsifiable concentrate formulations in lieu of suspension concentrate formulations. Such a substitution of formulation-categorized mass would result in equivalent gains in water quality (Figure 5) while allowing pest-control operators to continue postconstruction pest-control treatments in current fashion. Such a switch, however, would have environmental and economic effects. Manufacturers of pesticide products have moved away from solvent-based formulations to reduce flammability and phytotoxicity, to improve safety in handling and transport [16], and to

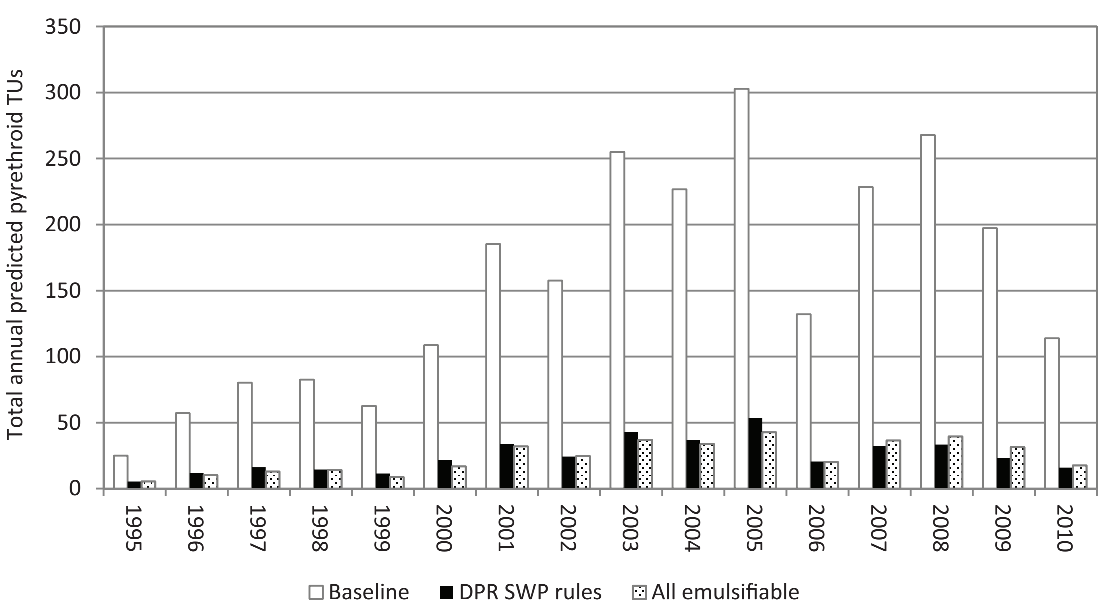

Figure 5. Comparison of hypothetical mitigation on a total annual predicted pyrethroid toxic unit (TU) basis. Department of Pesticide Regulation (DPR) surface water protection (SWP) rules as adopted with stricter provisions applied to bifenthrin applications. All emulsifiable = no change in annual pyrethroid mass applied, but all mass is applied as an emulsifiable concentrate.

reduce volatile organic emissions with ozone forming potential [17]. Pest-control applicators have similarly moved away from solvent-based formulations because of odors and customer complaints [18]. Consumer acceptance would likely represent a formidable obstacle to postconstruction emulsifiable concentrate–based pest control. In addition, the model-predicted gains of switching to emulsifiable concentrate formulations were based almost entirely on the observed difference in washoff function of emulsifiable concentrate as opposed to suspension concentrate treatments on concrete. The suspension concentrate washoff function used in the exposure model was derived from a single suspension concentrate–formulated product, yet the categorizing of suspension concentrate–formulated products in the PUR data aggregated all nonsolvent–based liquid formulations, including micronencapsulated suspensions and wettable powders (Supplemental Data, Table S1). We are uncertain whether these formulations would yield similar washoff functions as derived for the suspension concentrate formulation.

On the basis of the model predictions presented in the present study, the Department of Pesticide Regulation's surface-water protection rules appear to address the principal-use behavior. However, even after simulating mitigation measures, model-predicted pyrethroid concentrations would still occasionally exceed proposed aquatic life criteria. Furthermore, given the comparatively high dilution capacity of the American River, regulatory protected surface waters such as urban creeks would have even higher predicted pyrethroid concentrations.

CONCLUSION

We developed a watershed-level pyrethroid insecticide exposure model for the lower American River watershed and used it to develop retrospective predictions of in-stream pyrethroid concentrations and toxic unit exposure. Model predictions suggested that since 2000, approximately 70% of the predicted total toxic unit exposure in the watershed was associated with the pyrethroids bifenthrin and cyfluthrin/β-cyfluthrin. Pyrethroid applications for aboveground structural pest-control purposes utilizing suspension concentrate–categorized product formulations accounted for more than 97% of the total toxic unit exposure. Given the excedence of toxicity thresholds, impairment of invertebrate biota may occur, particularly in storm-water events. The relationship to declines of fish populations within the Delta is still unclear.

Modeled implementation of mitigation strategies, such as those recently adopted by the Department of Pesticide Regulation, yielded an approximate 84% reduction in predicted total toxic unit exposure in all modeled years. The exposure model assumes that all aboveground exterior structural pest control is in the form of a perimeter barrier spray, and as such, the gains derived from implementing the recently adopted Department of Pesticide Regulation surface-water protection rules are through application mass reductions imposed by the severe curtailment of currently permissible structural pest-control applications. Such curtailment could possibly drive pest-control operators to use permitted insecticides that do not contain pyrethroids. Products containing imidacloprid and fipronil would likely increase their market share for urban pest control. The environmental effects of such a shift are unclear.

Similar reductions in toxic unit exposure could be achieved through a movement toward pyrethroid-containing emulsifiable concentrate formulations. Based on our model predictions, such a shift would allow the continued use of pyrethroids as they are applied today, thus avoiding a potentially harmful or environmentally net-neutral switch to the use of other active ingredients. However, there would likely be manufacturer and consumer opposition to such a shift given various human health and environmental concerns related to the solvents used in emulsifiable concentrate formulations.

On the basis of our results, we suggest that a concerted effort be made to monitor the effects of the California Department of Pesticide Regulation's surface-water protection regulations, including in Delta surface waters. We suggest monitoring not only concentrations of pyrethroids and their potential replacement active ingredients in ambient surface water but also market trends in pesticide use. The PUR database summarizes pesticide-use market trends and is available to pesticide regulators and water-quality managers. However, use of the PUR data can lead to incorrect generalizations given that it contains potentially erroneous entries that can cause substantial errors in watershed modeling. Collecting additional information on indoor versus outdoor application and aboveground versus belowground application also would be valuable. Such additions would significantly improve the utility of the PUR database.

SUPPLEMENTAL DATA

Figures S1–S2.
Tables S1–S4. (164 KB DOCX).

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