Published in final edited form as:
Environ Toxicol Chem. 2013 November ; 32(11): 2469–2477. doi:10.1002/etc.2352.

Predicted Transport Of Pyrethroid Insecticides From An Urban Landscape To Surface Water

Brant Jorgenson[1], **Larry Brown**[2], **Erica Fleishman**[3], **Kate Macneale**[4], **Daniel Schlenk**[5,*], **Nat Scholz**[4], **Julann Spromberg**[4], **Inge Werner**[6], **Don Weston**[7], **Thomas M. Young**[1], **Minghua Zhang**[8], and **Qingfu Zhao**[9]

[1]Agricultural and Environmental Chemistry Graduate Group, University of California, Davis, CA USA

[2]U.S. Geological Survey, Sacramento, CA USA

[3]John Muir Institute of the Environment, University of California, Davis, CA USA

[4]Northwest Fisheries Science Center, NOAA Fisheries Service, Seattle, WA USA

[5]Department of Environmental Sciences, University of California, Riverside, CA USA

[6]Swiss Centre of Applied Ecotoxicology, EAWAG/EPFL, Dubendorf, Switzerland 8600

[7]Department of Integrative Biology, University of California, Berkeley, CA USA

[8]Department of Land, Air and Water Resources, University of California, Davis, CA USA

[9]Electrical and Computer Engineering, University of California, Davis, CA USA

Abstract

We 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. We 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 above-ground structural pest control on the basis of suspension concentrate 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.

*Corresponding Author: Daniel Schlenk, Department of Environmental Sciences, University of California, Riverside, Riverside, CA 92521 USA, Tel: (951) 827-2018, Fx: (951) 827-3393, Daniel.schlenk@ucr.edu.

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.

Pyrethroid use in urban settings affects the ultimate fate and environmental relevance of pyrethroids in exposed surface waters. Whether use is over pervious or impervious surfaces and the particular product formulation can affect off-target transport [4,5]. In this paper, 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 versus structural perimeter).

We focused on the lower American River below Folsom Reservoir 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. Here, we document development of the model and use its predictions of pyrethroid washoff to evaluate how patterns of pesticide use may affect organism exposure in the river. We compared the baseline results of the model to alternative mitigation scenarios, including regulations for protection of surface waters recently adopted by the California Department of Pesticide Regulation (DPR). 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 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

NIH-PA Author Manuscript
NIH-PA Author Manuscript

River from January 1, 1995 through December 31, 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 one-hour precipitation events with storm intensities of 25 mm/hr and 50 mm/hr. The elapsed time between application and rainfall simulation (i.e., set time) of products ranged from 1.5 hours to 49 days. In total, 49 experiments were conducted with a range of product formulations, including emulsifiable concentrate (EC), suspension concentrate (SC), and granular (GR) 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 (Eq. 1) to standardize the washoff calculation:

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

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

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

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

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. Eq. 3 was assumed 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 process are provided in Table 1. In deriving these coefficients, the dataset 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 (CDEC) for Lake Natoma Reservoir (http://cdec.water.ca.gov). We obtained daily accumulated precipitation depth from the California Irrigation Management Information System (CIMIS) for Fair Oaks and Davis, California (http://wwwcimis.water.ca.gov).

PUR Database

We downloaded raw pesticide user report (PUR) data for 1995 through 2009 from the PUR database maintained by DPR (http://www.cdpr.ca.gov). We obtained provisional data for 2010 via direct communication with DPR. To prepare the pesticide use data for model input, we applied four 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 pyrethroid active ingredients (Table 2). 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 DPR label finder (http://www.cdpr.ca.gov)to categorize each entry in the filtered database as a suspension concentrate, emulsifiable concentrate, granular, or other formulation type (Table 3). 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 below-ground application screening procedure, discussed in greater detail in Supplemental Materials.

Watershed Properties

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 U.S. Geological Survey level II classification scheme [7]. The land cover classes were tree and shrub canopy, irrigated grass and ground, water, roof, and other impervious and pervious covers such as bare soil and non irrigated 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 stormwater discharge to the American River during precipitation events; the total flow at the modeling point (Discovery Park) was determined by adding this flow to the daily discharge at the upstream boundary of the domain (Folsom Dam).

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 above-ground 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 from xxxx. We used the Urban Forest Effects (UFORE) random plot selection tool [9] to select 104 sample parcels stratified among four major urban land use types on the basis of their proportional cover within the watershed. We selected 77 low-density residential parcels, four 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 above-ground 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 a kilometer 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, five had detectable concentrations of pyrethroids. All of the five contained bifenthrin at concentrations from 1.1 to 5.6 ng/L, and two of the samples had detectable concentrations of permethrin (Table 4). Although the exposure model could only be calibrated to bifenthrin, model predictions fit these data reasonably well (Table 4). Additionally, model predictions for the other pyrethroids were near or below the reported analytical quantification limit of 1 ng/L, consistent with the non-detections in the published monitoring data [2].

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 2). The screening of below-ground structural pest control applications was responsible for the majority of this mass difference.

The below-ground screening procedure was rational in its formulation because pyrethroids have high Koc 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 pre-construction whole-house termite treatment. Such treatments are required for all Federal Housing Administration (FHA) 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 pre-construction termite treatment, as would be required by a FHA insured loan, we expected to observe a strong correlation between housing starts (i.e., permits for new singlefamily home construction) and mass of below-grade pyrethroid screened from the PUR database.

Total annual pyrethroid mass removed and total annual housing starts were highly correlated (Pearson's $r = 0.768$, two-sided $p < 0.001$) (Figure 2c). Although the screening procedure resulted in a substantial removal of applied mass, this removal appeared to be well supported.

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 use increased steadily. This steady increase was most likely related to the US Environmental Protection Agency (EPA)-negotiated phase-out of two 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 1990s, 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 in the mid- to late-2000s (Figure 2c). The change in active ingredient could be due to their respective efficacies towards 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 non-agricultural 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 3). 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 April 18, 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 kilograms ($n = 9{,}733$). Similarly, the two predicted cyfluthrin concentrations above 20 ng/L on February 7 and 8, 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 to 7.1 ng/L (Table 5), 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 EPA has not yet developed water quality criteria for pyrethroids. Fojut *et al*. [8] developed pyrethroid water quality criteria by modifying the EPA's method of criteria derivation.. Consistent with EPA's method, Fojut et al. created a species sensitivity distribution on the basis of data for all aquatic species with suitable EC_{50}/LC_{50} data, and established the acute criterion at one-half the 5th percentile of that distribution. For two pyrethroids (cyfluthrin and cypermethrin), Fojut *et al*. [8] made an *a posteriori* adjustment to the criteria by using the 1st percentile of the distribution, believing the 5th 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 a focus of this study, and to retain consistency with established use of the 5th percentile. Fojut et al. derived both acute (1-hour average concentration) and chronic (4-day average concentration) water quality criteria on the basis of whether the criterion was exceeded more than once every three years on average [8]. 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 three days [2]. Thus, although we do not have sufficient data to support use of the chronic criteria, exposure is likely to be well over one hour, and use of the acute criteria is well justified (Table 6).

We used the acute water quality criteria to express model-predicted pyrethroid concentrations as toxic units (TU), that is, the ratio of the predicted concentration to the criteria. TUs for deltamethrin and fenvalerate/esfenvalerate could not be determined due to 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 among the pyrethroids. Because pyrethroids share the same mode of action, effects of pyrethroid insecticides often are assumed to be additive [1,9], and summing pyrethroid toxicities has been recommended in applying the water quality criteria [8]. Therefore, the model-predicted sum of TUs 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 TUs indicated that pyrethroid concentrations in the American river far exceeded the water quality criteria (Figure 4). 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 concentrations, the sum of the TU metric reflects the sensitivity of the exposure model to individual data points. Nevertheless, the watershed exposure model predicted frequent excursions in water quality exceeding 5 TU 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 use of many organophosphates. On days when the exposure model predicted pyrethroid discharge to the river (i.e., during precipitation events), concentrations exceeded 5 TU from 1995 through 1999 on 1% of days, whereas concentrations exceeded 5 TU on 12% of days from 2000 through 2010. Moreover, when total TU exposure was predicted to be its greatest, between 2003 and 2008, bifenthrin and cyfluthrin/beta 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 versus structure) and product formulation (e.g., SC, EC, GR). The percent distribution of toxic units across surface type and formulation type varied little amongst modeled years. Accordingly, we summarized the distribution as an average of all years modeled. Application of SC categorized products for exterior, above-ground structures accounted for an average of 97.1% of the accumulated toxic exposure (Figure 5) despite the fact that SC categorized products comprised 26.7% of the total average mass of pyrethroid applied in the watershed. This model prediction is a product of three factors. First, TU is a weighted metric. Permethrin comprised about 25% of the total pyrethroid mass applied in most years, but permethrin is about 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 EC categorized products. Third, the prediction in part reflects that in our washoff functions, SC categorized products applied to impervious surfaces yield the greatest fractional washoff. The dominance of SC structural applications in the model-predicted effects on water quality in the American River fundamentally limits mitigation options.

Mitigation Options

In July 2012, DPR announced new regulations that restricted pyrethroid applications in a non-agricultural 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 (Table 7). The DPR placed additional limitations on bifenthrin use given its prevalence in monitoring data and estimated fractional contribution to toxicity.

A key assumption of the model is that all above-ground 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 DPR-adopted surface water protection rules would reduce mass applied to the pervious and impervious perimeter fraction of structural pest control by about 50% and 80%, respectively. The model predicted that these regulations would have resulted in a reduction in total annual TU exposure of nearly 84% (Figure 6). Due to the model's assumption that structural pest control is only a perimeter treatment, these estimated reductions in TU exposure likely represent an upper bound.

To obtain these reductions in total annual TU exposure requires a substantial change in current pest control practices. Above-ground pyrethroid applications in Sacramento County are overwhelmingly for structural pest control purposes and use SC categorized products. The new surface-water protection rules drastically curtail the permitted use of these products for the post-construction treatment of building perimeters. Such a substantial limitation could possibly promote a change in active ingredients applied for post-construction structural pest control. Products already available for pest control include imidacloprid and fipronil. Given the recent controversy of potential effects of neonicotinoids on honey bees (*Apis mellifera*) [12,14] or non-target toxicity of fipronil, 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 [10.11].

An alternative to the rules adopted by DPR would be a shift to the use of EC formulations in lieu of SC formulations. Such a substitution of formulation-categorized mass would result in equivalent gains in water quality (Figure 6) while allowing pest control operators to continue post-construction 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 [14], and to reduce volatile organic emissions with ozone forming potential [15]. Pest control applicators have similarly moved away from solvent based formulations due to odors and customer complaints [16]. Consumer acceptance would likely represent a formidable obstacle to post-construction EC-based pest control. Additionally, the model-predicted gains of switching to EC formulations were based almost entirely on the observed difference in washoff function of EC as opposed to SC treatments on concrete. The SC washoff function used in the exposure model was derived from a single SC formulated product, yet the categorizing of SC formulated products in the PUR data aggregated all non-solvent based liquid formulations, including micronencapsulated suspensions and wettable powders (Table 2). We are uncertain whether these formulations would yield similar washoff functions as derived for the SC formulation.

On the basis of the model predictions presented here, DPR'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 (California, USA) 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/beta cyfluthrin. Pyrethroid applications for above-ground structural pest control purposes utilizing SC 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 stormwater 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 DPR, yielded an approximate 84% reduction in predicted total toxic unit exposure in all modeled years. The exposure model assumes that all above-ground exterior structural pest control is in the form of a perimeter barrier spray, and as such, the gains derived from implementing the recently adopted DPR surface water protection rules are through application mass reductions imposed by the severe curtailment of currently permissible structural pest control applications. Such curtailment could possible 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 towards pyrethroid-containing EC 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 EC formulations.

On the basis of our results, we suggest that a concerted effort be made to monitor the effects of the California DPR'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 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 it contains potentially erroneous entries that can cause substantial errors in watershed modeling. Collecting additional information on indoor versus outdoor application and above-ground versus below-ground application also would be valuable. Such additions would significantly improve the utility of the PUR database.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The research described in this paper was supported by the California Department of Pesticide Regulation under contract number 06-0086C, by the National Institute of Environmental Health Sciences under award number P42E5004699, and by cooperative agreement no. 113325G004 between the University of California, Santa Barbara and the US Fish and Wildlife Service. The content is solely the responsibility of the authors and does not necessarily represent the official views of the California Department of Pesticide Regulation, the National Institute of Environmental Health Sciences, or the National Institutes of Health. Thanks to Frank Spurlock and Kean Goh, California Department of Pesticide Regulation, for providing provisional PUR database data for 2010.

References

1. Weston DP, Lydy MJ. Urban and agricultural sources of pyrethroid insecticides to the Sacramento-San Joaquin Delta of California. Environ Sci Technol. 2010; 44:1833–1840. [PubMed: 20121184]
2. Weston DP, Lydy MJ. Stormwater input of pyrethroid insecticides to an urban river. Environ Tox Chem. 2012; 31:1579–1586.
3. Werner I, Deanovic LA, Markiewicz D, Khamphanh J, Reece CK, Stillway M, Reece C. Monitoring acute and chronic water column toxicity in the northern Sacramento-San Joaquin Estuary, California, USA, using the euryhaline amphipod. Hyalella azteca. 2010:2006–2007.Environ Toxicol Chem. 29:2190–2199.
4. Jorgenson BC, Young TM. Formulation effects and the off-target transport of pyrethroid insecticides from urban hard surfaces. Environ Sci Technol. 2010; 44:4951–4957. [PubMed: 20524665]
5. Jorgenson BC, Wissel-Tyson C, Young TM. Factors contributing to the off-target transport of pyrethroid insecticides from urban surfaces. J Agric Food Chem. 2012; 60:7333–7340. [PubMed: 22784034]
6. Xiao, Q.; Wu, C. Report of the Department of Land, Air, Water Resources. University of California at Davis; Davis, CA, USA: 2008. Urban forests for clean air demonstration project – land cover, land use, and urban forest analysis, report 1: Analysis and mapping of current land use.
7. U.S. Geological Survey. Land use and land cover digital data from 1:250,000- and 1:100,000-scale maps: Data User Guide. 1986; 4:25. This document is out of print, but was available online on July 1, 2005 at http://www.vterrain.org/Culture/LULC/Data_Users_Guide_4.html.
8. Xiao, Q.; Wu, C.; Simpson, JR.; McPherson, EG. Report of the Department of Land, Air, Water Resources. University of California at Davis and Center for Urban Forest Research, US Forest Service; Davis, CA, USA: 2009. Urban forests for clean air demonstration project – land cover, land use, and urban forest analysis: Data collection, analysis and mapping of current land cover classification and urban forest structure.
9. Nowak, DJ.; Crane, DE.; Stevens, JC.; Hoehn, R. The Urban Forest Effects (UFORE) model: field data collection procedures. U.F. Service. , editor. Syracuse, NY.: 2003. p. 30
8. Fojut, TL.; Palumbo, AJ.; Tjeerdema, RS. Aquatic life water quality criteria derived via the UC Davis method: II. Pyrethroid insecticides. In: Tjeerdema, RS., editor. *Aquatic Life Water Quality Criteria for Selected Pesticides* Rev Environ Contam Toxicol. Vol. 216. 2012. p. 51-103.
9. Trimble AJ, Weston DP, Belden JB, Lydy MJ. Identification and evaluation of pyrethroid insecticide mixtures in urban sediments. Environ Toxicol Chem. 2009; 28:1687–1695. [PubMed: 19245272]
10. Aajoud A, Ravane P, Tissut M. Fipronil metabolism and dissipation in a simplified aquatic ecosystem. J Agric Food Chem. 2003; 51:1347–52. [PubMed: 12590480]
11. Gunasekara AS, Truon T, Goh KS, Spurlock F, Tjeerdema RS. Environmental fate and toxicology of fipronil. J Pestic Sci. 2007; 32:189–99.
12. Hassani AKE, Dacher M, Gauthier M, Armengaud C. Effects of sublethal doses of fipronil on the behavior of the honeybee (*Apis mellifera*). Pharmacol Biochem Behav. 2005; 82:30–39. [PubMed: 16102801]
13. Tingle CC, Rother JA, Dewhust CF, Lauer S, King WJ. Fipronil: environmental fate, ecotoxicology, and human health concerns. Rev Environ Contam Toxicol. 2003; 176:1–66. [PubMed: 12442503]

NIH-PA Author Manuscript

NIH-PA Author Manuscript

14. Rebmann, V.; Fiquet, L. Pyrethroid microemulsions. In: Berger, PD.; Devisetty, BN.; Hall, FR., editors. Pesticide Formulations and Application Systems. Vol. 13. American Society for Testing and Materials; Philadelphia, PA, USA: 1993. p. 30ASTM STP 1183
15. Kumar A, Howard CJ, Derrick D, Malkina IL, Mitloehner FM, Kleeman MJ, Alaimo CP, Flocchini RG, Green PG. Determination of volatile organic compound emissions and ozone formation from spraying solvent-based pesticides. J Environ Qual. 2011; 40:1423–1431. [PubMed: 21869504]
16. Van Steenwyk, D. Presentation at the Pyrethroid Forum. Vol. 30. California Department of Pesticide Regulation; California EPA: 2007 Apr. Industry perspectives: From a representative of Pest Control Operators of California. 2007

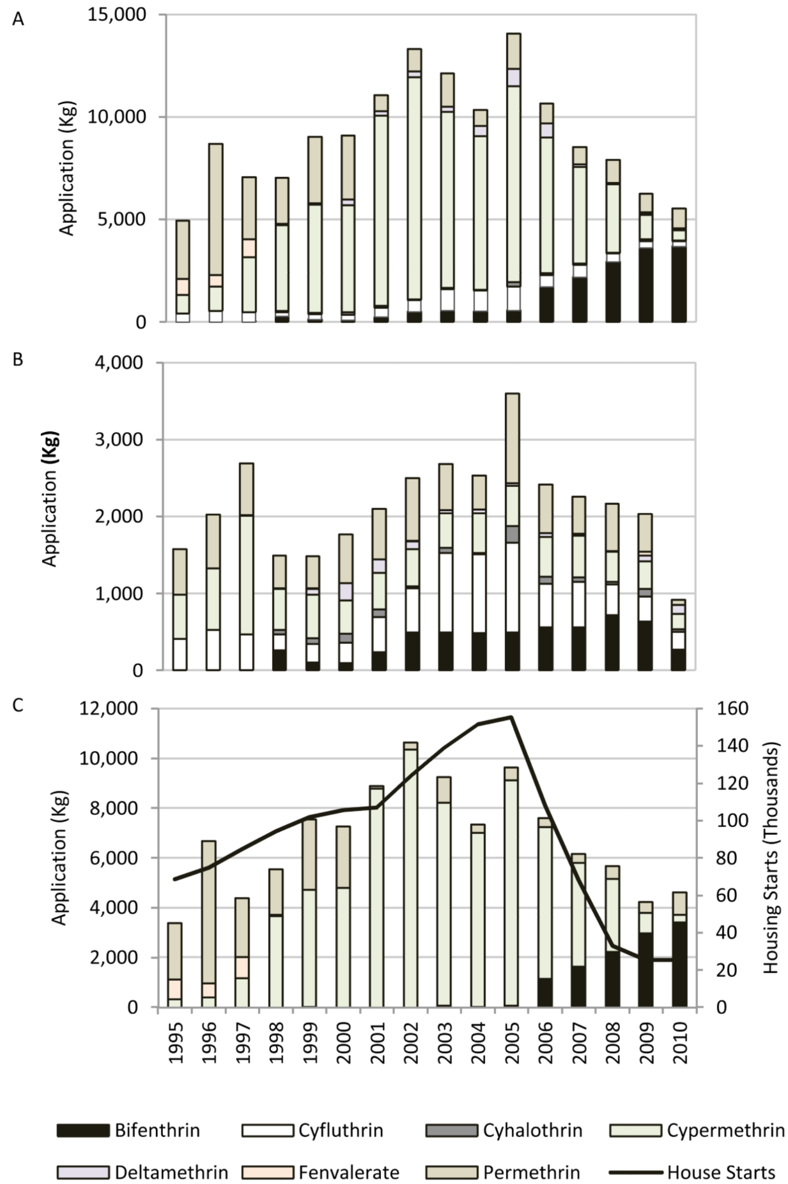

Figure 1.

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 above-ground applications. C) California housing starts compared to whole house pre-construction termite application totals removed from the Pesticide Use Report (PUR) data.

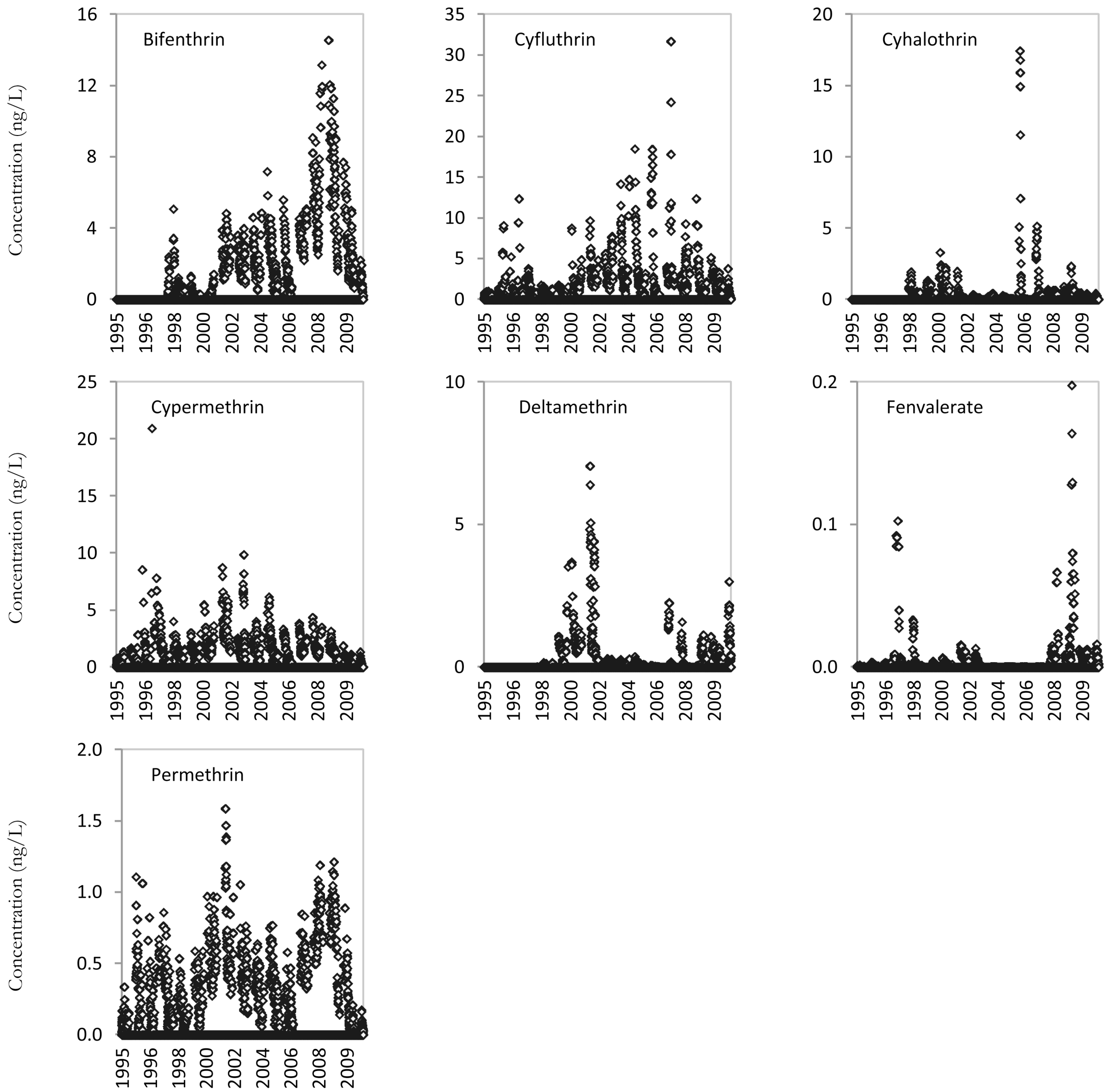

Figure 2.
Baseline predictions of chemical concentrations generated by an exposure model for 1995-2010. Symbols represent predicted daily concentration in the lower American River.

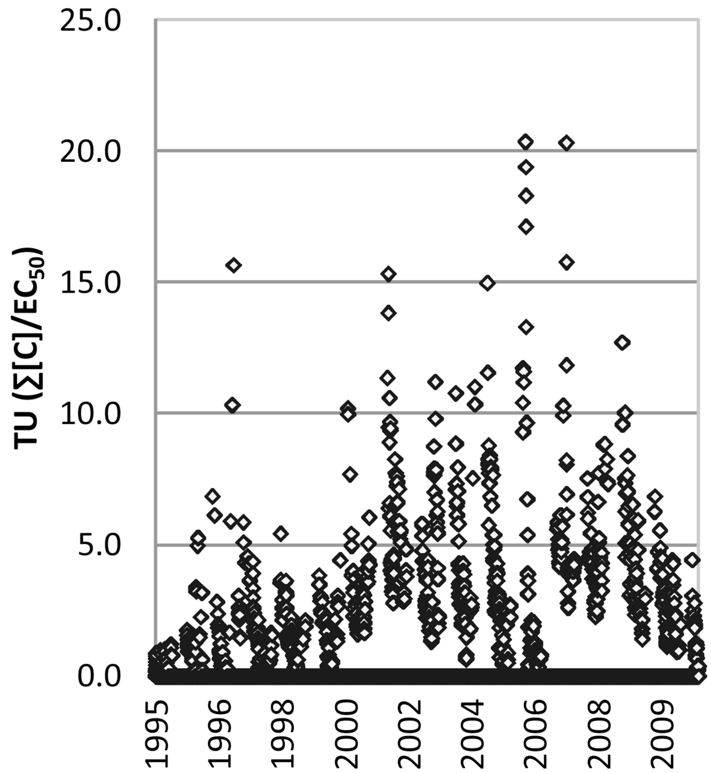

Figure 3.

Exposure model-predicted daily sum of Toxic Units (TUs).

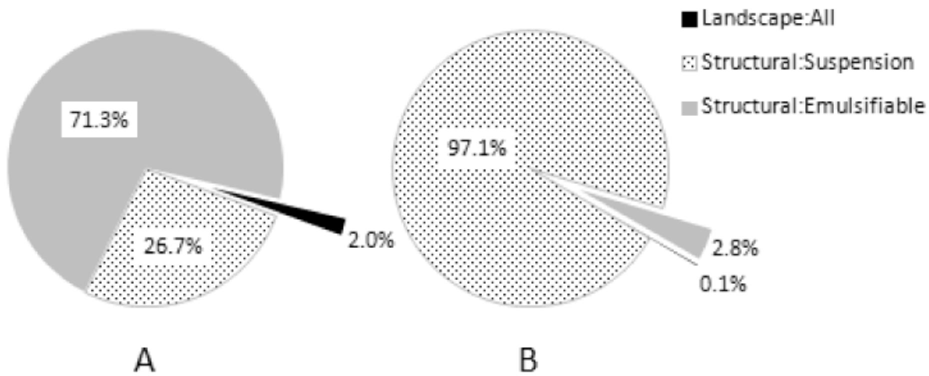

Figure 4.
Comparison of mass applied versus accumulated toxic units as a function of dominant surface and formulation type (surface:formulation). A) Distributed mass applied aboveground (average of all years modeled). B) Distributed total toxic units (average of all years modeled).

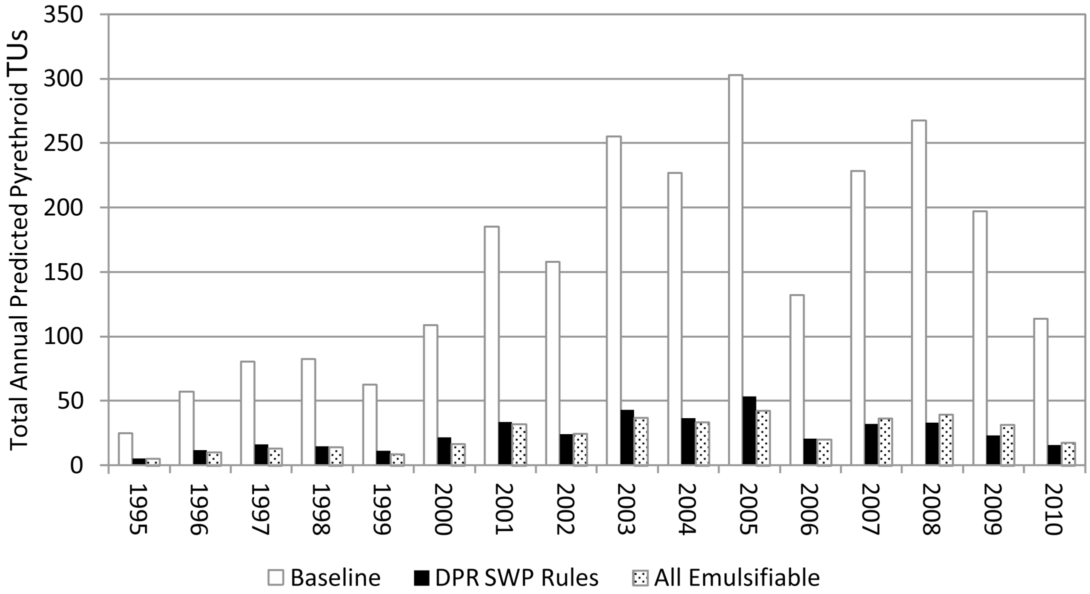

Figure 5.
Comparison of hypothetical mitigation on a total annual predicted pyrethroid Toxic Unit (TU) basis. DPR surface water protection rules as adopted with stricter provisions applied to bifenthrin applications. All Emulsifiable: no change in annual pyrethroid mass applied, but all mass is applied as an emulsifiable concentrate.

Table 1

Washoff function coefficients for formulations on various surfaces.

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

EC – emulsifiable concentrate, GR – granule, SC – suspension concentrate

Table 2

Comparison of observed and predicted pyrethroid concentrations

Monitoring Date	Measured Concentration (ng/L)		Model Predicted Concentration (ng/L)						
	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

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

Measured concentration data from [2]

NIH-PA Author Manuscript
NIH-PA Author Manuscript

Table 3

Daily average river concentration in ng/L (std dev)[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)

Bif – bifenthrin, Cyf – cyfluthrin/beta cyfluthrin, Cyhal – cyhalothrin/lambda cyhalothrin, Cyper – cypermethrin, Delta – deltamethrin, Fenv – fenvalerate/esfenvalerate, Perm - permethrin

[a] Calendar year average of predicted pyrethroid concentrations for days of measured precipitation.

Table 4

Published 5th percentile acute criteria values (ng/L) [a]

Bif	Cyf	Cyhal	Cyper	Delta	Fenv	Perm
4	2	1	6	--	--	10

Bif – bifenthrin, Cyf – cyfluthrin/beta cyfluthrin, Cyhal – cyhalothrin/lambda cyhalothrin, Cyper – cypermethrin, Delta – deltamethrin, Fenv – fenvalerate/esfenvalerate, Perm - permethrin

[a] Acute criteria values from [8]

Acute criteria values for deltamethrin and fenvalerate/esfenvalerate were not derived.