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Biofilms Provide New Insight into Pesticide Occurrence in Streams and Links to Aquatic Ecological Communities

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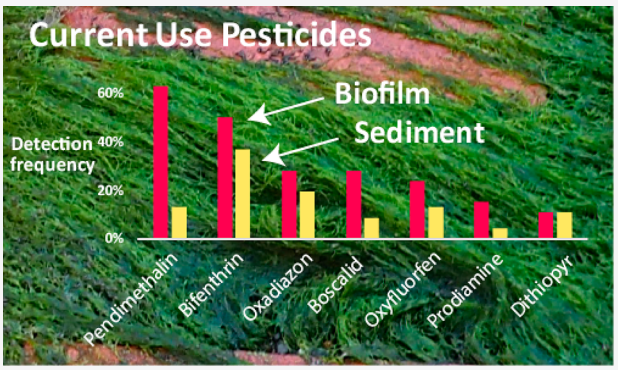
ABSTRACT: Streambed sediment is commonly analyzed to assess occurrence of hydrophobic pesticides and risks to aquatic communities. However, stream biofilms also have the potential to accumulate pesticides and may be consumed by aquatic organisms. To better characterize risks to aquatic life, the U.S. Geological Survey Regional Stream Quality Assessment measured 93 current-use and 3 legacy pesticides in bed sediment and biofilm from 54 small streams in California across a range of land-use settings. On average, 4 times as many current-use pesticides were detected in biofilm at a site (median of 2) as in sediment (median of 0.5). Of 31 current-use pesticides detected, 20 were detected more frequently in biofilm than in sediment and 10 with equal frequency. Pyrethroids as a class were the most potentially toxic to benthic invertebrates, and of the 9 pyrethroids detected, 7 occurred more frequently in biofilm than sediment. We constructed general additive models to investigate relations between pesticides and 6 metrics of benthic community structure. Pesticides in biofilm improved fit in 4 of the 6 models, and pesticides in sediment improved fit in 2. The results indicate that the sampling of stream biofilms can complement bed-sediment sampling by identification of more current-use pesticides present and better estimation of ecological risks.



■ INTRODUCTION

More than 6000 chemicals are currently used to control unwanted organisms, including insects, fungi, and weeds.[1,2] Many legacy pesticides (i.e., those no longer in use), such as DDT, aldrin, dieldrin, and chlordane, sorb to sediment, and because of their persistence they (or their degradates) continue to be widely detected.[3−5] Although current-use pesticides (CUPs) generally are characterized as being less persistent, more water-soluble, and less likely to bioaccumulate than legacy organochlorine compounds,[6] many also partition to sediment.[7] While occurrence of dissolved pesticides generally is episodic,[8,9] pesticides associated with bed sediment provide a continuous source of exposure to benthic invertebrates. Many sediment-associated current-use insecticides are more toxic to benthic invertebrates than the legacy insecticides they were designed to replace. For example, the pyrethroid insecticide bifenthrin is more than 300 times more toxic to *Hyalella azteca* than the legacy organochlorine insecticide *p,p′*-DDT (DDT).[10]

Analysis of bed sediment has long been a standard approach to evaluate the occurrence of hydrophobic pesticides (as extensively reviewed in ref 11), and CUPs have been widely detected in stream sediment (e.g.,[12−17]). Compounds with a water solubility less than 1 mg/L or a log Kow greater than 3 and with a soil half-life greater than 30 d have potential to accumulate in sediment.[11] Classes of CUPs that include compounds that meet these criteria include chloroacetanilides, triazines (herbicides); organophosphates, pyrethroids, phenylpyrazoles (insecticides); and triazoles (fungicides). Changes in benthic invertebrate communities have been linked to sediment-associated insecticides, particularly bifenthrin (e.g.,[7,18,19]), although other factors have been cited as influential.[20,21] Legacy pesticides have been reported to enhance the toxicity of mixtures to biota.[22] Both water and diet cause legacy contaminants to bioaccumulate in the food web, with rates varying by contaminant and by organism.[23]

Biofilms offer an alternative to bed sediment for integrative sampling of hydrophobic pesticides in streams. Stream biofilms consist of fungi, bacteria, algae, and microfauna enclosed in a mucopolysaccharide matrix attached to a surface; biofilms are continuously exposed to streamflow and hyporheic exchange and the chemicals they contain. Biofilms also trap fine sediment that settles out of the water column, which tends

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to be more recently delivered to the stream than bed sediment.[24] Biofilms have been identified as one of three exchange zones between surface water and hyporheic water, the other two being fine bed sediment and the hyporheic zone itself.[25] The presence of a pesticide in biofilm should indicate that the pesticide was recently in transport in the water column or the hyporheic zone, either in the dissolved phase or sorbed to suspended sediment. Because of the role biofilms play at the interface between flowing water and the stream bed and their importance as a basal resource for many invertebrates (and some fish),[26,27] they have been recommended as a suitable medium to evaluate the effects of chemicals on stream ecosystems.[28]

Numerous studies have investigated the uptake and metabolism of pesticides by biofilms and the effect of chemical uptake on biofilm composition, community structure, and function.[29−35] In a few studies (as reviewed in ref 33), algae has been observed to bioconcentrate pesticides by a factor of 100 to 1000 times relative to water concentrations and the elevated algal concentrations have persisted for days after the last detection in water.[36] Most studies of pesticides and biofilms, however, (1) have tended to consider one or a small number of pesticides; (2) have been undertaken in controlled conditions; and (3) focus on the effect of toxicants on the biofilms rather than on use of biofilms as an integrative sampler. For example, studies have investigated individually glyphosate,[34] lindane and norfloxacin,[37] diuron,[35] carbofuran,[38] and methomyl[39] among others. Most of these studies have been done using microcosms and mesocosms, which allow detailed evaluation in a controlled environment.[37,40,41] The objectives of many studies have been either better understanding of the mechanisms and kinetics of pesticide degradation by biofilms or the effects of pesticides on biofilm function, structure, and consortia.[31,32,34,35,38,39]

Although biofilms have rarely been used as an indicator of contaminant concentration in streams,[42] a few studies have taken advantage of biofilms as a monitoring tool. Huerta et al.[43] identified numerous pharmaceuticals and endocrine disruptors in biofilms downstream from a wastewater treatment plant and concluded that biofilms were a useful integrative monitoring tool for these compounds. Hobbs et al.[44] used biofilms to track sources of PCBs and metals to streams and rivers in Washington State, USA. They further reported that the metal burden in biofilms was strongly related to adverse impacts on periphyton and ecological integrity of the macroinvertebrate community. Rooney et al.[45] documented bioconcentration of 20 pesticides in periphyton in a coastal marsh and reported that more pesticides were detected in periphyton than in sediment.

In this study, we monitor concentrations of pesticides in biofilm in the context of the potential for risk to invertebrate community structure. To our knowledge, this is the first field study to both compare concentrations of a wide range of current-use and legacy pesticides in biofilm and bed sediment in a suite of streams and investigate how the occurrence of pesticides in biofilms is related to the structure of the benthic invertebrate community. We hypothesized that biofilms, by reason of their more heterogeneous structure and position within the food web, would provide a more comprehensive view of the occurrence of hydrophobic pesticides and a closer linkage to invertebrate community structure than bed sediments.

■ METHODS

Site Selection, Sample Collection, and Ecological Surveys. A bed sediment sample and a biofilm sample were collected at each of 54 wadeable stream sites in the Central California Foothills and Coastal Mountains ecoregion (https://www.epa.gov/eco-research/ecoregions) (Supporting Information (SI) Figure S1; Table S1).[46] The sites are a subset of those chosen for the U.S. Geological Survey (USGS) California Stream Quality Assessment (CSQA) (https://webapps.usgs.gov/rsqa/#!/region/CSQA),[47] which was designed to assess relations between stressors and stream ecology across a region.

Biofilm and sediment samples were collected in May 2017 to target the period following the growing season and peak pesticide use. Unglazed ceramic tiles for colonization by epilithic biofilm were deployed in streams in February or March 2017, 60 to 90 days prior to retrieval; the tiles provide a uniform substrate for colonization among sites.[48] Sediment samples were composites of material collected from multiple depositional locations along the 150 m stream sampling reach and were collected on the same day as biofilm. Details on streambed sediment and biofilm collection are provided in SI.

An ecological survey was done along each 150 m stream reach on the same day as bed sediment and biofilm collection. Invertebrate communities were sampled by the reach-wide benthos method using protocols from the Surface Water Ambient Monitoring Program (SWAMP) of the California State Water Resources Control Board.[49] At each stream site, subsamples were collected along 11 transects, using a D-frame 500 μm mesh net, composited, and preserved with 95% ethanol. Identification and enumeration of taxa were done at the USGS National Water Quality Laboratory in Lakewood, CO, following methods recommended by the California State Water Resources Control Board.[50] Benthic invertebrates were identified to the lowest practical taxon, that is, to the species or genus level where possible, or, for difficult groups or damaged or immature individuals, to family or order.

Analytical Methods and Quality Assurance. Streambed sediment and biofilm were analyzed for pesticides to document the occurrence, distribution, and magnitude of pesticide concentrations in sediment and biofilm in small California streams. Analysis of 118 (sediment) and 96 (biofilm) mostly CUPs and of organic carbon (OC) content was done at the USGS Organic Chemistry Research Laboratory (OCRL) in Sacramento, California. Details on analytical methods are provided in SI and results are provided in SI Tables S2 and S3 and as a USGS data release.[46] Results for only the 96 pesticides analyzed in both media are discussed here. The compounds analyzed and their chemical classes, molecular weights, method reporting levels (MRL), and benchmarks for benthic invertebrates are provided in SI Table S4. Quality control for streambed sediment and biofilm analysis consisted of laboratory blanks (baked sodium sulfate),[51] field replicate samples, and matrix spike samples; results are discussed in SI. We note that the MRLs for biofilm are for 5 g of sample, but most samples had less than 5 g of mass (range 0.01−5.34 g; median 0.8 g; interquartile range 0.22−3.0 g) (SI Table S3). There was no relation between the duration of deployment and biofilm mass. Insufficient mass can result in the nondetection of a compound, and the 8 sites with a biofilm mass <0.1 g had no detections. Samples from these 8 sites were therefore deemed not to be representative and were excluded

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from the data analysis. Given the relatively low sample masses, reported detections in biofilm should be considered a lower bound on the actual number of pesticides present in that medium.

Sediment Toxicity Benchmarks and Sediment-Pesticide Toxicity Index. Published freshwater sediment-toxicity benchmarks for pesticides (Threshold Effect Benchmark [TEB] and Likely Effect Benchmark [LEB])[10] were used to evaluate potential toxicity of pesticides in sediment to benthic invertebrates (SI Table S4). The TEB is the concentration of a pesticide in sediment below which adverse effects to benthic invertebrates are unlikely, and the LEB is the concentration above which adverse effects are highly probable. The toxicity of the mixture of pesticides in a sample was evaluated following the approach described in Nowell et al.[10] In brief, the ratio of the OC-normalized concentration of each pesticide detected in a sediment sample to its LEB was computed; this ratio is the toxic unit (TU). An OC value of 0.2% was used for samples with OC content <0.2%, consistent with equilibrium partitioning methodology.[52] The largest TU for a pesticide in a sample is the TU_{max}, which corresponds to the pesticide responsible for the greatest amount of potential toxicity associated with that sample. TUs for detected pesticides in each sample are summed to obtain the Sediment-Pesticide Toxicity Index (Sediment-PTI), which assumes additive toxicity, to screen for potential toxicity of the sample mixture.

Pesticide Use Data. Pesticide use data, used to investigate the relation between use and occurrence, were obtained from the California Department of Pesticide Regulation (CDPR) Web site (https://calpip.cdpr.ca.gov/main.cfm; additional information and documentation at https://www.cdpr.ca.gov/docs/pur/purmain.htm). Pesticide use data for urban and nonproduction agricultural uses are reported monthly on a county basis to the CDPR; use data for production agriculture are reported for the day and time of application on a Public Land Survey System (PLSS) 1 square mile section basis.[53] Data on specific crops on which pesticides were used were available only for production agriculture. Use data for January, February, March, and April 2017 were obtained for (a) the 10 most frequently detected pesticides ("top 10") or (b) those pesticides with a concentration in sediment that exceeded a TEB at any site. Nonagricultural uses were estimated for each stream site based on land use and the area of the watershed, and agricultural and nonagricultural uses were summed. Additional details on the data and the process used to estimate use within each basin are provided in SI.

Statistical Analyses. General additive models (GAMs) were used to explore associations between metrics of invertebrate community structure and pesticides in sediment and biofilm. GAMs relate a univariate response variable (invertebrate metric) with predictors that depend on unknown smoother functions. Variables entered into the models are defined in SI Table S5. We used the six invertebrate metrics included in the State of California's index of stream quality, which is used to assess ecological condition,[54] as response variables. The pesticide metrics (n = 26) included concentration of a pesticide in sediment or biofilm for the top 10 pesticides; other pesticide metrics (e.g., number of pesticides detected, Sediment-PTI) and total organic carbon (TOC) (sediment only) also were tested. Also used in the model are 10 natural covariates that represent measures of site location (latitude, longitude, elevation, elevation range), basin size, long-term air temperature, precipitation (long-term average and summer average), bulk soil density, and soil erodibility.[54] In brief, for each invertebrate model, a GAM was developed using the natural covariates only.[55,56] A pesticide stressor metric was then added to determine whether it improved the covariate-only model based on Akaike information criteria (AIC)[57] and was evaluated for significance of slope ($p \leq 0.05$). Nondetections were incorporated as zero values. The process was repeated for each pesticide stressor. Analysis was done in R version 3.6.0 using the "mgcv" package. Additional details on the GAM models are provided in SI.

Tobit regression methods, also called censored regression analysis, were used to identify relations between potential explanatory variables and concentrations of bifenthrin in sediment and biofilm. Bifenthrin was chosen as the response variable because it had relatively high detection frequency in both sediment and biofilm and because it occurred more frequently than any other pesticide in the 6 models of metrics of benthic invertebrate community structure. Models were developed using a stepwise procedure similar to stepwise regression, except that the AIC was used to select variables for inclusion in the model. Potential explanatory variables were considered in four groups: pesticide use, land use, precipitation, and landscape. Analysis was done in R version 3.6.1 using the "survival" package. Additional details on the regression analysis are provided in SI text.

RESULTS AND DISCUSSION

Pesticide occurrence. Of the 96 pesticide compounds analyzed in streambed sediment and biofilm from the 46 sites with sufficient biofilm sample mass, 25 were detected in one or more bed-sediment samples and 34 were detected in one or more biofilm samples (Figure 1; SI Tables S2, S3, and S6).

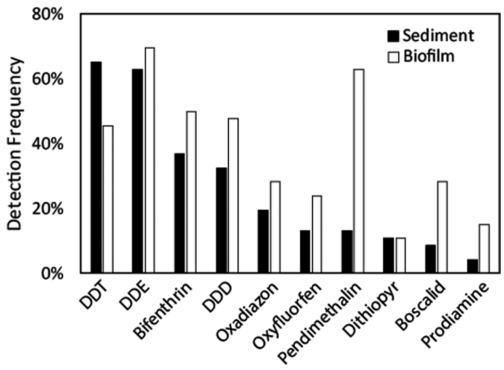

Figure 1. Of the 10 most frequently detected pesticides in sediment or biofilm, 8 occurred more frequently in biofilm than sediment. Compounds are ordered by decreasing detection frequency in sediment. (n = 46).

The most frequently detected pesticides (sum of detections in both media) were in descending order: DDE, DDT, bifenthrin, DDD, pendimethalin, oxadiazon, oxyfluorfen, boscalid, dithiopyr, and prodiamine ("top 10"); all were detected in 10% or more samples in one or both media.

Detection frequency (DF) in sediment of the top 10 pesticides was significantly related ($p < 0.05$) to the log of the octanol−water partition coefficient (log Kow) of the compound (Kendall tau = 0.76); for biofilm samples, there was no significant relation between DF and log Kow (Figure 2). There was no correlation between DF in either sediment or biofilm and solubility in water or typical half-life in soil

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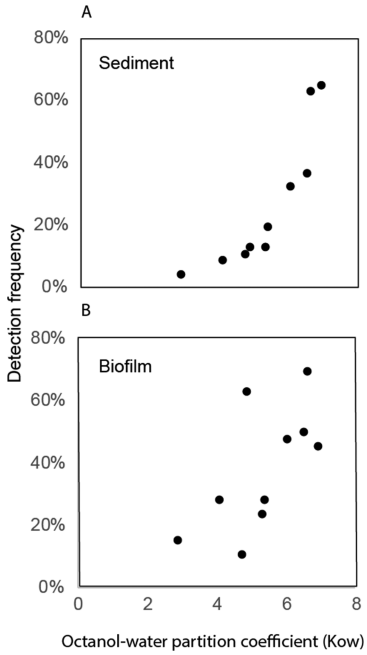

Figure 2. There was a significant relation (Kendall's tau = 0.76) between detection frequency in sediment and the octanol−water partition coefficient (Kow) of a pesticide; for biofilm samples, the relation was not significant. Pesticides included in the analysis, from low Kow to high, were prodiamine, boscalid, dithiopyr, pendimethalin, oxyfluorfen, oxadiazon, DDD, bifenthrin, DDE, and DDT.

(pesticide properties from https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm).

Sorption of organic contaminants to sediment is strongly controlled by partitioning into organic carbon and therefore is strongly associated with the Kow of the compound,[11] but bioconcentration of pesticides by biofilms in a natural setting has been observed to be unrelated to Kow.[45] Similarly, no relation was observed between the octanol−water distribution ratio (Dow) of pharmaceuticals and the bioconcentration factor in biofilm.[43] The lack of a relation between Kow or Dow and chemical uptake by biofilms likely is related to the heterogeneous nature of biofilm, as the wide range of charged and hydrophobic−hydrophilic sites within biofilms allows participation of different types of contaminants in a range of interactions.[30]

The relatively strong relation between the Kow of a compound and detection frequency in sediment but not biofilm suggests that interpretation of pesticide occurrence from sediment samples may be biased toward more hydrophobic compounds. For example, the dinitroaniline herbicide pendimethalin, with a low Kow (4.86) relative to several of the other frequently detected pesticides, was detected in 63% of biofilm samples, indicating relatively high occurrence, but was detected in just 13% of sediment samples, indicating relatively low occurrence. The biofilm results indicate that pendimethalin is present and bioavailable at the majority of the sampling sites; analysis of sediment samples only would lead to a different conclusion. Similarly, the fungicide boscalid (Kow = 0.41, the second lowest Kow of the top 10 pesticides) is more prevalent (detected in 28% of biofilm samples) in the streams than its occurrence in sediment samples (9%) would lead one to believe.

Current-Use Pesticides. Biofilm tended to accumulate a greater number of CUPs than sediment. At 67% of sites, the number of CUPs detected in the biofilm sample exceeded the number detected in the sediment sample; detections in sediment exceeded those in biofilm at 7% of sites; at 26% of sites, there were an equal number of detections of CUPs in the two media (Figure 3). On average, about 4 times as many CUPs were detected in biofilm as in sediment (medians of 2.0

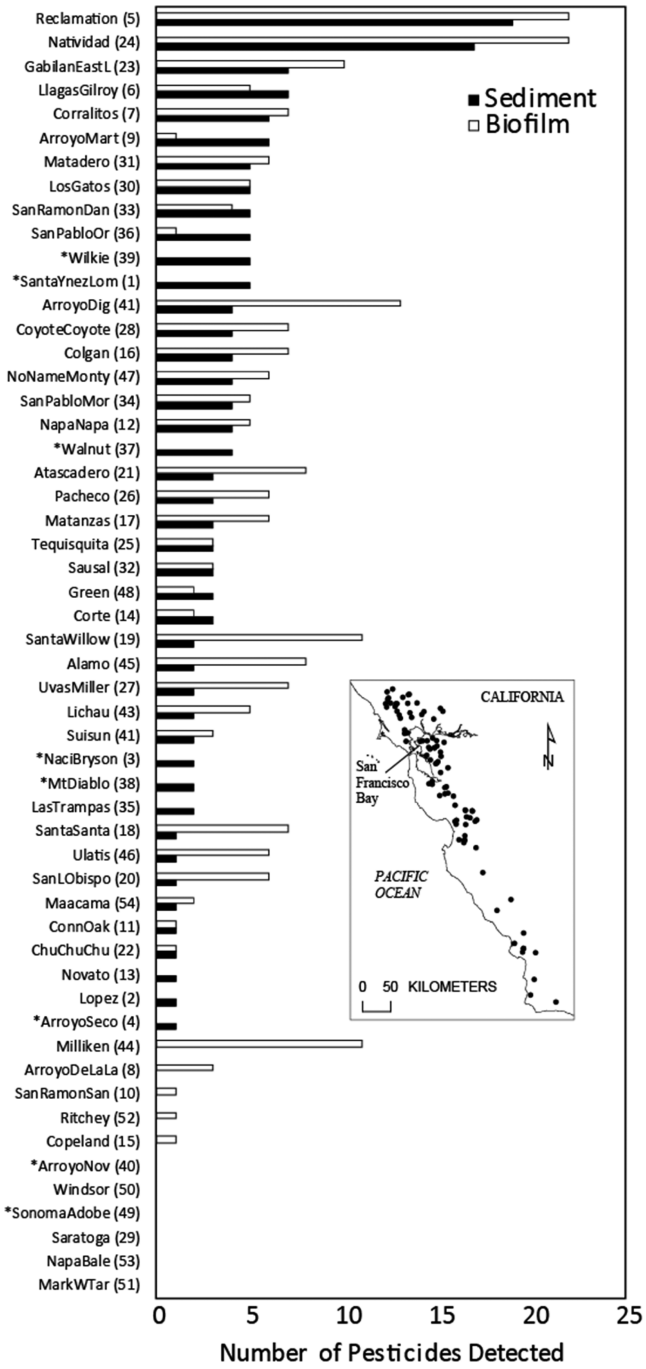

Figure 3. Number of pesticides detected in streambed-sediment (filled bars) and biofilm (open bars) samples at the 54 sites considered. Sites are ordered by descending number of pesticides in sediment; one sample of each medium was collected at each site. The numbers in parentheses denote site location on the detailed map in Supporting Information (Figure S1). An asterisk next to a site name indicates low biofilm sample mass (<0.1 g) at that site.

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and 0.5, respectively). Of the 31 CUPs detected in either medium, all but one (azoystrobin) were detected more frequently (n = 20) in biofilm than sediment or with equal frequency (n = 10). In some cases, the difference was extreme; for example, the insecticide permethrin and the herbicide pendimethalin were detected about 5 times more frequently in biofilm than sediment (SI Table S6). Of the 9 pyrethroids detected in either medium, 7 were detected more frequently in biofilm than sediment. Bifenthrin was the most frequently detected CUP in sediment (37% of sites); pendimethalin was the most frequently detected CUP in biofilm (63% of sites), followed by bifenthrin (50% of sites).

The greater frequency of occurrence of CUPs in biofilm than sediment indicates that some CUPs present in streams may go undetected by traditional sediment-sampling methods. As a result, the contribution of those pesticides to environmental risk assessment likely would not be considered. This phenomenon appears to be particularly important for pendimethalin, prodiamine, and boscalid, which were detected 3 or more times more frequently in biofilm than in sediment. Several factors likely affect detection frequencies of pesticides in sediment and biofilm. Differences in physical and chemical properties of the pesticide compounds, such as hydrophobicity, might cause a compound to favor one sampling medium over the other because, for example, of differences in the amount and nature of organic carbon in sediment and biofilm. Variation in sediment source might play a role in detection frequency in that eroded streambank material can dilute sediment-associated-contaminant concentrations,[24] and high flow can resuspended and transport contaminated sediment away from the sampling site.[58] As a result, benthic invertebrate and other aquatic communities may continue to be exposed to pesticides through contact with and ingestion of biofilm even when concentrations in sediment are not detectable; insight into this exposure is one of the benefits of analyzing biofilm.

Legacy pesticides: DDT and its metabolites. The legacy insecticide DDT and its metabolites DDE and DDD were among the 5 most frequently detected pesticides in both sediment and biofilm. The common occurrence of DDT and its metabolites is evidence of the persistence and past widespread application of this organochlorine insecticide, whose use was canceled in 1972.[59] The detection frequency of total DDT (DDT+DDE+DDD; nondetections counted as zero) (ΣDDT) in bed sediment was 70% with maximum and median concentrations of 185.4 and 2.9 ng/g, respectively. Concentrations of DDT compounds in both media are similar to those of the other frequently occurring pesticides (SI Tables S2 and S3). The levels of occurrence of ΣDDT measured, 45 years after cessation of use, indicates that DDT compounds continue to be a common contaminant in California streams. Many other studies have highlighted the persistent occurrence of DDT and its metabolites in stream sediment in California and elsewhere.[2,24,60]

The ratio of DDT to ΣDDT (DDT:ΣDDT) in bed sediment reflects the amount of time since the parent chemical entered the hydrologic system.[11] The California State Water Resources Control Board classifies DDT:ΣDDT of >0.6 and <0.4 to be typical of soil and sediment, respectively.[61] The median DDT:ΣDDT of 0.49 for this study indicates a transition in which the ratio is shifting from that of a recently eroded soil to that of a weathered streambed sediment. A 1985 study of 99 agricultural soil samples from 32 counties in California, however, reported an average DDT:ΣDDT of 0.49,[62] indicating that the source of the DDT in the streambed sediment collected for this study could be recently eroded soil.

Relative proportions of DDT and DDD in sediment and biofilm indicate the likely breakdown of DDT to DDD within biofilm: considering only those samples for which ΣDDT was not zero, DDT:ΣDDT exceeded DDD:ΣDDT in 32 of 34 sediment samples but only 17 of 32 biofilm samples. Several studies have demonstrated that biologically mediated degradation of DDT can occur at the time scale of our study. For example, 81% of DDT was degraded in 7 days in a *Pleurotus ostreatus* culture.[63] In another study, DDT was degraded by 77−61% over 10 days by hairy root cultures of *Cichorium intybus* and *Brassica juncea*.[64] Although the breakdown of DDT by biofilms has not been studied, other organic contaminants, such as methomyl, carbaryl, and carbofuran,[31,38] have been shown to be degraded by river biofilms. The difference in DDT ratios between sediment and biofilms might occur because, in the original soils, over time DDT has migrated into the recalcitrant organic matter fraction, and these soils are the source of the DDT in the bed sediment. It also might occur because biofilms are a more biologically active and complex medium than soils and sediment.

Screening-Level Risk Assessment. Sediment-quality benchmarks indicate the predicted likelihood (low, intermediate, or high) of toxicity of pesticides associated with streambed sediment to benthic invertebrates.[10] One or more LEBs were exceeded at 3 sites, and one or more TEBs were exceeded at 13 sites (SI Table S7). Of the pesticides measured, bifenthrin exceeded its TEB most frequently (eight sites), followed by chlorpyrifos (five sites). The Sediment-PTI, which screens for potential toxicity of pesticide mixtures, offered little additional insight into the potential toxicity of the streambed sediment to benthic invertebrates. A Sediment-PTI of 1.0, assumed to represent a potentially toxic mixture, was exceeded at the same three sites with an exceedance of an LEB. Inclusion of the legacy pesticide DDT and its degradates had a negligible influence on the computed Sediment-PTI, in contrast to results reported in ref 22.

Pyrethroids as a class were the most potentially toxic to benthic invertebrates. Pyrethroids were responsible for 11 of the 13 TU_{max} computed for sites with at least one exceedance of a TEB (SI Table S8). The preponderance of pyrethroids among the TU_{max} is largely because pyrethroids are highly toxic to *Hyalella azteca*, which usually is the basis of pyrethroid TEB and LEB values,[10] and because the pyrethroid bifenthrin occurred frequently in sediment (37% of sites). Despite relatively low concentrations, bifenthrin was the pesticide responsible for the most TU_{max} (n = 6). The pyrethroid esfenvalerate was not among the top 10 pesticides, but at the four sites where it was detected, it was responsible for the TU_{max} and exceeded its LEB by a factor of as much as 12. Esfenvalerate in California streambed sediment has been reported to be toxic to *Hyalella azteca*.[65] Contamination of agricultural and urban stream sediment by pyrethroids has been extensively documented, including in California, and linked to toxicity to benthic organisms.[15,66−69]

Although sediment samples at more than two-thirds of the sites did not have a pesticide that exceeded its TEB, sublethal effects from exposure to sediment- or biofilm-associated pesticides cannot be excluded. Toxicity tests generally last 10 or fewer days, focus on single species test organisms such as the crustacean *Hyalella azteca*, and do not reflect the complex conditions present in stream ecosystems.[19] For example, in

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Table 1. Results for Top General Additive Models (GAM) for Each of Six Invertebrate Metrics[c]

Invertebrate metric[a]	Covariates included in model[b]	Pesticide stressor in best performing model	Medium	*p*-value	Adj. R^2
RICH	PPT	oxyfluorfen	biofilm	4.47×10^{-05}	0.66
SH-rich	Elev_atQWsite, ELEV_RANGE, SumAve_P	oxadiazon	biofilm	0.004	0.75
Intol_richp	KFCT_AVE, PPT	bifenthrin	sediment	0.016	0.78
EPTRp	Elev_atQWsite, BDH_AVE, SumAve_P	bifenthrin	biofilm	0.026	0.77
cn_richp	BDH_AVE, SumAve_P	oxyfluorfen	sediment	0.035	0.41
COLEOPRp	Elev_atQWsite, SumAve_P	bifenthrin	biofilm	0.009	0.46

[a]RICH, total richness (number of taxa); SH-rich, Richness of taxa with the shredding feeding trait (number of taxa); Intol_richp, intolerant class: percentage of taxa with TVi ≤ X, where X is the user-specified criteria for the intolerant class;[71] EPTRp, number of Ephemeroptera, Plecoptera, and Trichoptera taxa, as a percentage of RICH; cn_richp, richness of taxa with the clinging behavior, as a percentage of RICH; COLEOPRp, number of Coleoptera taxa, as a percentage of RICH. [b]PPT, 10-y (2000−09) average precipitation at the sampling site; Elev_atQWsite, elevation at the sampling site, in m; ELEV_RANGE, difference between elevation at sampling site and maximum elevation in the basin, in m; SumAve_P, mean June to September 1971−2000 monthly precipitation, averaged across the basin; KFCT_AVE, average soil erodability factor (k); BDH_AVE, average bulk soil density; all variables tested for the model are defined in SI Table S5. [c]Top models were chosen on the basis of the Akaike information criteria (AIC) and *p*-value.

stream mesocosms, bifenthrin has been demonstrated to result in altered emergence patterns and trophic cascades,[19] phenomena not reflected in standard laboratory toxicity tests. Additionally, standard toxicity tests do not consider dietary exposure through feeding on biofilms: Reduction in growth of nymphs of the grazing scraper *Cinygmula reticulata* was observed when algae were exposed to the pyrethroid pesticide esfenvalerate.[70] Accumulation of hydrophobic pesticides in biofilms therefore might have sublethal effects on organisms even if the pesticide is not detected in the sediment.

Potential Effects on Stream Ecology. We investigated associations between pesticide occurrence in sediment and biofilm by evaluating the relation between 6 metrics of invertebrate community structure used by the State of California to determine stream biological condition[54] (Table 1) and 26 pesticide stressor metrics. Prediction of the 6 benthic invertebrate community metrics from GAMs based on natural covariates (basin characteristics) was significantly improved (decrease of ≥2 AIC units) when a pesticide metric was included in the models (Table 1, SI Figures S2−S7). Four of the 6 models (one for each invertebrate metric) had good predictive power, explaining from 66 to 78% of the variance (adjusted R^2) in the invertebrate metric. The other two models, for clinger (behavioral and morphological adaptive traits to cling to rocks) and Coleoptera richness, were significant but were less robust, explaining less than one-half of the variance (adjusted R^2 of 0.41 and 0.46, respectively). Both clinger and Coleoptera richness likely indicate hydrologic conditions and thus are expected to be less closely related to contaminant exposure than to habitat alteration.

The inclusion of a biofilm metric as the pesticide stressor in 4 of the 6 models, and 3 of the 4 most robust models, is another indication that biofilms may be a more effective medium than sediment for evaluating the effects of chemicals on aquatic invertebrate communities. There are at least two reasons why biofilms might better characterize chemical exposure risks to invertebrate communities than sediment. First, invertebrates directly consume biofilms on rocks or on coarse organic matter, preferentially exposing themselves to biologically available pesticides,[72] but only indirectly consume associated sediments. Second, because in this study biofilm tended to accumulate a greater number of pesticides than did sediment, biofilms expose invertebrates to a wider range of chemical contamination than sediment. The results of this study indicate that the toxic effects of pesticides on invertebrate communities might be underestimated or missed entirely if only concentrations of pesticides in sediment are measured.

The inclusion of a bifenthrin metric in three of the six models of invertebrate community metrics (example shown in Figure 4) is consistent with research indicating the deleterious

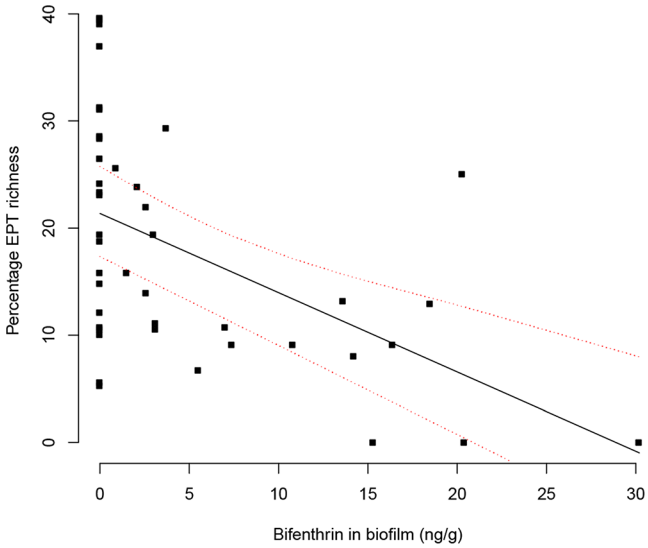

Figure 4. Bifenthrin in biofilm was the pesticide stressor in the top general additive model (GAM) for percent Ephemeroptera-Plecoptera-Tricoptera (EPT) richness. Black line is the model, and red dashed lines are the 95% confidence interval. This model also included three natural covariates (Elev_atQWsite, BDH_AVE, and SumAve_P; defined in Table 1); the adjusted R^2 for the total model was 0.77. Similar graphs for other top models are provided in Supporting Information.

effects of bifenthrin on benthic invertebrate communities. Worldwide, bifenthrin has been identified as a primary contributor to toxicity to benthic invertebrates[69] and has been demonstrated to reduce larval macroinvertebrate abundance, richness, and biomass in mesocosm experiments with native benthic communities at OC-normalized concentrations similar to those measured at many of the sites for this study.[19] In the California Stream Quality Assessment (CSQA) watersheds, bifenthrin use was reported primarily for artichokes, broccoli, and raspberries. Other pyrethroids, such as esfenvalerate, cyhalothrin, and fenpropathrin, might also be contributing to toxicity at some sites but their detection

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Table 2. Results of Tobit Regression Models for Concentrations of Bifenthrin in Sediment and Biofilm

Model	Significant explanatory variables[a]	Transformation	Regression slope	*p*-value	Individual R^2	Pseudo R^2 for model[b]
Sediment	CSQA_Total_Urban	square root	+	0.006	0.13	0.385
	Crops	square root	+	0.003	0.07	
Biofilm	LB_CSQA_Total_Urban	square root	+	0.0001	0.29	0.53
	PPT_Apr_2017	none		0.0011	0.17	

[a]CSQA_Total_Urban, percentage of basin with urban land use; Crops, percentage of basin with cultivated crops; LB_CSQA_Total_Urban, percentage of the lower basin (within a 5-km straight-line distance of the sampling point) with urban land use; PPT_Apr_2017, total depth of precipitation at the sampling location for April 2017. [b]Note that individual R^2 do not sum to model R^2 because variables are not orthogonal.

frequency was insufficient for inclusion in the statistical analysis. The herbicide oxyfluorfen appeared as the pesticide stressor in two of the models. Although herbicide effects on invertebrates could be either direct or indirect, oxyfluorfen is reported to be toxic to highly toxic to aquatic invertebrates and some uses of oxyfluorfen may result in acute and chronic toxicity to those species.[73] Oxyfluorfen use in the CSQA watersheds was reported primarily for grapes and broccoli. The herbicide oxadiazon was identified as the significant stressor in one model, although the risk of acute toxicity to invertebrates is considered low.[74] In the CSQA watersheds, oxadiazon was reported as used on outdoor-grown transplants. The summed concentration of pyrethroid TUs, which has been associated with toxicity to *Hyalella azteca*,[75] did not appear in top models for any invertebrate metric. OC content was not identified as a significant explanatory variable when added to the covariate-only model in contrast to results reported in ref 21 nor was Sediment-PTI identified as a significant explanatory variable.

Relations between Bifenthrin Occurrence and Potential Explanatory Variables. The relation between bifenthrin in sediment and in biofilm and a wide range of potential explanatory variables was explored to determine whether concentrations in the two media were affected by different factors. Bifenthrin was chosen for the analysis because it occurred relatively frequently in biofilm and sediment and was identified as significant in four of the six benthic invertebrate community structure models. Censored regression analysis (Tobit model) was used to explore contributions of potential explanatory variables in four broad classes (pesticide use, land use, precipitation, and landscape (SI Table S9)) to the occurrence of bifenthrin in sediment and biofilm. The Tobit model considers censored data, i.e., nondetections, in the analysis.

The optimal model for the concentration of bifenthrin in sediment contained two land-use variables (Table 2). The model explained 38.5% of the variance, indicating that factors not considered in the model contribute to most of the occurrence of bifenthrin in the sediment samples. Of the two significant explanatory variables, urban land use in the watershed was the most important. The optimal model for the concentration of bifenthrin in biofilm contained a land-use variable and a precipitation variable and explained 53% of the variance in bifenthrin concentration. The land-use variable (urban land use in the lower part of the basin) explained more of the variance than the precipitation variable.

Models for both sediment and biofilm contained an urban land-use variable (Table 2). Land-use variables can be considered as surrogates for pesticide use, and relations between urban land use and pyrethroid occurrence have been reported previously.[15,68,76] The retention of an urban land-use variable in regression models into which an urban pesticide-use variable was also entered indicates that reported urban pesticide use in California may not adequately represent actual urban use. Urban-use reporting in California is substantially less comprehensive than agricultural-use reporting: the California Pesticide Use Reporting (PUR) Database does not include residential home and garden uses, veterinary uses, and most industrial and institutional uses in urban areas. While most of the agricultural use is reported for square mile sections, urban use is reported on a county-wide basis; as a result, apportionment of use at the basin scale is likely to be substantially less accurate for urban use than agricultural use. The results suggest that, although California is more proactive than other states in terms of requiring some reporting of urban pesticide use, urban use in individual basins remains difficult to quantify accurately.

We hypothesize that the precipitation variable included in the biofilm model (but not the sediment model) is a surrogate for flow and might indicate that slower flow rates contribute to higher concentrations of bifenthrin in biofilm. This does not reflect simple dilution of chemical concentration from higher flow, which would affect biofilm and sediment. Higher flow rates are associated with loss of organic matter in biofilm, leading to reduced pesticide uptake.[35] The loss is attributed to shear stress thinning the biofilms;[77] greater biofilm biomass increases biofilm storage of solutes.[78] An additional consideration is that biofilms can increase the residence time of water in the stream channel, allowing more time for interaction between the biofilm and dissolved contaminant and enhancing uptake.[79] This phenomenon may be more pronounced during periods of slow flow, given that biofilm biomass has been shown to be the main control on the exchange rate between the main channel and transient storage in the hyporheic zone.[79]

Sediment and Biofilms As Integrative Samplers of Current-Use Pesticides. Sediment and biofilms each have some advantages and some shortcomings as integrative samplers of pesticides. Sediment sampling is simpler logistically. The collection of a sediment sample requires a single site visit (although biofilm can be collected in one visit if natural substrate suitable for colonization and sampling), sufficient mass for analysis is assured (although finding depositional areas with fine-grained sediment is sometimes a challenge), and there is no concern for vandalism, destruction, or loss of a colonization substrate. Additionally, pesticide concentrations in sediment can be compared to sediment-quality guidelines for a screening-level assessment of potential toxicity to benthic biota, and sediment is suitable for use in ambient sediment toxicity testing. However, streambed-sediment composition, storage, and transport can be highly variable spatially and temporally,[58,80−82] and contaminated sediment from the land surface can be diluted by sediment from streambank erosion[24] or resuspended and transported with an increase in streamflow velocity.[58] These processes can

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result in inconsistent or undetectable concentrations of pesticides in sediment.

Biofilms have the advantage of being an integral part of the aquatic food web, and any pesticides taken up are by definition bioavailable. Biofilms are unlikely to be removed from the substrate except under extreme conditions; therefore, dilution of sequestered pesticides is unlikely. However, biofilms respond to changes in environmental conditions such as light, temperature, and flow.[83−85] Additionally, biofilms can degrade pesticides,[34,38,39] and the capacity to do so can vary on a seasonal time scale.[31] The degree to which both sediment and biofilm samples represent contamination of small streams, therefore, will vary across time and space.

The various benefits and shortcomings of sediment and biofilm as integrative samplers indicate that their use in tandem may be complementary. If the goal of an investigation is evaluation of pesticide occurrence and relations to benthic invertebrate community structure, the CSQA data support the use of biofilms to provide a unique perspective of current stream contamination by hydrophobic CUPs. Biofilm more consistently accumulated the 93 CUPs analyzed for this study than bed sediment, and in some cases the difference was large (pendimethalin, prodiamine, boscalid). More CUPs were detected in biofilm than in sediment at almost 10 times as many sites as the reverse, and the median number of CUPs detected in biofilm at a site was 4 times that for sediment. Most of the top 10 pesticides and most of the pyrethroid compounds were detected more frequently in biofilm than in sediment at any given site. In many cases, therefore, biofilms provided evidence of the presence of a bioactive pesticide in a stream where a sediment sample did not.

Statistical analysis indicated that pesticides in biofilms were better indicators of the structure of the benthic invertebrate communities measured for this study than pesticides in sediment. Four of the six models for a metric of invertebrate community structure included a variable representing a pesticide in biofilm rather than sediment. This supports the assumption of many studies that biofilms reflect the effects of chemical contaminants on stream ecosystems[28,86,87] and goes further to quantify that effect. The presence of a biofilm-related pesticide metric in the models also indicates that a significant relation between pesticides and benthic invertebrate community structure might be overlooked if only concentrations in sediment are considered.

Potential toxicity metrics and statistical analysis indicate that the pyrethroid insecticide bifenthrin may be adversely affecting the benthic invertebrate community structure in the California streams sampled. This finding is consistent with numerous studies that identify bifenthrin as a primary contributor to toxicity to benthic invertebrates.[69,76,88] The agricultural use of bifenthrin in the United States has increased nearly an order of magnitude since the 1990s[89] and urban uses, although not reported for most of the country, are common. Bifenthrin, like its predecessor DDT, is strongly hydrophobic. Despite efforts to better target the use of pyrethroids and reduce transport to streams in California,[90] pyrethroids continue to pose a risk to stream organisms.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b07430. Machine-readable data files are available as a USGS data release at https://www.sciencebase.gov/catalog/item/5dfa73fee4b0cdded73d1b4f.

Details of biofilm and streambed-sediment sample collection; description of analytical methods and quality assurance; approach used to retrieve and process pesticide-use data; use of general additive models (GAM) and Tobit regression statistics; detailed map of the study area; figures illustrating the results of the GAM (PDF)

Tables that provide a numerical key to sites shown on the map, pesticide data for sediment and biofilm samples, information on the pesticide compounds analyzed, definition of variables used in the GAMs, detection frequencies for the pesticides analyzed, the number of benchmarks exceeded by site, the maximum toxic units measured, definition of variables used in the Tobit regression (XLSX)

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Notes

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