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SPATIAL RELATIONSHIPS BETWEEN WATER QUALITY AND PESTICIDE APPLICATION RATES IN AGRICULTURAL WATERSHEDS

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Abstract. Pesticide applications to agricultural lands in California, USA, are reported to a central data base, while data on water and sediment quality are collected by a number of monitoring programs. Data from both sources are geo-referenced, allowing spatial analysis of relationships between pesticide application rates and the chemical and biological condition of water bodies. This study collected data from 12 watersheds, selected to represent a range of pesticide usage. Water quality parameters were measured during six surveys of stream sites receiving runoff from the selected watershed areas. This study had three objectives: to evaluate the usefulness of pesticide application data in selecting regional monitoring sites, to provide information for generating and testing hypotheses about pesticide fate and effects, and to determine whether in-stream nitrate concentration was a useful surrogate indicator for regional monitoring of toxic substances. Significant correlations were observed between pesticide application rates and in-stream pesticide concentrations ($p < 0.05$) and toxicity ($p < 0.10$). In-stream nitrate concentrations were not significantly correlated with either the amount of pesticides applied, in-stream pesticide concentrations, or in-stream toxicity (all $p > 0.30$). Neither total watershed area nor the area in which pesticide usage was reported correlated significantly with the amount of pesticides applied, in-stream pesticide concentrations, or in-stream toxicity (all $p > 0.14$). In-stream pesticide concentrations and effects were more closely related to the intensity of pesticide use than to the area under cultivation.

Keywords: land use, pesticide use reports, diazinon, chlorpyrifos, pyrethroid, toxicity, *Ceriodaphnia dubia*, *Hyalella azteca*, GIS, watershed

1. Introduction

Management of non-point source pollution from urban, residential, industrial, and agricultural landscapes is complicated by the diversity of contaminant sources, constituents, and transport processes. Runoff containing mixtures of nutrients, sediments, industrial chemicals, and pesticides has contributed to a variety of significant impacts on aquatic systems and the ecological services they provide (NRC, 1999; Postel and Carpenter, 1997). Numerous studies have implicated pesticide runoff as a cause of biological effects in aquatic habitats (deVlaming *et al.*, 2000; Anderson *et al.*, 2003a, b; Thiere, 2004; Schulz, 2004; Liess and Von Der Ohe, 2005). In the USA, about 450 million kg of pesticides are used each year, with agriculture accounting for 70 to 80% of total pesticide use (USGS, 1999). The relative risk to aquatic resources posed by pesticides depends on a variety of factors, including landscape application rates, application methods, irrigation and storm water management, soil type, topography, erosion, and land management practices (NRC, 1999). Pesticide application rates can be estimated by analysis of surrogate indicators such as land use or cropping patterns (Black *et al.*, 2000; Dabrowski *et al.*, 2002; Evans, 2002; Staten *et al.*, 2003; Jongbloed *et al.*, 2004; Houlahan and Scott, 2004), but substantial uncertainty exists in the absence of reliable pesticide use data.

In California, a pesticide use reporting system has been developed, which provides information that can be combined with water quality data to evaluate relationships between land use and aquatic resource condition. Some level of pesticide use reporting has been required in California since the 1950s. In 1989, the State Legislature passed Assembly Bill 2161 (Section 12979 of the California Food and Agriculture Code), requiring that all pesticide applications for agricultural purposes be reported monthly to County Agricultural Commissioners. The County Commissioners transfer this information to a statewide data base managed by the Department of Pesticide Regulation (DPR). This data is available to the public, and its dissemination is facilitated by various university and agency programs (UC IPM, 2005; CDPR, 2002).

While this system documents pesticide usage, other programs monitor water quality throughout California's streams and coastal waters (e.g., Puckett, 2002; Belitz *et al.*, 2004; USEPA, 2005). Successful water quality assessments depend both on the selection of appropriate monitoring indicators and on the selection of appropriate sampling locations in monitoring designs. Monitoring indicators often include synoptic measurements that allow toxicologic information to provide the link between measured stressors and observed ecological effects (USEPA, 2000a; Scherman *et al.*, 2003; Anderson *et al.*, 2003b). Sampling locations are often selected to characterize watershed conditions at scales appropriate for known stressors and critical habitats. Because pesticide use data and water quality monitoring locations are both georeferenced, the present study was designed to determine whether the geographic distribution of known stressors (pesticides, as applied to the landscape) could be used to direct monitoring effort towards potentially degraded sites in critical habitat (stream networks). Evaluation of these spatial patterns may also be useful for generating and testing hypotheses about pesticide fate and effects processes. An additional objective of this study was to evaluate whether in-stream concentrations of nitrate, an inexpensively measured chemical often indicative of intensive land use, could be a useful surrogate for directing site selection in regional monitoring for toxic substances.

The study was conducted in primarily agricultural watersheds along California's central coast. Agriculture in this region is intensive and highly productive. Year-round cultivation supports a \$3.5 billion/year industry that produces more than 85% of the nation's lettuce, artichokes, and broccoli, and more than one-third of the nation's strawberries, celery, and mushrooms (AWQA, 2004). Approximately 8,640 metric tons of pesticide active ingredient were applied in this region in 2002, the year this study was initiated (CDPR, 2002). Rainfall is seasonal, with a winter wet season and summer drought. Summer flow in many small streams can be dominated by runoff from irrigated agriculture. Regional watersheds drain to important wildlife habitats, such as those found in the Elkhorn Slough National Estuarine Research Reserve, the Salinas River National Wildlife Refuge, and the Monterey Bay National Marine Sanctuary.

2. Materials and Methods

Data were collected from twelve watersheds, ranging in size from 15 to 480 km^2. These were selected to represent a variety of agricultural activities and a range of pesticide usage. One stream sampling site was selected at the loading point of each watershed (see below), and these twelve sites were sampled on six dates: 08 July 2002, 03 Sept. 2002, 17 Mar. 2003, 27 May 2003, 06 Mar. 2004, and 02 June 2004. Dates were scheduled within that portion of the primary growing season when sufficient stream flow was available at all sites.

2.1. Geographic information

A geographic information system (GIS) was used to quantify pesticide application rates in the selected watersheds. The base map for the study area was a mosaic of eight US Geological Survey (USGS) 30 m digital elevation models (30 M DEMs), that were transformed into hillshades for ease of topographic visualization using ArcGIS 8.3 (ESRI, Redlands, CA, USA). These were overlain by stream segment features from the U.S. Environmental Protection Agency (USEPA) Reach File 3 national hydrologic database (USEPA, 2004). Boundaries for the watershed areas draining to study sites were heads-up digitized from the 30 M DEM hillshade projections (Figures 1–4). Boundaries were manually drawn at scales selected to optimize visualization of the individual watersheds, with views varying from approximately 125 to 1,000 km^2. Watershed delineation took advantage of drainage patterns displayed by the stream reach layer, as well as knowledge of local landforms, such as alluvial fans. The authors consider the accuracy sufficient for this analysis in areas with moderate to high topographic relief. However, delineation of watershed boundaries over flat terrain may have substantial inaccuracies. Identifying drainage boundaries in these areas is confounded by the presence of levees and by agricultural

Figure 1. Map of California, USA, with rectangles showing the location of the two study areas.

land management practices that often include the re-routing of drainage networks, both of which may affect runoff to the sampling points. These complications are in addition to the inherent difficulty of identifying natural drainage divides on flat terrain. The relevance of this potential error is enhanced because flat land is often the most intensively cultivated, with resulting potential for greater pesticide usage. Adequate ground-truthing of drainage patterns was infeasible due to the size of the land area and the difficulty gaining access to private property.

2.2. Pesticide application data

Pesticide use data are transferred regularly from DPR to the Central Coast Regional Water Quality Control Board (Regional Board) as a series of text files via CD-ROM. Data for pesticide applications that occur within the Regional Board's jurisdiction are imported into an MS Access database. Pesticide usage is georeferenced in the public land survey system (PLSS) of township, range, and section, with spatial resolution of 2.6 km^2 per grid cell. This database was queried to retrieve application rates of the organophosphate (OP) pesticides diazinon and chlorpyrifos, and the pyrethroid pesticides permethrin, cypermethrin, bifenthrin, lambda-cyhalothrin,

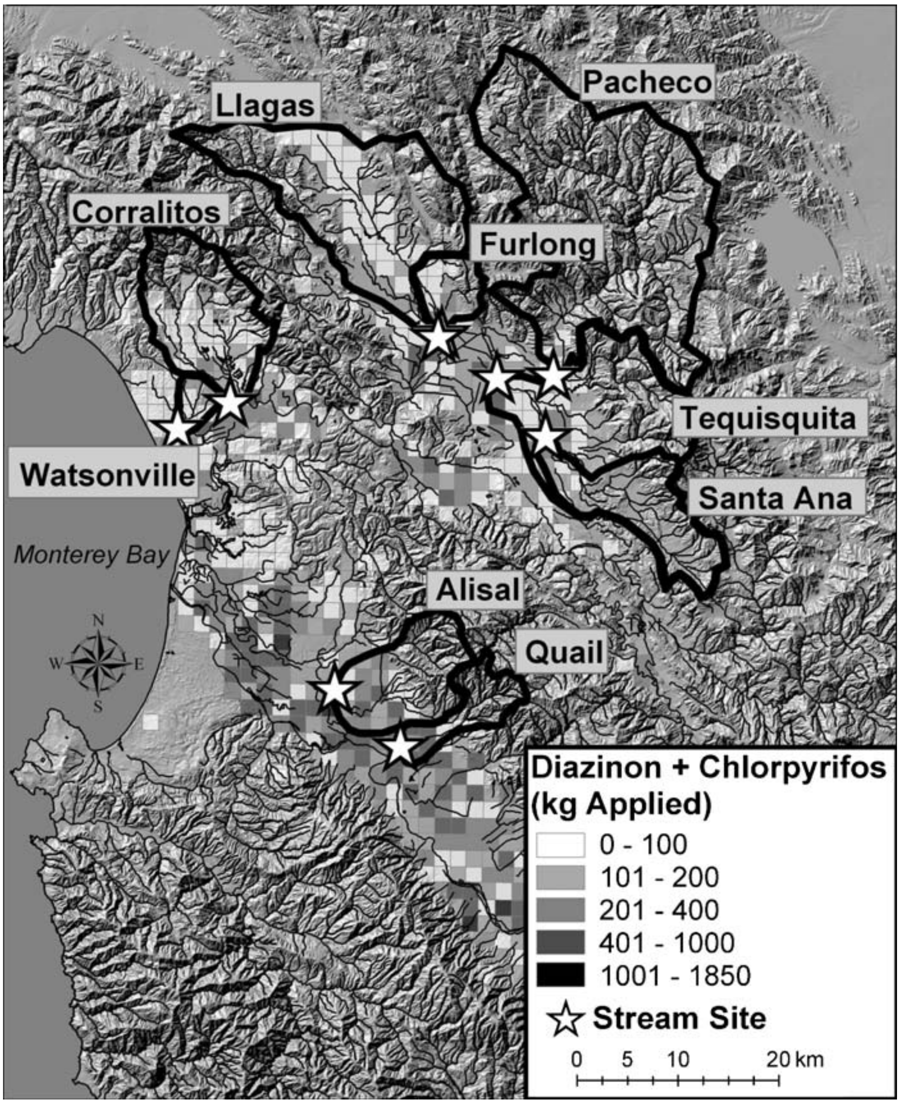

Figure 2. Map of the northern study area, showing the sampling sites, the boundaries of watershed areas draining to them, and application rates of the organophosphate pesticides diazinon and chlorpyrifos in public lands survey system squares (2.6 km^2).

and esfenvalerate. The study focused on these chemical classes because of their high toxicity, their common usage in the region, and their previously reported association with biological effects in regional stream systems (Hunt *et al.*, 2003; Anderson *et al.*, 2003a (in press); Kelley and Starner, 2004). These two groups were also useful for study because they vary in their solubilities and persistence. The organophosphates are more water soluble, and have half lives in freshwater streams on the

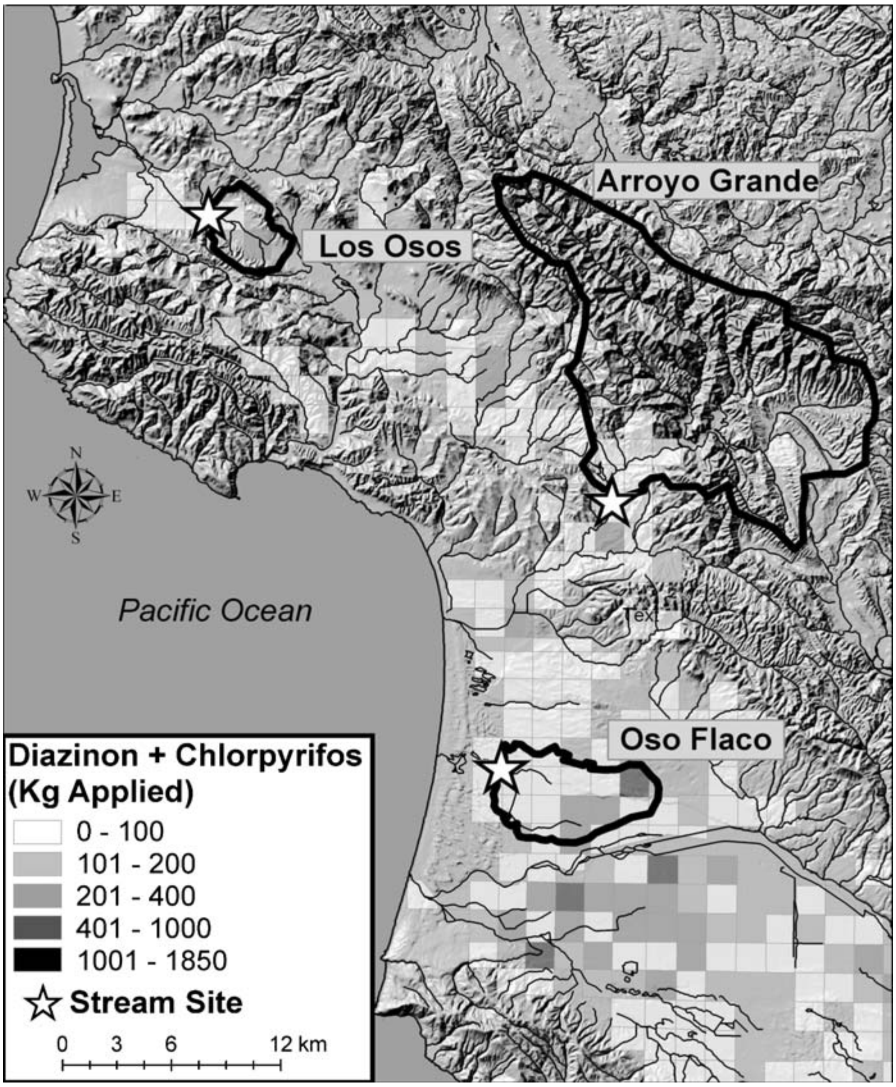

Figure 3. Map of the southern study area, showing the sampling sites, the boundaries of watershed areas draining to them, and application rates of the organophosphate pesticides diazinon and chlorpyrifos in public lands survey system squares (2.6 km^2).

order of one to four weeks (Bondarenko *et al.*, 2004). The pyrethroids are highly insoluble, and have half lives on the order of 8 to 17 months (Gan *et al.*, 2005). Monthly pesticide use data were summed to provide annual values for 2002, the year in which stream surveys were initiated. The query tables were exported to an ArcMap data frame, and were joined to a PLSS shape file using the common field of combined township, range, and section attributes. This allowed each PLSS section to be both analyzed and visualized according to its annual pesticide use.

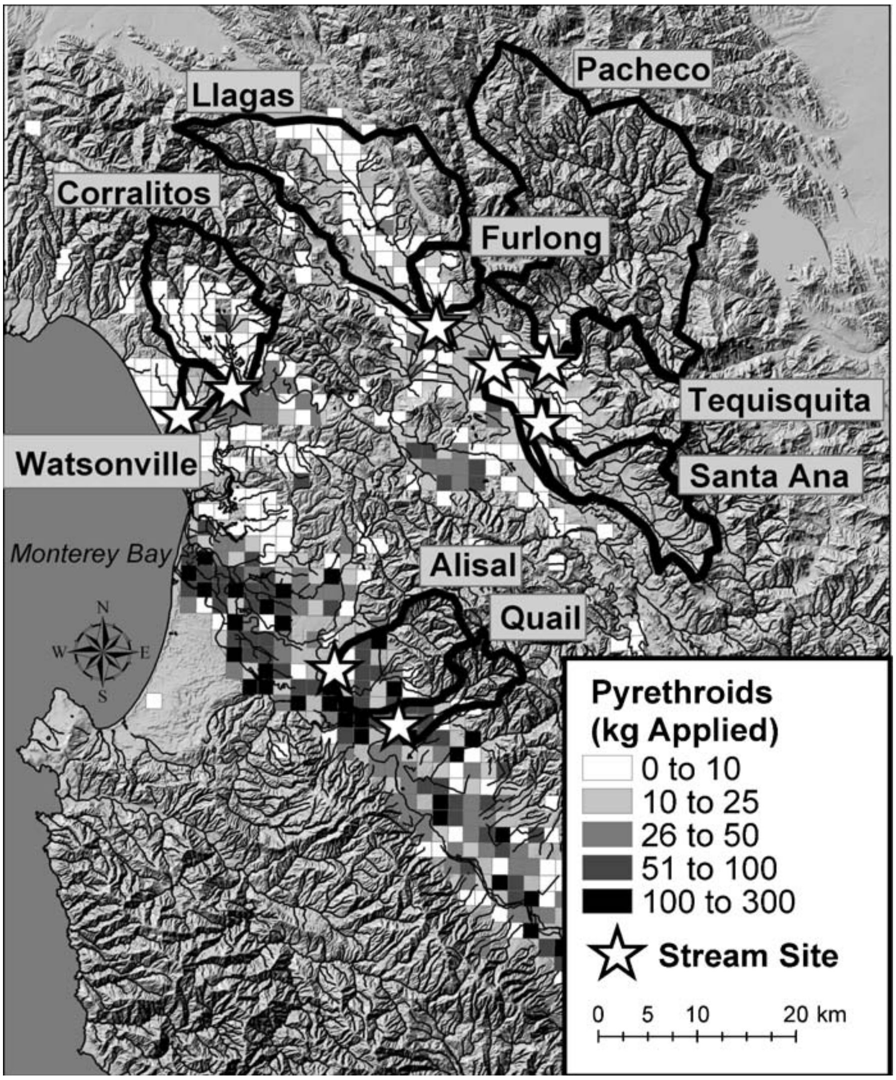

Figure 4. Map of the northern study area, showing the sampling sites, the boundaries of watershed areas draining to them, and application rates of pyrethroid pesticides in public lands survey system squares (2.6 km^2). Pyrethroids were represented by five compounds: permethrin, cypermethrin, bifenthrin, lambda-cyhalothrin, and esfenvalerate.

To quantify the pesticide mass applied within study watersheds, the PLSS sections were intersected with the watershed polygons (including an 0.8 km buffer, representing half the width of the PLSS section). Pesticide applications within the selected PLSS cells were then summed to characterize total usage on land draining to the stream study sites (e.g., Figures 2–4).

2.3. Water and sediment toxicity

The toxicity of water samples collected during the six surveys from all 12 sites was determined using the USEPA 7-day survival and reproduction toxicity test with the Cladoceran *Ceriodaphnia dubia* (USEPA, 2002). Each undiluted grab sample was tested using 10 replicates, each containing one *C. dubia* neonate (<24-h-old). Daphnid survival and neonate production were monitored daily in each replicate of each sample.

The toxicity of one sediment sample (June 2002, mid growing season) from each of six sites was assessed using the 10-day survival and growth toxicity test with *Hyalella azteca*, a resident epibenthic amphipod (US EPA, 2000b). Each sample was divided among eight laboratory replicates, each with ten 7- to 14-day-old amphipods. The amphipods were exposed to 100 ml of sediment in 300 ml beakers, each containing 175 ml of overlying water. The test temperature was 23 °C (±1 °C). Overlying water was renewed twice daily, and 1 ml of YCT food (Yeast, Cerophyl, Trout Chow) was added daily to each test container. The containers were not aerated. After surviving animals were dried at the end of the test, growth was measured as change in mean dry weight per individual amphipod per replicate. Sediment samples were stored in the dark at 4 ± 1 °C. Tests were initiated within 96 hours of sample collection.

2.4. Conventional parameters

Dissolved oxygen (mg/L), specific conductance (μs/cm), pH, temperature (°C) and turbidity (NTU) were measured *in situ* using a Hach Sension 156 and Hach 2100 P portable turbidimeter. These instruments were calibrated in the laboratory as per manufacturer's recommendations. Alkalinity (total as $CaCO_3$) and hardness (calcium as $CaCO_3$) were measured in field-collected samples in the laboratory. Nitrate and phosphate concentrations were measured on a Hach 2010 spectrophotometer.

2.5. Chemical analyses

Water samples from the September 2002 and May 2003 surveys were analyzed for organophosphate, organochlorine and pyrethroid pesticides; polychlorinated biphenyls (PCBs); and trace metals. Organochlorine compounds were measured using gas chromatograph/electron capture (EPA Method 8080), with detection limits ranging from 0.3 to 5 ng/l. Organophosphate compounds were measured using a nitrogen-phosphorus specific detector (EPA Method 8140/8141), with detection limits ranging from 0.04 to 33 μg/l (chlorpyrifos MDL = 0.05 μg/l, diazinon MDL = 0.04 μg/l). PCBs were analyzed as arochlors using EPA Method 8080-PCBs, with detection limits ranging from 0.04 to 0.11 μg/l. Selected water samples were also analyzed for trace metals (As, Ag, Cd, Cr, Cu, Hg, Mg, Ni, Pb, Zn) by inductively coupled plasma mass spectroscopy (ICP MS; EPA Method 200.7), with detection limits ranging from 0.33 to 4.1 μg/l.

Sediment samples from the June 2002 survey of all sites were analyzed for polycyclic aromatic hydrocarbons (PAHs), organophosphate, organochlorine, and pyrethroid pesticides. Selected samples were analyzed for trace metals. Standard quality assurance procedures including measurement of standard reference materials and quantification of surrogate recoveries and matrix spikes were used in all analyses. All chemical and toxicological analyses met prescribed quality assurance guidelines (Puckett, 2002).

2.6. ELISA TESTS

All water samples were analyzed for chlorpyrifos and diazinon using enzyme-linked immunosorbent assays (ELISAs) following procedures recommended by Sullivan and Goh (2000). ELISA readings were compared to a 5-point standard curve prepared using standards provided by the manufacturer. Accuracy was determined for each batch using external standards and matrix spikes. Measured values for all standards were within $\pm 20\%$ of the expected value. Precision was determined by duplicate measurement of one sample per batch. Duplicate coefficients of variation (sd/mean) were always less than 20%. A combined bottle-blank/process-blank was included during one sampling period, with no contamination detected. Samples were tested at full strength unless initial readings indicated that the chemical was at concentrations above the range of the test kits. In such cases, samples were diluted to known concentrations before definitive analysis. The ELISA lowest detectable dose was 30 ng/l for diazinon and 50 ng/l for chlorpyrifos.

2.7. CORRELATION ANALYSIS

Pearson correlation analyses were used to identify significant linear relationships between pesticide application rates and measured water quality parameters. Toxicity test proportion data were transformed to their arcsine square root prior to analysis. All data sets had distributions that were not significantly different from normal (Shapiro-Wilks, $p > 0.05$), with the exception of the distribution of ELISA measurements. The relationship between ELISA measurements and pesticide application rates was evaluated using the Spearman rank test. Application rates for the two pesticide classes (OPs and pyrethroids) were highly correlated ($r^2 = 0.89$), indicating a similar pattern of application (Figures 2 and 4). Because of the similar usage patterns, OP pesticide application data were used to characterize overall pesticide use for all correlations with water quality parameters. Using OPs in the analysis was also advantageous because all water samples were analyzed for diazinon and chlorpyrifos, so application rates could be compared to in-stream concentrations. Both pyrethroid and OP data were used in correlations with sediment toxicity, because the two compound classes have widely varying solubilities, and thus different soil/water partitioning characteristics.

In order to best characterize overall conditions at stream sites, data used in these analyses consisted of annual totals for pesticide use and mean values across all surveys for the in-stream parameters. ELISA diazinon and chlorpyrifos concentrations were averaged and summed using a value of zero for non-detects. Concentrations, rather than toxic units, of the two pesticides were summed because the intent was to compare the mass of pesticides applied with the mass of two common easily measured pesticides in streams.

3. Results

3.1. Water and Sediment Chemistry

A broad suite of analytes were measured in water samples during two surveys. Of the analytes measured, only diazinon and chlorpyrifos were measured above literature LC50 values or similar toxicity thresholds (e.g., Bailey *et al.*, 1997). These two pesticides were measured by ELISA in every sample, and those results are described below. Two pyrethroid pesticides were measured above reporting limits. Bifenthrin, with a reported *C. dubia* 48-h LC50 value of 0.07 ug/L, was detected in two of six samples, 0.010 ug/l at Alisal Creek and 0.025 ug/l at Oso Flaco Creek. Lambda cyhalothrin, with a reported *C. dubia* 48-h LC50 value of 0.30 ug/L (Mokry, 1990), was measured in one of six samples, 0.011 ug/l at Oso Flaco Creek. The Oso Flaco Creek watershed had the highest reported pyrethroid application rate, at 9.9 kg applied per km^2 of watershed area; Alisal Creek had 8.5 kg applied per km^2 (Table I).

A number of organochlorine and pyrethroid pesticides and PAHs were detected in sediment samples. Of these, the organochlorines DDE, DDT, dieldrin, and endrin were found above consensus Threshold Effects Concentrations, indicating the possibility of biological effects (MacDonald *et al.,* 2000). Dieldrin was measured in one sample (Corralitos Creek) at 110 ng/g dry weight, nearly twice the consensus Probable Effects Concentration of 61.8 ng/g DW, above which harmful effects are considered likely to be observed. *H. azteca* survival in this sample was 79%, and amphipod growth was 42% of that in test controls. Lambda cyhalothrin was measured at 12.1 ng/g in a sample from Alisal Creek, about twice the *H. azteca* LC50 value (Amweg *et al.*, 2005). *H. azteca* survival in this sample was 12% (Table I).

The ELISA measurements of diazinon plus chlorpyrifos, averaged over all six surveys, combined with average water column toxicity data, show the 12 sites falling into two main groups. Three sites had mean diazinon plus chlorpyrifos concentrations above 1 ug/l: Santa Ana Creek (28% mean *C. dubia* survival), Quail Creek (20%), and Alisal Creek (17%). The nine other sites all had OP concentrations below 0.16 ug/l and mean survival rates above 60% (Table I). The results were the

TABLE I

Watershed area, pesticide applications on land draining to stream sites, and selected parameters measured in stream samples

	Drainage area (km^2)[a]		Reported use (kg/y)[b]		ELISA (ug/l)	*C. dubia* Mean response (%)		Nitrate mean	*H. azteca* mean response (%)	
Watershed	Total	Reported	pyrethroids[c]	diazinon + chlorpyrifos	diazinon + chlorpyrifos	Survival	Repro.[d]	(mg/l)[e]	Survival	Growth[d]
Corralitos Creek	144	86	160	2052	0.075	98	108	33.9	79	42
Santa Ana Creek	112	13	76	425	6.708	28	42	4.8	ns	ns
Furlong Creek	39	23	57	914	0.115	64	95	134.2	ns	ns
Llagas Creek	271	83	172	974	0.023	97	118	47.2	94	47
Pacheco Creek	480	8	2	55	nd	97	112	19.7	ns	ns
Tequisquita Slough	297	78	582	2916	0.097	82	92	26.3	99	62
Watsonville Slough	18	10	106	495	0.157	100	108	17.8	95	64
Alisal Creek	108	47	920	4380	1.012	17	23	49.2	12	24
Quail Creek	50	26	439	3294	1.244	20	28	121.4	ns	ns
Arroyo Grande Cr.	203	21	11	68	0.023	75	82	15.3	ns	ns
Los Osos Creek	15	5	15	242	0.036	97	114	30.0	ns	ns
Oso Flaco Creek	35	35	340	1674	0.093	68	74	138.1	71	42

[a]Areas were derived from geographic information system counts of public lands survey system sections, with and without pesticide use reported, within digitized watershed boundaries.
[b]Reported use is as active ingredient applied in 2002.
[c]Sum of five synthetic pyrethroid pesticides: permethrin, cypermethrin, bifenthrin, lambda-cyhalothrin, and esfenvalerate
[d]*C. dubia* reproduction and *H. azteca* growth are given as percent of control response.
[e]Nitrate is given as total NO_3. "nd" = not detected. "ns" = not sampled.
ELISA, *C. dubia* toxicity, and nitrate are mean values from six surveys per site. *H. azteca* toxicity is from one sample per site.

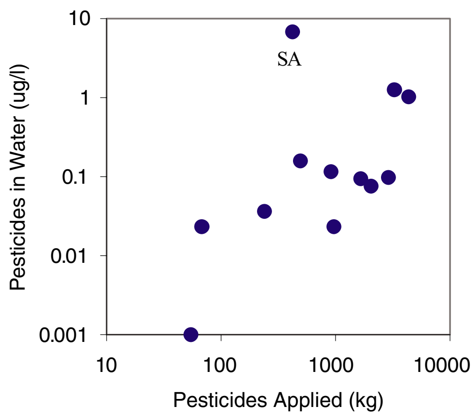

Figure 5. Graph of the annual (2002) mass of diazinon and chlorpyrifos pesticide active ingredient applied in the watershed area versus the mean concentration of these two pesticides in water samples from the study sites. SA = Santa Ana Creek.

same when viewed in terms of combined diazinon and chlorpyrifos toxic units (TU = concentration(LC50). Santa Ana Creek water samples averaged 20.6 TU, Quail Creek averaged 19.4 TU, and Alisal Creek averaged 4.4 TU.

3.2. Water quality and pesticide applications

Rates of pesticide application varied widely among watersheds, as did mean values for in-stream toxicologic and chemical parameters (Table I). This range of values was sufficient to resolve significant trends. There was a significant correlation ($p < 0.05$) between the annual use of diazinon and chlorpyrifos in the watersheds and the mean concentrations of the two pesticides measured in water samples from the corresponding stream sites (Figure 5). The correlation between watershed pesticide application rate and mean in-stream toxicity to *C. dubia* was significant at the $p < 0.10$ level (Figure 6).

Linear relationships between sediment toxicity to amphipods and watershed application rates of both OP and pyrethroid pesticides were significant at the $p < 0.10$ level, despite the low number of data points available (Figures 7 and 8). These sediment correlation analyses included Quail Creek toxicity data obtained in a separate study, as discussed below.

Data for the Santa Ana Creek water samples did not follow the general trend observed in the other watersheds (Figures 5 and 6). All six surveys found Santa Ana Creek diazinon concentrations above the *C. dubia* LC50, with one extremely high value of 37 ug/L (∼100 toxic units) measured in Sept 2002. Mean *C. dubia* survival was 28% at this site. This high diazinon and associated toxicity might be caused by a source close to the sampling site, since total watershed usage of diazinon and chlorpyrifos was low relative to the other watersheds. On the other hand, the

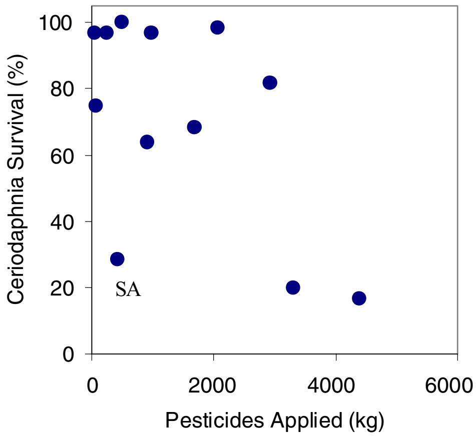

Figure 6. Graph of the annual (2002) mass of diazinon and chlorpyrifos pesticide active ingredient applied in the watershed area versus the mean survival rate of *Ceriodaphnia dubia* in water samples from the study sites. SA = Santa Ana Creek.

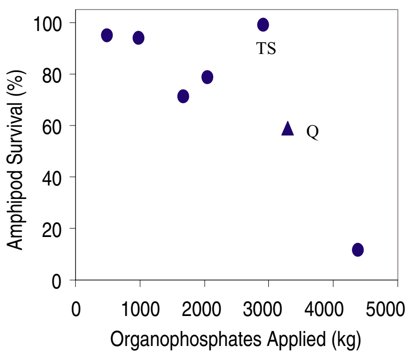

Figure 7. Graph of the annual (2002) mass of diazinon and chlorpyrifos pesticide active ingredient applied in the watershed area versus the mean survival rate of the amphipod *Hyalella azteca* in sediments from the study sites. TS = Tequisquita Slough

Tequisquita Slough site had lower sediment toxicity than the overall trend might indicate, based on pesticide usage in the watershed (Figures 7 and 8). This site is actually downstream of the Santa Ana Creek site (Figure 2), but is hydrologically complex, as it lies in a broad flat basin with poor subsurface drainage, a high water table, and undocumented flow patterns.

Nitrate concentration did not significantly correlate with any of the following parameters: the amount of pesticides applied, in-stream pesticide concentration, in-stream toxicity to *C. dubia*, watershed area, or watershed area in which pesticide usage was reported (all $p > 0.10$). Additionally, watershed size (both total area and area in which pesticide usage was reported) did not correlate significantly with any of the following parameters: amount of pesticides applied, in-stream pesticide

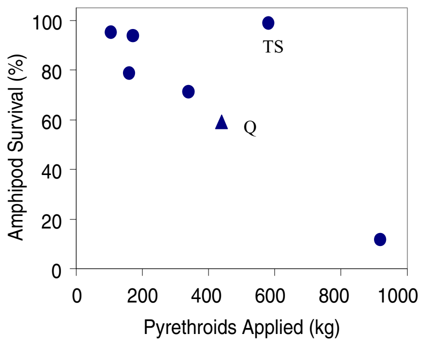

Figure 8. Graph of the annual (2002) mass of pyrethroid pesticide active ingredient applied in the watershed area versus the mean survival rate of the amphipod *Hyalella azteca* in sediments from the study sites. Pyrethroids were represented by five compounds: permethrin, cypermethrin, bifenthrin, lambda-cyhalothrin, and esfenvalerate. TS = Tequisquita Slough.

concentration, or in-stream toxicity (all $p > 0.10$). The weakness of these relationships suggests that the in-stream occurrence and effects of pesticides were more strongly related to the intensity of their application than to the extent of the drainage area or area under cultivation. It also indicates that nitrate behaves differently than do the measured pesticides in terms of application rate, environmental fate, or both.

4. Discussion

While there are numerous factors affecting the relationships between land use and water quality, this regional study of 12 watersheds indicated that the application rates of selected pesticides were generally associated with in-stream pesticide concentrations and toxicity. Watersheds with larger total pesticide inputs tended to have higher water column OP concentrations (Figure 5) and toxicity (Figure 6) in their streams. This analysis illustrates the value of having accurate pesticide use data when designing water quality monitoring programs for assessing the effects of land use on aquatic habitat.

The spatial and temporal scales of this study were coarse relative to the pesticide fate and effects processes under consideration. Spatially, the scale was determined by the reporting format for pesticide use, which consisted of 2.6 km^2 PLSS sections. Temporally, the pesticide use data were summed over the 2002 reporting year, and measured water quality parameters were averaged over the two year study period (July 2002 to June 2004). This temporal averaging provided a generalized characterization of land use and stream condition, and the results suggested that pesticide use data may be a useful predictor for site selection in regional water quality monitoring. Monitoring designed for status and trends analysis, for example, could consider watershed pesticide use in the development of levels for stratified random sampling. Studies of water body impairment, causes of biological effects, or sources of chemicals of concern could use the broad scale patterns seen in this study to focus sampling efforts. More intensive studies of pesticide fate and transport could make use of the more specific date and time information available in the pesticide use data base, though finer spatial resolution would require active collaboration with pesticide applicators. Similarly, the inclusion into the analysis of factors known to affect chemical fate and transport (precipitation, irrigation, soils, slope, permeability, vegetation, etc.) would allow more detailed modeling and likely provide more information useful for monitoring site selection.

There were significant linear relationships between sediment toxicity and watershed applications of both pyrethroid and OP pesticides ($p < 0.10$), despite the small size of the data set. Six sites were sampled for sediment toxicity, and data were available from a previous study of Quail Creek, in which *H. azteca* survival was measured in September 2000 (Anderson *et al.*, 2003a). Matching that result (59% survival) with the 2002 pesticide application data (Table I), produced the triangular point 'Q' that fits well within the linear relationships of both graphs (Figures 7 and 8). Review of pesticide application data for Monterey County, in which the Quail Creek watershed is located, indicated that application rates changed only moderately between 2000 and 2002. Applications of permethrin, the most widely used pyrethroid, increased 2%, while combined diazinon and chlorpyrifos applications increased 11% (PAN 2005). The point with lowest amphipod survival on both graphs (12% at Alisal Slough), is not likely to be unique in the region. Another watershed in the region with similar land use, but for which pesticide usage was not quantified in this study, had *H. azteca* survival of 4% in a previous study (Anderson *et al.*, 2003b). These and related data indicate the existence of high sediment toxicity in intensively cultivated regional watersheds.

While the occurrence of significant correlations is of interest, this study is also useful for identifying cases that did not fit the trends. The Santa Ana Creek watershed, for example, had relatively low rates of pesticide application within the watershed, but had extremely high concentrations of the same pesticides in water samples, accompanied by high toxicity (Table I, Figures 5 and 6). GIS visualization is helpful for examining this situation; it appears that the highest OP pesticide application rates in the watershed occur just upstream of the sampling site (Figure 2). Identifying such anomalous situations is a useful first step in designing studies to better understand processes of pesticide fate and effects, as well as in identifying runoff sources in need of management.

While spatial analysis found significant associations between agricultural pesticide use and in-stream effects, consideration must also be given to other human activities that can affect water quality but are not included in the available data. Principal among these is the application of pesticides for residential, urban, and industrial use. These uses are not reported in the current system, and are therefore not included in the analysis or visualization of pesticide effects. In the case of Santa Ana Creek, for example, land use just upstream of the sampling site includes both industrial and high density residential areas. Diazinon spikes in water samples could be the result of improper residential use or urban runoff, phenomena that are completely ignored in the present analysis. As mentioned above, however, this analysis does help to highlight situations not easily explained by agricultural applications, and may lead to consideration of appropriate alternative hypotheses.

The results of this study did not support the use of nitrate as an indicator of chemical contamination or toxicity. Nitrate is relatively inexpensive to measure, and is commonly applied to soils as part of input-intensive agricultural or residential activities. However, it is far more water-soluble than non-polar organic contaminants, and is expected to be transported through the environment via different pathways and at different rates. It is seldom found in streams at concentrations toxic to macroinvertebrates, and its ecological effects are primarily related to eutrophication. Nitrate may be a useful general indicator of intensive land use, and clearly must be monitored to evaluate potential water quality impairment, but the present study indicated it is not suitable for use in site selection when monitoring for ecological effects of toxic chemicals. Toxicity testing, on the other hand, did correspond reasonably well with watershed pesticide application rates, tends to be predictive of ecological effects (deVlaming *et al.*, 2000; Anderson *et al.*, 2003a), and provides a single integrative measure to detect toxic concentrations of both measured and unmeasured chemicals.

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