Ph.D. research prospectus for the Qualifying Exam

A multi-scale evaluation of agricultural best management practices for the control of pesticides

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Introduction and Background

Modern conventional agriculture, exemplified by large scale agriculture in California, uses chemical inputs such as pest control chemicals to maintain high levels of production. A fraction of applied pesticides are mobilized into surface waters by irrigation and stormwater runoff, negatively impacting California surface water quality with toxicity to biota and humans (Foe, 1995; Domagalski et al., 1997; Kratzer, 1999). Such is the case in the San Joaquin River Valley where the four counties of the valley are ranked in the top ten nationally for both agricultural production and pesticide use and the San Joaquin River and its tributaries are on the California 303(d) List for impairment by diazinon, chlorpyrifos and chlorinated pesticides (SWRCB, 2003; USDA-NASS, 2005; DPR, 2008). Orestimba Creek is a pesticide-impaired western tributary of the San Joaquin River and the focus of many monitoring studies by state, federal, and private entities. The high spatial and temporal resolution of data available for Orestimba Creek makes it an excellent case study to assess the impact of Best Management Practices (BMPs) on surface water quality. The results of this research will be useful in many other watersheds around the world dominated by agricultural land uses and with similar challenges to water quality.

Recent regulatory scrutiny and monitoring efforts have focused on chlorpyrifos, diazinon, and the pyrethroid pesticides such as lambda-cyhalothrin, esfenvalerate, and bifenthrin (CVRWQCB, 2003; Domagalski and Munday, 2003; deVlaming et al., 2006). Because of their similar chemical structure and mode of action, chlorpyrifos and diazinon are often managed similarly, but this may not be appropriate. A meta-analysis of available chlorpyrifos and diazinon monitoring, pesticide applications, and streamflow data revealed different patterns of diazinon and chlorpyrifos concentrations in Orestimba Creek. High concentrations of chlorpyrifos in Orestimba Creek reliably occurred after applications within one mile of the creek, but high concentrations of diazinon were not correlated with nearby applications, indicating diazinon was transported to the creek over greater distances due to its moderately hydrophilic nature. Chlorpyrifos management might be most useful when considered a case study for hydrophobic pesticide management.

Natural treatment systems, such as constructed wetlands and vegetated ditches, have been proposed as structural BMPs for the control of pesticides, suspended sediments, and nutrients and have a demonstrated ability to remove chlorpyrifos from irrigation and stormwater (Moore et al., 2001; Schulz and Peall, 2001; Bouldin et al., 2004; Cooper et al., 2004; Bennett et al., 2005). Beyond their intended use as natural treatment systems, structural BMPs could provide ancillary services to the agricultural landscape as islands of biodiversity in fields planted in monoculture. Though current pilot-scale natural treatment systems in the San Joaquin Valley have achieved reductions in aqueous chlorpyrifos concentration, before the commitment involved with adopting a full scale network of cost-effective BMPs, further research is necessary on several fronts to assess the applicability of natural treatment systems for the control of chlorpyrifos. Chlorpyrifos has been found to significantly sorb to soils and plants in BMPs, with preferential sorption to plants (Brock et al., 1992; Moore et al., 2002). A key to understanding the functioning of BMPs for hydrophobic pesticide removal is to understand the role of plants as surfaces for the sorption of pesticides and for intercepting particles and how differences in plant species selection and planting density can affect removal efficiency at a watershed scale.

The interactions of pesticides with soils have been the subject of much study, with well established theory and approach quantifying sorption using isotherms (Cheng, 1990). To characterize the sorption of pesticides to soil, it is assumed that at a given concentration an equilibrium is established between the pesticide sorbed onto the soil surface and the pesticide in solution, with the ratio of the two expressed as a distribution coefficient, K_d. The distribution coefficients of chlorpyrifos to a variety of soils have been measured, ranging from 45 to 1300 $L \cdot kg^{-1}$ (Garcia et al., 1992; Huang and Lee, 2001; Baskaran et al., 2003; Wu and Laird, 2004; Yu et al., 2006). There is sufficient variation in experimental data to suggest that sorption should be measured for each location of proposed BMP construction.

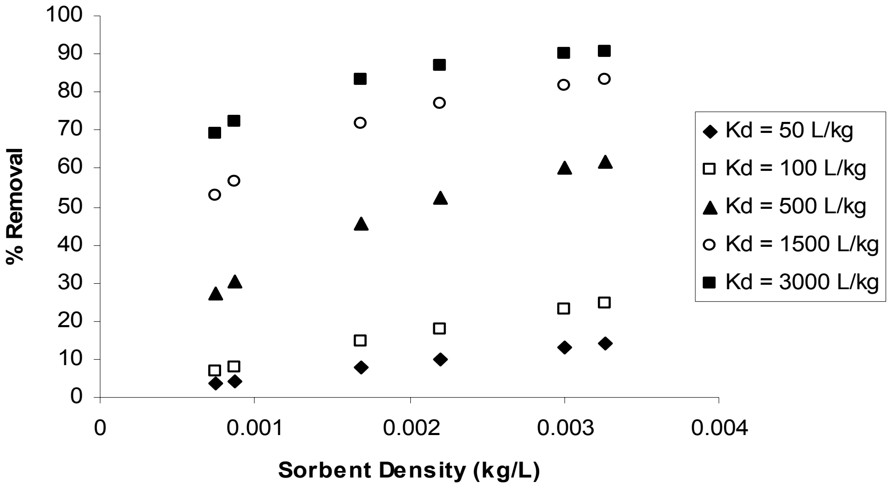

Figure 1. Percent removals as a function of sorbent mass per volume and distribution coefficient, Kd, in a completely stirred batch reactor at equilibrium. Sorbent densities were calculated from wetland plant mass per area (Emery and Perry, 1995; Koottatep and Polprasert, 1997; Horowitz, 1999; DeBerry and Perry, 2004) and soil bulk density, assuming a wetland depth of 0.5 m and a saturated soil bed depth of 0.1 cm.

The interaction of pesticides with plants is more complicated because there can be reactions with both external and internal surfaces as well as possible uptake into plant tissues. Chlorpyrifos sorption to plants has been measured in only one study with distribution coefficients for submergent aquatic plants ranging from 1660 to 2150 $L\cdot kg^{-1}$ (Crum et al., 1999). The greater affinity of chlorpyrifos for plants and the sheer amount of plant-derived surfaces in a natural treatment systems (e.g. live stems, thatch, litter, peat, etc.) indicate plant associated sorption is an unmeasured but dominant process in the functioning of natural treatment systems for chlorpyrifos control (Figure 1). With average half-lives for chlorpyrifos transformation reactions ranging from 10 to 170 days, much slower than the residence time of many BMPs, it can be inferred that sorption is the primary mechanism of observed chlorpyrifos removal in natural treatment systems (Racke, 1993).

Datasets publicly available in California represent an unrealized opportunity for watershed managers in the state and an example for others areas of the types of analysis that could be conducted given sufficient data reporting (CMCC, 2006; DPR, 2006, 2008). These data sources and new Geographical Information System (GIS) tools can answer such fundamental questions for BMP implementation as how much removal is needed, how to size and site BMPs, and how water quality is effected. Analysis of data from individual monitoring studies has been published and Guo *et al.* (2004) used the compiled datasets to correlate hydrophilic pesticide loads in the Sacramento River watershed to pesticide use and rainfall. Dabrowski *et al.* (2002)used a GIS-based model to assess chlorpyrifos transport in agricultural watershed subcatchments. Cryer *et al*. (2001) modeled Orestimba Creek and assessed the efficacy of several spray modification BMPs. Modeling using these databases has not been implemented in the San Joaquin Valley for the management of hydrophobic pesticides with constructed BMPs. Site selection criteria for natural treatment systems have not been extensively managed with a GIS.

Research Objectives

The overarching goal of this research is to understand chlorpyrifos sorption in natural treatment systems and to assimilate that knowledge into field scale and watershed scale models for improved BMP site selection. I hypothesize that sorption processes are the most important removal processes over the timescale of chlorpyrifos transport to surface waters. Even in non-engineered existing systems, the residence time in drainage ditches acts as a primitive BMP, but chlorpyrifos mitigation can be improved by sizing and siting treatment systems to intercept chlorpyrifos-containing runoff with sufficient sorbent mass and residence time. I propose to confront this problem at four spatial scales: bulk phase-surface interactions; field scale transport; watershed scale fluxes and loading; and regional BMP site selection and impact. I will achieve these broad goals by answering three specific research questions:

1. *Does sorption to plants predominate chlorpyrifos sorption in natural treatment systems and can observed sorption be correlated with measurable plant physical or chemical properties?*

2. *Can models be used to quantify the fluxes of chlorpyrifos in a watershed and reductions in chlorpyrifos load necessary to meet water quality criteria, thus enabling estimates of land area required for conversion to BMPs in order to meet water quality goals?*

3. *Where in the watershed should BMPs optimally be employed, what will the impact to the San Joaquin River be, and how might results from Orestimba Creek be applied to other watersheds?*

This research will contribute to a better understanding of the role of vegetation in chlorpyrifos sorption in BMPs. The combined results of the modeling components of this research will be beneficial to watershed managers to comply with pesticide water quality criteria. Establishing metrics for BMP site selection will allow allocation of limited funds to achieve the greatest amount of remediation. This research could establish the framework for a chlorpyrifos trading scenario, whereby growers with minimal chlorpyrifos emissions or high construction costs could offset the construction costs of BMPs with a greater net impact, similar to other pollutant trading systems.

Proposed Research

Research will consist of laboratory experimental and modeling components. Sorption experiments and measurement of plant biochemical composition will be conducted in the laboratory of William Stringfellow at LBNL, under controlled conditions with established quality control procedures. Microscopic imaging and analysis will be conducted at the Biological Imaging Facility, Koshland Hall, UC Berkeley. Modeling will be performed using established models and software available for use on a standard PC, as detailed below.

Objective I: Chlorpyrifos sorption in natural treatment systems

The first research objective is to quantify distribution coefficients for surfaces in agricultural BMPs, establish kinetics for selected sorbents, and explain differences in sorption by correlation to physical or chemical characteristics of the sorbents.

Sorption experiments will be conducted on two soils and six plants. Soils for this experiment are a composite soil sample collected from a proposed pilot-scale vegetated ditch site and a reference San Joaquin Soil obtained from NIST. Plants to be measured are wheat (*Triticum aestivum)*, ryegrass (*Lolium sp*.), alfalfa (*Medicago sativa)*, cattail (*Typha sp*.), Tule bulrush (*Schoenoplectus acutus),* and California gray rush (*Juncus patens*) which represent species common to local agricultural and wetland environments. Plant stems in 5-cm and 1-cm are used to assess if there is a difference between sorption to intact plant stems and broken plant tissues. Alvord and Kadlec (1995) observed increased atrazine sorption by degraded wetland plant matter, thus I will also measure sorption to a wetland sediment and a decomposed plant sample.

The sorption of chlorpyrifos to soils and plants will be measured using a batch equilibrium method similar to Wu and Laird (2004). Sorbent samples are exposed to solutions of chlorpyrifos in Ultrapure water buffered to pH 7.4 and placed in shaker at 25°C in the dark for 16 hours. A HP 6890 gas chromatograph with micro-cell electron capture detector (μ-ECD) will be used to analyze extracts and report chlorpyrifos peak data using a method based on Zaugg et al. (1995). The low solubility of chlorpyrifos poses a challenge to experimental work and I chose a maximum concentration of 2.85 μM chlorpyrifos, well within the range of reported solubility.

Given the significantly larger distribution coefficients for plants than for soils (Crum et al., 1999), I am particularly interested in measuring sorption to plants nominated for planting in vegetated BMPs. I aim to establish independent metrics that can be used to normalize observed distribution coefficients for plants and aid in the selection of plants for natural treatment systems for chlorpyrifos management. I hypothesize that observed differences in plant sorption are due to differences in plant stem morphology and the ratio of carbohydrate:lipid:protein between plant species. Visual inspection of plant stem cross-sections reveals differences in surface area to volume ratios and internal surface areas. Correlation between partitioning and lipid content have been reported (Schwarzenbach et al., 1993; Karnchanasest et al., 2002; Lin et al., 2007). I will measure these physical and chemical characteristics of plant species and perform correlations to observed distribution coefficients.

Results to date

In a preliminary kinetics experiment, sorption of chlorpyrifos to soil was rapid, with 70.3 and 94.9 percent of the maximum sorbed concentration reached in 1.7 and 8.3 hours respectively (data not shown). It appears that much of the sorption occurred rapidly (<20 minutes), perhaps reaching a "pseudo-equilibrium" in less than eight hours. Further kinetic studies with finer temporal resolution are required to establish the kinetics of chlorpyrifos sorption to soils and plants.

Sorption to plants in 1-cm and 5-cm lengths and to soils was fit to both linear and Freundlich equations (Tables 1 and 2). If R^2 values are used as a measure of goodness of fit as in previous studies, for all samples the linear fit was superior. No isotherms asymptotically approached saturation, as would be expected for Freundlich isotherms, over the experimental range of chlorpyrifos concentrations. Because the chlorpyrifos concentrations were bracketed by the solubility limit and environmentally relevant concentrations, it can be concluded that, for all practical purposes, the partitioning of chlorpyrifos between solids and water in the environment can be described by a linear relationship.

Linear distribution coefficients for chlorpyrifos were 40.0 and 71.4 $L \cdot kg^{-1}$ for composite vegetated ditch soil and San Joaquin Standard Soil respectively (Table 2). The values derived experimentally were within the range of values reported in the literature. For plants, linear distribution coefficients for chlorpyrifos ranged from 571.1 to 1303.4 and 637.1 to 2557.1 $L \cdot kg^{-1}$ in 5-cm and 1-cm plant stems respectively (Table 1). These values

Table 1. Distribution coefficients of chlorpyrifos to plants

Adsorbate	5-cm					1-cm				
	K_d ($L \cdot kg^{-1}$)	R^2	K_f ($L \cdot kg^{-1}$)	n	R^2	K_d ($L \cdot kg^{-1}$)	R^2	K_f ($L \cdot kg^{-1}$)	n	R^2
Cattail	1303.4	0.96	1088.2	0.92	0.83	2557.1	0.98	2610.5	1.02	0.79
California gray rush	932.4	0.92	352.2	0.60	0.67	1507.2	0.99	1397.9	0.97	0.97
Wheat	957.9	0.98	608.5	0.95	0.94	1141.4	0.96	726.6	0.81	0.82
Ryegrass	629.5	0.99	454.7	0.82	0.92	677.2	0.99	476.9	0.82	0.94
Alfalfa	571.1	0.94	364.8	0.80	0.64	637.1	0.97	466.0	0.84	0.91

Table 2. Distribution coefficients of chlorpyrifos to soils

	K_d ($L \cdot kg^{-1}$)	R^2	K_f ($L \cdot kg^{-1}$)	n	R^2	K_{om} ($L \cdot kg^{-1}$)
Composite Vegetated Ditch Soil	40.0	0.98	39.6	0.95	0.94	2819.4
NIST San Joaquin Standard Soil	71.4	0.99	68.3	0.94	0.98	5214.2

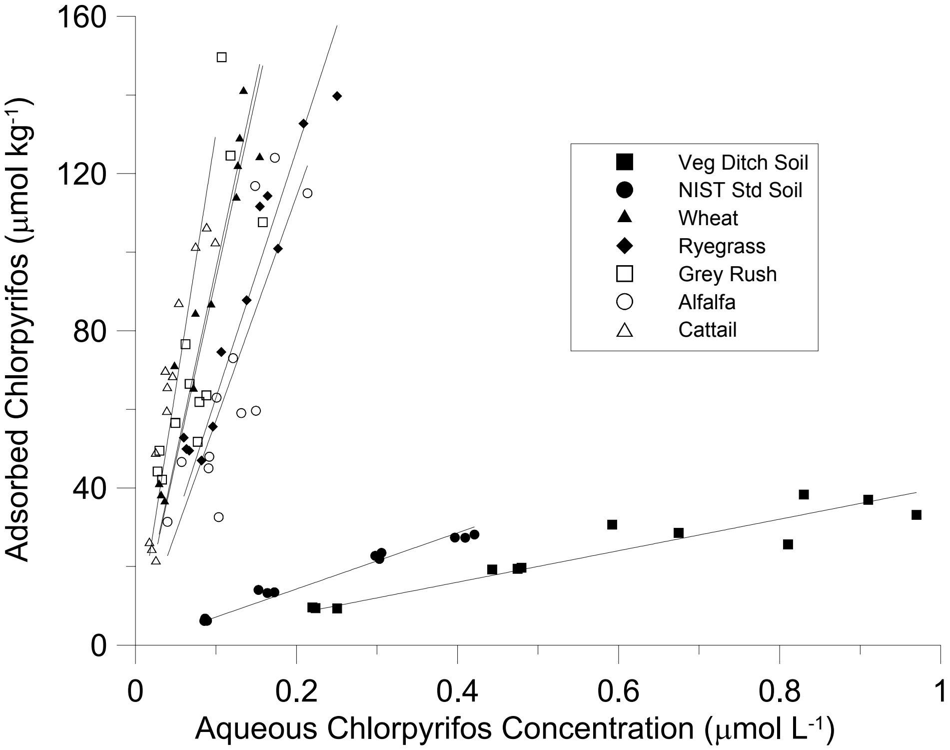

Figure 2. Isotherms for the sorption of chlorpyrifos to soils (particles 1.18 mm in diameter or less) and plants (5-cm stem lengths)

are approximately equal to those reported by Crum et al (1999). As shown by the isotherms for the five plants (5-cm lengths) and two soils (Figure 2), chlorpyrifos affinity was at least an order of magnitude greater for plants than for soils. To two significant figures the organic matter content of the two soils were equal and therefore the distribution coefficients were not correlated to organic matter content. The K_{OM} values calculated using the measured organic matter for composite vegetated ditch and San Joaquin Standard soils were 2819 and 5214 $L \cdot kg^{-1}$ respectively (Table 2). These values are equal in magnitude to K_d for plants and are comparable considering plants to be made up entirely of organic matter.

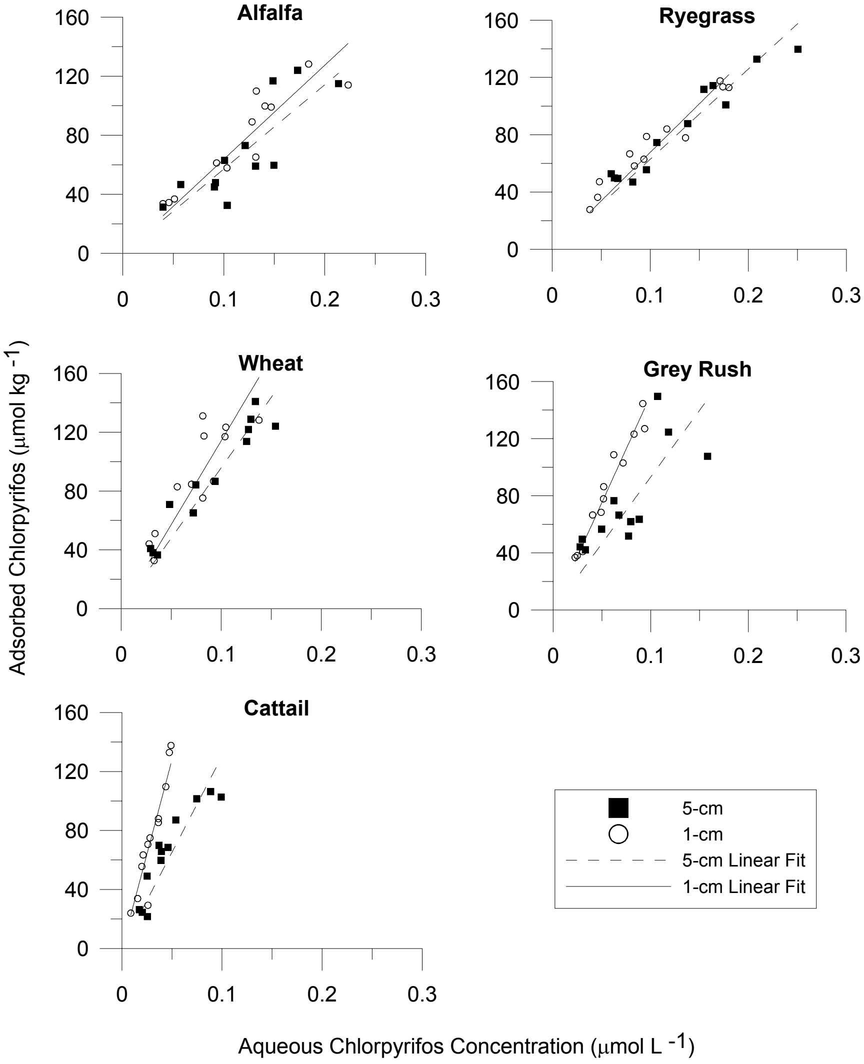

Figure 3. Isotherms for the sorption of chlorpyrifos to 1-cm and 5-cm plant pieces

Variation was observed between plant species and for all plant species 1-cm plant pieces had greater distribution coefficients than 5-cm plant stems (Figure 3). Chopping the plant material increased K_d by 11.6, 7.6, 19.2, 61.2, and 96.2 percent for alfalfa, ryegrass, wheat, grey rush, and cattail respectively. Chopped plant materials can be divided into two groups: plants with a hollow cylindrical structure (alfalfa, ryegrass, and wheat) that exhibited increases in K_d less than 50% and plants with an internal porous cellulose structure (grey rush and cattail) where K_d increased by more than 50%. I am pursuing measurement of plant tissue lipid, carbohydrate, lignin, and protein content as well as microscope imaging and analysis for plant surface area to volume ratio and internal surface area per mass. I expect these parameters will explain differences between plant species and among plant particle sizes and be used to normalize distribution coefficients. The initial meaning of these results is that the wetland species are better sorbents for chlorpyrifos and the increased surface area and porosity of the broken stems and thatch in a permanent wetland or ditch may increase the chlorpyrifos retention capacity of the system.

Objective II: Watershed modeling

For the second research objective, a GIS watershed model of Orestimba Creek will be used to quantify the flux of applied chlorpyrifos reaching the stream and estimate the chlorpyrifos mitigation required to meet regulatory requirements. The information gained in Objective (1) and a reactor model for chlorpyrifos treatment in a vegetated ditch BMP will be integrated into the watershed model to estimate the total land required for conversion to BMPs to meet water quality objectives.

The California Department of Pesticide Regulation (DPR) Pesticide Use Reporting (PUR) database is a collection of publicly accessible and searchable raw data on pesticide use (DPR, 2004). The DPR Surface Water Database (SWDB) is an annually updated collection of downloadable files containing the entire dataset (>183,000 records) of DPR records since 1991 of surface water and sediment monitoring for pesticides (DPR, 2006). ArcGIS with Tracking Analyst and ArcHydro extensions (ESRI, Redlands, CA) provides the functionality to combine data on pesticide applications and monitoring with publicly available hypsography, hydrography, streamflow, land use, and meteorology data to define the watershed and its surface water network, then model spatial and temporal patterns of chlorpyrifos occurrence and transport in the watershed (DWR, 2005; CMCC, 2006; USGS, 2006).

I will define sub-catchments and model the watershed at a scale more relevant to pesticide applications and transport. Current data allows for a resolution for applications data of approximately one square mile. These data can often be combined with land use surveys to identify individual fields where applications occur. These fields can then be connected to their associated drains and integrated into the watershed model.

I will incorporate BMPs into the watershed model and analyze impacts. I will model vegetated ditch BMPs as a series of stirred tank reactors or a packed bed reactor. This model will be tuned with bench-scale experiments and field data provided by my collaborators at DPR. I will use this model to address the impact of plant species selection and species-dependent plant growth density on removal. This model will be used to determine the mass removal of chlorpyrifos per unit of BMP area under three or more planting scenarios. Real vegetated ditch or constructed wetland systems will have lower chlorpyrifos removal than predicted by this model, due to non-ideal behavior such as hydraulic short-circuiting. Modeling an idealized vegetated ditch is a best-case scenario, but nevertheless provides a simple estimate of the land area required for BMPs.

Results to date

A preliminary meta-analysis of the chlorpyrifos and diazinon applications, monitoring data, rainfall, land use, and streamflow has been conducted from the above identified sources. This analysis has exposed several limitations in the dataset:

- The data are left-censored with a non-normal distribution, owing to a large number of non-detects
- Sampling dates are biased towards the winter dormant spray season
- Sampling intensity is not equal from year to year
- The number of samples varies greatly from site to site
- The limit of detection of the studies varied widely
- Several studies had limits of detection above WQC

Only Orestimba Creek has a sufficient temporal data resolution to allow for the type of analysis proposed in Objective (2). Due to a scarcity of data, it is unclear if other west San Joaquin tributaries have similar patterns of chlorpyrifos use and occurrence but Orestimba Creek can be used as a test case of a watershed with high chlorpyrifos use.

Objective III: BMP site selection and regional impact

The third research objective is to use site suitability analysis techniques to identify most promising locations for BMP construction and model the impact of BMPs on chlorpyrifos concentrations in the San Joaquin River.

Site suitability analysis is an established GIS technique, applied often in the urban planning and landscape architecture fields, to rank criteria such as site slope and adjacency to streams or roads in order to determine sites of highest suitability for further investigation. These techniques will be applied to BMPs for chlorpyrifos by ranking sites according to their chlorpyrifos application rate, vegetative cover, crop type, and distance from the receiving water. Land areas meeting criteria to a determined minimum degree will be identified. Suitable land area will be compared with the needed area calculated from Objective (2) to determine if sufficient chlorpyrifos can be achieved in the watershed. If the suitable sites exceed needed area, the sites best fitting the selection criteria will be identified for further investigation. I hypothesize that a large area could be used for BMPs but only a few sites will be identified as the most effective for chlorpyrifos removal.

The San Joaquin River Model Interface of the Watershed Analysis Risk Management Framework (WARMF) is the currently accepted model for hydrology and water quality in the San Joaquin River basin. The model defines watersheds using U.S. EPA BASINS and uses both modeled and gauge data to describe conditions in the San Joaquin River and tributaries. Analyses are performed and results reviewed using a GIS-based graphical user interface. The Orestimba Creek watershed in this model is currently treated as a flat plane with the actual data from the Orestimba Creek at River Road gauging station fed to the model. This form of modeling likely underestimates the contribution of Orestimba Creek on the San Joaquin River chlorpyrifos load.

This Orestimba Creek GIS watershed model will be inserted into the San Joaquin WARMF to better model Orestimba Creek. The San Joaquin WARMF model will be run with and without the inclusion of this module to consider the impact of Orestimba Creek with and without BMPs on chlorpyrifos loads in the San Joaquin River. The impact several scenarios for BMP implementation will be modeled.

Conclusion

This research will quantify distribution coefficients of chlorpyrifos to soils and plant to be used in BMPs of the San Joaquin Valley. These basic values are necessary for the design of BMPs locally and worldwide. Relating sorption to physical and chemical properties is a novel method to assess potential of new species for use in BMPs. The site selection and watershed modeling techniques developed can be emulated in other watersheds for hydrophobic pesticides management. The multi-scale framework developed for assessing the applicability of natural treatment systems will guide other watershed managers in implementing BMPs. The solution to controlling chlorpyrifos in runoff requires the application of the fundamentals from several disciplines and this project reflects this multidisciplinary approach.

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