Environmental Fate of Organophosphate Pesticides in Constructed Wetlands Treating Non-point Source Agricultural Drainage

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Abstract

Chlorpyrifos and diazinon, organophosphate pesticides, are found on the state 303(d) list for the San Joaquin River and its tributaries. Elevated levels of pesticides in surface waters are attributed to agriculture, a major industry in the region. Methods to reduce the levels of pesticides in agricultural irrigation water are called Best Management Practices (BMPs). This study will investigate the ability of one agricultural BMP, constructed wetlands, to remove organophosphate pesticides. Focused scientific studies will analyze and evaluate the impact of constructed wetlands on improving agricultural drainage water quality by reduction of pesticide and sediment concentrations. The overall removal rates and efficiencies of chlorpyrifos and diazinon in constructed wetlands will be determined. The physical, chemical, and biological removal processes will be identified and removal kinetics will be determined. Macrocosm studies will be utilized to determine how engineering design parameters affect chlorpyrifos and diazinon removal. Guidelines will be written to improve the efficiency of constructed wetlands used as agricultural BMPs for pesticides. Understanding the chlorpyrifos and diazinon removal mechanisms and kinetics in wetlands will enhance their applicability as a BMP. Locally, this project will improve the ability of stakeholders to manage their watershed to comply with TMDL and Ag Waiver Program requirements. Published guidelines will allow growers on a local and national level to evaluate constructed wetlands as management practices and implement the most beneficial solutions.

A. Specific Aims

My hypothesis is that a combination of physical, chemical, and biological processes remove pesticides from irrigation drainage water treated in constructed wetlands. The objectives of this project are:

1. Quantify the chlorpyrifos and diazinon removal rates and efficiencies for constructed wetlands treating agricultural drainage.
2. Determine if pesticide removal is accomplished by physical, chemical, or biological means.
3. Examine the mechanism(s) of pesticide removal and determine removal pathways and kinetics.

4. Determine how engineering design parameters such as flow, installation size, site management practices, and environmental factors affect chlorpyrifos and diazinon removal.
5. Create guidelines to improve the pesticide removing potential of constructed wetlands used as agricultural Best Management Practices (BMPs).

B. Relevance to the UC TSR&TP

Agriculture is a major contributor to the California economy. California's agricultural system requires irrigation and the use of pesticides, chemicals that are toxic by design. When irrigation drainage water containing pesticides enters surface waters, it becomes a potential human health and environmental risk. Elevated levels of pesticides have been found in the San Joaquin River and its tributaries, an agricultural region. Water from this river system is distributed throughout California for a multitude of uses. Pesticides in the San Joaquin River are thus a concern for all Californians and the management of pesticide-containing irrigation water is the responsibility of California's large agriculture industry.

This study will investigate constructed wetlands, an agricultural Best Management Practice, in remediating irrigation drainage water. Fundamental knowledge will be gained in the applicability of wetlands as a pesticide remediation strategy. Technology developed through this project will allow farmers and irrigation districts to meet future management restrictions from upcoming state and federal water quality regulations.

C. Background

Agriculture is a major contributor to the U.S. economy, with $197 billion in market value of agricultural products sold. California agricultural alone accounts for $30.6 billion (California Agricultural Statistics Service, 2003). Farms also figure predominantly in the American landscape, covering 931 million acres, or 40% of the U.S. landmass (USDA, 2003; CIA, 2003). To maintain a high level of production, U.S. agriculture applies over 700 million pounds of pesticide active ingredients per year (Donaldson et al., 2002). Over 180 million pounds of pesticide active ingredient was applied in California in 2000 (*California Pesticide Use Summaries Database*, 2003). Runoff carries some of the applied pesticides into surface waters, where water quality can be impaired. The U.S. EPA 303(d) list of impaired water bodies includes 1518 bodies of water impaired by pesticides (U.S. EPA, 2003). Impaired waters are those that do not meet water quality guidelines, even after reduction of point sources. To meet water quality standards, the EPA and state agencies are implementing Total Maximum Daily Load (TMDL) rules for pollutants for each impaired water body. The TMDL limits the total load of pollutants that a water body can receive and still meet water quality standards. Since 1996, 200 TMDLs have been approved for pesticides (USEPA, 2003).

Many states are now requiring individual farmers and agricultural organizations to comply with TMDLs. The Central Valley Regional Water Quality Control Board has adopted a temporary the conditional waiver of Waste Discharge Requirements for “irrigation return water” dischargers. This Waiver Order (Ag Waiver Program) requires that agricultural surface discharges are monitored and management practices implemented to achieve water quality objectives (CRWQCB, 2003). The trend in accountability for agriculture dischargers will continue. One method of meeting agricultural discharge water quality requirements is through Best Management Practices. Agricultural BMPs are management practices developed with water quality standards in mind to reduce non-point source pollution. This project will evaluate one commonly employed BMP, constructed wetlands, for pesticide and sediment removing potential.

The Wingsetter Ranch is located adjacent to the San Joaquin River in West Stanislaus County, California, in the Panoche-San Luis Reservoir Watershed (USGS #18040014) (Surf Your Watershed, 2003). A constructed wetland at Wingsetter Ranch was built to control sediment runoff from approximately 4,000 acres of agricultural land. The organophosphate insecticides chlorpyrifos and diazinon are applied to alfalfa, almond, apricot, walnut, and tomato crops grown in the Wingsetter Ranch drainage. The San Joaquin River above Vernalis and Orestimba Creek and four of its tributaries in West Stanislaus County are on the State 303(d) list of impaired water bodies for chlorpyrifos and diazinon (Central Valley RWQCB, 2003). In 2000, Stanislaus County applied 88,384 lbs. of chlorpyrifos and 73,483 lbs. of diazinon active ingredient (California Pesticide Use Summaries Database, 2003).

This project will investigate the efficacy of the Wingsetter Ranch wetland in removing chlorpyrifos and diazinon pesticides from agricultural drainage. Pesticides are often closely associated with sediments; the removal of sediments by wetlands will also be investigated. Domagalski et al. (1997) and Kratzer (1999) found that, in the study region, pesticides are mobilized by irrigation and drain water and carried into the San Joaquin River and its tributaries. Wetlands have been constructed upstream of agricultural discharge outlets to the San Joaquin River to intercept and remove pesticides before they enter the river. However, the pesticide removing abilities of wetlands have not been extensively studied (Moore et al., 2002; Schulz and Peall, 2001; Rodgers and Dunn, 1992),

The environmental fate of chlorpyrifos and diazinon are not well understood. Previous work shows that chlorpyrifos is adsorbed strongly onto sediment particles, reducing the aqueous concentration (Howard, 1999). The fate of sorbed chlorpyrifos is not known. For chlorpyrifos dissolved in water, volatilization, photolysis, and hydrolysis are major removal mechanisms (Howard, 1999; Racke, 1993). The role of biodegradation in chlorpyrifos removal is not well understood. Giddings et al. (1997) did find that the degradation of chlorpyrifos in water followed a first-order decay model. The environmental fate of diazinon is less known, but it is more soluble than chlorpyrifos and undergoes pH-dependent decomposition in water (Howard, 1999; EXTOXNET, 2003).

D. Research Design and Method

The overall efficacy of the Wingsetter Ranch wetland at removing pesticides and sediments will be determined with a mass balance approach. I will install sampling stations at the inlets and outlets of the wetland. Flow measurements and water samples will be collected at the sampling stations. Collected water samples will be analyzed for chlorpyrifos and diazinon with GC/FPD using EPA Method 1657. Sediments will be collected and analyzed for the organophosphate pesticides also via EPA Method 1657. The expected detection limits for chlorpyrifos and diazinon with this method are 4 and 38 ng/L respectively (U.S. EPA, 1993). I will use this input/output study to calculate the pesticide and sediment removal rate and efficiency for the wetland.

Other water quality parameters will also be determined as part of the pesticide environmental fate studies. I will make field measurements for turbidity, algal chlorophyll fluorescence, temperature, electrical conductivity, dissolved oxygen, and pH. Water samples will also be analyzed for TOC, DOC, VSS, TSS, chlorophyll, nitrate and nitrite nitrogen, ammonia nitrogen, soluble ortho-phosphate, and total phosphate. These measurements will allow me to determine the environmental and water quality conditions in the wetland and relate those findings to the results of lab microcosm studies.

I will implement laboratory and field studies to determine the removal mechanism for chlorpyrifos and diazinon in wetlands. I will determine if physical processes remove these pesticides, causing accumulation in sediments, or if the removal mechanism is destructive. For destructive processes, I will determine if the process is chemical or biological.

I will utilize field mesocosm studies and laboratory microcosm experiments under controlled conditions to identify specific chemical and biological removal mechanisms. These studies will allow further examination of the mechanisms of pesticide removal and determination of degradation kinetics. Temperature, spatial and temporal effects on the rate of removal will be determined. I will use macrocosm studies to determine how design parameters such as wetland dimensions, site hydrologic regime, and site management practices affect chlorpyrifos and diazinon degradation.

I will compare the results of this project to similar studies in other regions and states and create guidelines for implementing wetlands as agricultural BMPs. Guidelines will be published to assist design of constructed wetlands and improve existing water treatment wetlands nationwide.

E. Data Management

The software package JMP IN from the SAS Institute will be used for statistical analysis. Wetland mass balances will be modeled using Berkeley Madonna. Graphical representations of data will be created using Golden Software's Grapher package.

F. Future Importance of Research

The EPA and SWRCB are required by the Clean Water Act to address high pesticide levels in the San Joaquin River and its tributaries. Development of pesticide TMDLs and an end to the Ag Waiver Program will force farmers and irrigation districts to address pesticides in irrigation runoff. This study will evaluate the efficacy of constructed wetlands as a pesticide management strategy. Results of the study will enable stakeholders to meet the management goals of future irrigation discharge regulations.

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