In-stream pesticide loads in relation to agricultural pesticide applications

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By

Joy Larson

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ABSTRACT

Pesticides are a necessary component to successful agricultural production and are also the main source of toxicity in our state's surface waters. This study examines the transportation of two organophosphate insecticides in agricultural runoff. Three agricultural ditches in North Monterey County were sampled for chlorpyrifos and diazinon during a dry weather monitoring period in 2002 and the first storm event of the 2002/2003 season. Observed chlorpyrifos and diazinon concentrations were compared to published aquatic toxicity values. Loads of these two pesticides were estimated for the water column and pesticide adsorbed to suspended sediment in the water column. These loads were divided by the applications of these two pesticides in upstream and surrounding agricultural fields and greenhouses in the watershed. Application data were obtained from the Monterey County Agricultural Commissioner.

Chlorpyrifos estimated proportions of applications present in downstream loads ranged from 0.007% to 3.4%. Every sample collected exceeded acute and chronic toxicity values for chlorpyrifos (20 ng/L and 14 ng/L respectively). The estimated proportions of diazinon applications present in downstream loads ranged from 0.007% to 15%. Of all samples collected, 63% to 100% exceeded the acute toxicity value of 80 ng/L for diazinon and 100% exceeded the chronic toxicity value of 50 ng/L. Small proportions of pesticide applications can result in concentrations downstream that are known to be toxic to aquatic life. It is noted that these results are highly dependant on assumptions about the time period used to add up application data.

The general pattern of estimated loads in the waterways correspond to large or frequent applications upstream of the sample site. In two of the three watersheds, the highest estimated in-stream loads of chlorpyrifos and diazinon corresponded to peaks in the hydrograph of the storm, indicating that precipitation and runoff could have leached chlorpyrifos and diazinon that had been accumulating on the surfaces of the surrounding and upstream agricultural fields into the waterways. The highest estimated in-stream loads in the third watershed occurred during time of frequent large applications during the summer monitoring period. This could be due to greenhouse applications immediately upstream from the sampling site not influenced by precipitation and/or irrigation events that are not quantified in this study.

INTRODUCTION

The purpose of this study is to measure a relationship between agricultural applications of two pesticides, chlorpyrifos and diazinon, and amounts of these two pesticides downstream of the applications in three impaired surface water bodies.

Background

Agriculture and Water Quality in the Salinas River Watershed

The Salinas Valley along the Central Coast of California is known as the nation's salad bowl, and is the most productive vegetable producing region in the U.S.A. (CFBF, 2000). The Salinas River Watershed covers just over 10,000 km^2. It includes recognized aquatic habitats, as the river drains through the Salinas River National Wildlife Refuge estuarine area (Salinas Lagoon) and into the Monterey Bay National Marine Sanctuary (Figure 1). The river is a migration corridor for threatened salmonids, such as the steelhead (*Oncorhynchus mykiss)* and provides habitat for a diversity of waterfowl, mammal, and amphibian species. The northern portion of the watershed (the lower watershed) lies in Monterey County.

The Central Coast Regional Water Quality Control Board (CCRWQCB, Region 9), has placed the Salinas River on the federal Clean Water Act 303(d) list of impaired water bodies due to sediment and pesticide contamination (Ganapathy et al, 1997, Hunt et al, 2002, and Singhasemanon, 2003). Pesticide residues in surface water are a concern to the CCRWQCB and the Department of Pesticide Regulation (DPR) due to their possible effects on fish and wildlife. The DPR oversees environmental monitoring of pesticide contamination as it pertains to potential health hazards (as well as product evaluation and registration, residue testing of fresh produce, and local use enforcement through the county agricultural commissioners) (CDPR, 2003).

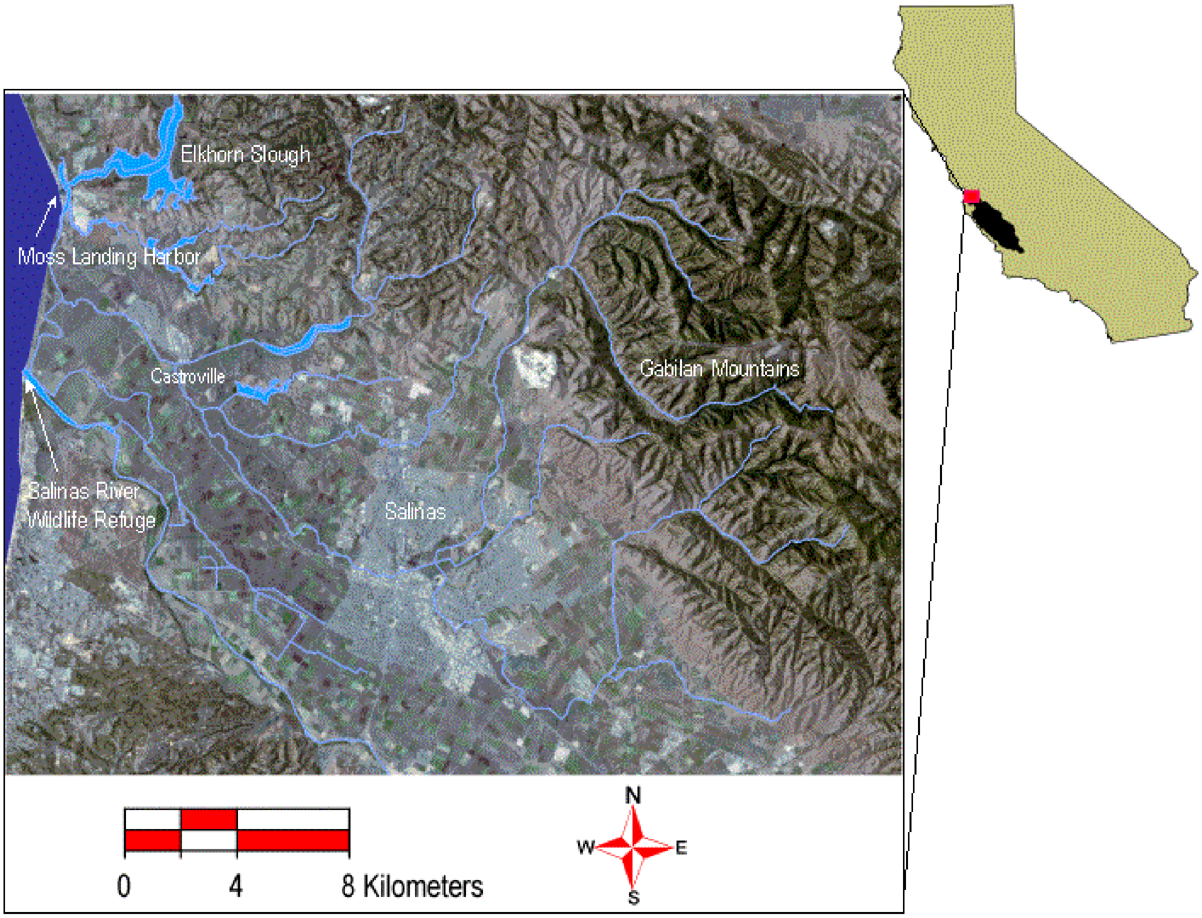

Figure 1 Map of study area. The Monterey Bay National Marine Sanctuary is immediately to the left of this image.

Two commonly used pesticides in the Salinas Valley are chlorpyrifos and diazinon. Though several studies have been completed regarding the toxicity of these two pesticides in Monterey County and the impacts these two pesticides may have on microinvertebrate communities (Rasmussen, 1995; Hunt et al., 2002; Anderson et al., 2003; Phillips et al., in press; Anderson et al., in press; and Ganapathy et al., 1997), a calculation of the percentage of applied pesticides being transported to downstream surface waters has yet to be done for this area. The purpose of this study is to measure the relationship between chlorpyrifos and diazinon applied to agricultural fields, and chlorpyrifos and diazinon concentrations detected in three impaired water bodies.

Chlorpyrifos and Diazinon

Chlorpyrifos (O,O-diethyl-O-(3,4,6-trichloro-2-pyridinyl) phosphorothioate) and diazinon (O,O-diethyl-O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate) are both organophosphate pesticides that are widely used in both agricultural and urban applications. Chlorpyrifos is a broadspectrum organophosphate insecticide and diazinon is a nonsystemic organophosphate insecticide (EXTOXNET, 2002). They are used in the Salinas Valley on lettuce, artichokes, greenhouse transplants, strawberries, broccoli, cauliflower (chlorpyrifos), and outdoor flowers (diazinon). Common product names for chlorpyrifos include Dursban, Lorsban, Brodan, Detmol UA, Dowco 179, and Scout. Common product names for diazinon include Basudin, Dazzel, Gardentox, Kayazol, and Spectracide.

Organophosphates work by interfering with the nervous system of insects, as well as mammals, birds, and fish. They block production of enzyme cholinesterase (ChE), which ensures that the chemical signal that causes a nerve impulse is halted at the appropriate time (Kegly, 1999).

Physical & chemical properties

The water solubility, half-lives, and soil absorption coefficient for chlorpyrifos and diazinon are presented in Table 1. Water solubility is the amount of pesticide in milligrams (mg) that will dissolve in one liter (L) of water. Larger numbers indicate that the substance is more soluble, more readily transported away from application site in water. Half-life is defined as the time required for half of the pesticides to break down into degradation products. Half-life is usually expressed as range because the rate is dependant on a variety of factors including temperature, soil pH, and exposure to light, water and oxygen. Breakdown products may be toxic and/or have significant half-lives as well (as cited in Kegley, 1999). Soil absorption coefficient (K_{oc}) is a measure of a chemical's tendency to adsorb to organic soil particles.

Chlorpyrifos adsorbs strongly to soil particles and is not readily soluble in water. Diazinon is more soluble in water and does not adsorb strongly to soil particles. In sediment/water systems, diazinon is less persistent than chlorpyrifos (Table 1). The environmental fate of both chlorpyrifos and diazinon is dominated by hydrolysis (the polar portion of the molecule is replaced by a water molecule; pesticide is broken down into degradation products) and microbial degradation (Montgomery, 1997).

Table 1. Physical and chemical properties of chlorpyrifos and diazinon.						
		Half-lives				
	Water solubility	**Soil & surface applications**	**Sediment/water systems**	**Volatility**	**Hydrolysis**	**Soil adsorption coefficient (K_{oc})**
Chlorpyrifos	2mg/L at 25°C **	7 - 56 days *	12 - 52 days *	3.5 and 20 days **	35 – 78 days (pH of 7.0 at 25°C) **	5300 – 14800 ***
Diazinon	40 mg/L at 20°C **	14 – 194 days *	8 – 10 days *			1007 – 1842 ***
* (Montgomery, 1997), ** (EXTOXNET, 2002), *** (Azimi-Gaylord et al, 2001)						

Acute Toxicity

Both chlorpyrifos and diazinon are considered moderately toxic (EXTOXNET, 2002). The LD_{50} and LC_{50} for a chemical is the lethal dose (LD) or lethal concentration (LC) that has been found in controlled experiments to kill 50% of a large number of test animals (LC_{50} is for aquatic organisms). The lower the LD_{50} or LC_{50}, the more toxic the chemical. It is an acute toxicity test that refers to the immediate (hours to a few days) effects of a pesticide when the subject is exposed to a particular dose, given orally (see Tables 1 & 2 in Appendix 1). The LD_{50} or LC_{50} of a chemical gives no information of the possible long-term health effects from repeated exposure at low levels. There is variability in susceptibility among individuals due to age and genetic makeup, and variability between laboratory test methods used to measure acute toxicity (Kegley, 1999). For these reasons, toxicities presented for chlorpyrifos and diazinon in Appendix 1 should not be viewed as precise numbers, rather, as an approximate concentration that causes the observable adverse effect.

Chlorpyrifos exhibits greater toxicity than diazinon. The data from a study designed to evaluate the joint acute toxicity of chlorpyrifos and diazinon suggest that chlorpyrifos (53 µg/L) may be 3 to 10 times more toxic than diazinon (320 µg/L) to the water flea *Ceriodaphnia dubia*, a frequently used test organism for LC_{50} determination (Bailey et al, 1997, also refer to Appendix 1). The data from this joint acute toxicity study suggested that diazinon and chlorpyrifos also exhibit additive toxicity when present together. (Bailey et al, 1997). The 96-hour LC_{50} values for rainbow trout are 3 µg/L for chlorpyrifos and 16 mg/L for diazinon (Montgomery, 1997). For comparison, the 96-hour LC_{50} value for rainbow trout is 7 µg/L for DDT (Montgomery, 1997).

The most commonly used guideline for toxicity in California for short-term exposure is the Criterion Maximum Concentration (CMC) (Siepmann and Finlayson, 2000). The CMC is the EPA national water quality criteria recommendation for the highest in-stream concentration of a toxicant or an effluent to which organisms can be exposed for a brief period of time without causing an acute effect (USEPA, 1991). The CMC value is a concentration that should not be exceeded more than once every 3 years. The short-term exposure CMC in terms of concentrations is 0.02 µg/L for chlorpyrifos and 0.08 µg/L for diazinon (Siepmann and Finlayson, 2000). These CMC values will be compared to concentrations observed in this study.

Chronic Toxicity

Chronic toxicity refers to the toxicity due to long-term or repeated exposure to a compound and results in the same effects as acute exposure including delayed symptoms. The guideline for longer-term exposure is the Criterion Continuous Concentration (CCC) (USEPA, 1991). The CCC is the 4-day average concentration of a pollutant in ambient water that should not be exceeded more than once every 3 years. The long-term exposure CCC is 0.014 µg/L for chlorpyrifos and 0.05 µg/L for diazinon (Siepmann and Finlayson, 2000). These CCC values will be compared to concentrations observed in this study.

Ecotoxicity

Birds and mammals that have been poisoned by the pesticides respond with uncontrolled nerve impulses (as cited in Kegley, 1999). Migratory waterfowl can ingest pesticides while preening, levels of pesticides ingested while preening is unknown. Birds are quite susceptible to diazinon poisoning (EXTOXNET, 2002); some birds have LD50 values for diazinon that are 100 times lower than those for mammals (Larkin, 2000).

There is more ecotoxicity information for diazinon than chlorpyrifos. Diazinon at concentrations below 0.5 µg/L can be toxic to aquatic organisms, especially zooplankton. (Amato et al, 1992). The diazinon water quality criterion for the protection of freshwater aquatic life is 0.080 µg/L (Menconi, et al, 1994; International Joint Commission Canada and United States, 1997). Steelhead (*Onchcorhynchus mykiss*) is a threatened salmonid that has potential habitat in the

Salinas River. Steelhead start out as rainbow trout and undergo the transformation into steelhead when a migration to the ocean is made. For this reason it is useful to compare chlorpyrifos and diazinon occurrence in the Salinas River to the published LC_{50} values for rainbow trout: 3 µg/L for chlorpyrifos and 16 mg/L for diazinon (Montgomery, 1997). Acute mortality in fish occurs at much higher concentrations; recent evidence suggests that diazinon affects sensitive salmonid olfactory organs at a concentration of 0.3 µL (Scholz, 2000). A hazard assessment of diazinon by the CDFG reported that freshwater organisms should not be adversely affected by exposure to diazinon if the 4-day average aquatic concentration did not exceed 40 ng/L, or if the 1-hour average did not exceed 80 ng/L more than one time every 3 years (Menconi & Cox, 1994).

In detailed chronic toxicity tests for diazinon, Allison and Hermanutz (1977) found the survival and growth of parental stock of fathead minnows continuously exposed to diazinon after 30 and 61 days showed decreasing average total body length with increasing diazinon concentration. The incidence of scoliosis in parental fathead minnow continuously exposed to diazinon was present at 13 weeks after hatch in concentrations between 69 and 1,100 µg/L and was present in fish at 19 weeks after hatch in concentrations between 3.2 and 60.3 µg/L. The incidence of scoliosis generally declined with decreasing concentrations. No spawning was observed in 60.3 µg/L, and spawning was very limited in 28.0, 13.5, and 6.9 µg/L. The survival and growth of parental stock of brook trout continuously exposed to diazinon after 91 and 173 days showed decreasing average total body length and weight with increasing diazinon concentration. The total number of brook trout eggs spawned decreased with increasing concentration, as did the total percent of mature males (Allison and Hermanutz, 1977).

In a study of amphibian population declines associated with pesticides, Sparling (2001) found that wildlife is also adversely impacted by aerial drift or over spray of these pesticides. Amphibians from populations downwind of intensive agricultural areas in California had tissue concentrations of diazinon and chlorpyrifos as high as 190 ppb wet weight, and a majority of individuals in the exposed populations exhibited acetylcholinesterase inhibition responses indicative of nervous system impacts (Sparling et al., 2001).

<u>Pesticide transport</u>

The agricultural application of diazinon and chlorpyrifos includes aerial spray or near-ground spraying from a tractor (Zamora et al, 2003). In Monterey County, granular pesticides are also applied with seeds at the time of planting (Patrick Brodrick with Pesticide Use Enforcement, personal communication, 2003). Irrigation and rainwater runoff can wash residual pesticides off fields and into nearby surface waters. Both occurrence and temporal distribution of pesticide residues in surface waters are influenced by a number of factors, including the amount and identity of pesticide applied, the physical and chemical properties of the pesticide (see solubility and half-life in Table 1), the type of soil and vegetation present in the application area, the occurrence of storms, and timing of application (Dubrovsky et al, 2000; Kegley, 1999).

On this latter point, potential problems associated with pesticide toxicity are not limited to storm runoff events, but may be present throughout the year (URS, 1999) as a result of irrigation runoff. And when seasonal river flow is low relative to inputs from tributary drains (or irrigation runoff), the likelihood of impacts to a larger portion of the aquatic community increases (Hunt et al, 2002).

Other ways that pesticides transported away from application sites are by over spray (drifting away through the air) or infiltrating groundwater by leaching through the soil. This study focuses on surface runoff.

Previous studies

To date, studies on diazinon and chlorpyrifos in the Salinas Valley have focused primarily on toxicity (Rasmussen, 1995; Hunt et al., 2002; Anderson et al., 2003; Phillips et al., in press; Anderson et al., in press). Studies that link applications on agricultural fields to downstream occurrence of chlorpyrifos and diazinon have taken place in other agriculturally intense regions of California (Dubrovski et al., 2000; Kratzer, 2000; Dileanis et al., 2002). The structure of the following review of previous studies will begin with a look at these studies outside of the study area and then identify the specific need for such a study in the Salinas Valley.

<u>Chlorpyrifos and diazinon applications and downstream occurrence</u>

In the San Joaquin River basin, Dubrovsky (2000) conducted a study designed to evaluate cropping patterns and pesticide applications and the occurrence of these pesticides downstream from the application site. Temporal variability in pesticide occurrence was evaluated by fixed interval sampling (year round) and by sampling across the hydrograph during winter storms. By examining the fate of pesticides after application, Dubrovski et al. (2000) found that both winter rainfall and irrigation tail water might transport pesticides from the site of application to the receiving river or stream. The highest concentrations of diazinon observed matched the period of application. However, chlorpyrifos exhibited maximum concentrations in the San Joaquin River during storms, rather than at the time of maximum application during the spring and summer. The overall amount of diazinon transported in the San Joaquin River during the January and February 1994 storms was about 0.05% of the amount applied during the preceding dry periods. The data also showed that concentrations of diazinon sufficient to be toxic to *C. dubia* could result from the transport of only a very small part of the total amount of pesticide applied (Dubrovsky et al, 2000).

In another study conducted in the San Joaquin River Basin, Kratzer (2000) found that two frequently sampled storms had much higher loading rates than the non-storm periods. The percentage of chlorpyrifos application found in downstream surface waters during the dry periods preceding the storms was 0.05 % and 0.07%. For the second storm, the percentage was 0.05%. For the months of January and February, the chlorpyrifos load was 0.16% of application. The percentage of diazinon application found in downstream surface waters during the dry periods preceding the storms was 0.04% and 0.11% of application. This is similar to the 0.05% calculated during to storms in January and February 1994. For months of January and February, the diazinon load was 0.17% of application (Kratzer, 2000).

In a similar study conducted on the Sacramento River (Dileanis et al., 2002), Dileanis found that the percentage of diazinon applied to agricultural fields that was transported to the lower Sacramento River ranged between 0.25 and 0.49% for individual storms, and a total for the monitoring period of 0.38% (Dileanis et al, 2002). This was compared to estimates of diazinon fluxes to seven rivers in the Mississippi River Basin during 1991 that were between 0.08% and 20% with a median of 0.13% (As cited in Dileanis et al, 2002).

Chlorpyrifos & diazinon in the Salinas Valley

Many pesticide toxicity tests and evaluations have been completed for the Salinas River (Rasmussen, 1995; Hunt et al., 2002; Anderson et al., 2003; Phillips et al., in press; Anderson et al., in press). In a study conducted by the State Mussel Watch Program (Rasmussen, 1995), seven of the eight clam samples analyzed from the Salinas River and tributaries had detectable residues of chlorpyrifos ranging from 3.1 to 288.0 ppb of wet weight. Of the four sediment samples collected, chlorpyrifos was detected twice at 1.1 and 4.1 ppb of wet weight. In 1992 one sample from the watershed was collected at the Salinas River at the Blanco Drain confluence (the Blanco Drain is included as one of the sites in the current study). The fish sample contained 61.0 ppb wet weight of chlorpyrifos (Rasmussen, 1995). This prompted further investigation into the fate of diazinon and chlorpyrifos, and the potential impacts these pesticides could have on aquatic ecosystems in the area they are used.

A team from the Marine Pollution Studies Laboratory has conducted a number of studies in the Salinas River Basin (Hunt et al., 2002; Anderson et al., 2003; Phillips et al., in press; Anderson et al., in press). A watershed-based assessment of ambient toxicity (Hunt et al, 2002) has identified urban runoff from residential areas and from irrigated fields as primary sources of diazinon and chlorpyrifos to the Salinas River. In 96-hour toxicity tests, significant *C. dubia* mortality was observed in 11% of the main river samples, 87% of the samples from a channel draining an urban/agricultural watershed, 13% of samples from channels conveying agricultural tile drain runoff, and in 100% of samples from a channel conveying agricultural surface runoff. Chlorpryrifos and diazinon were frequently found at concentrations causing *C. dubia* mortality in laboratory tests and toxicity identification evaluations (TIEs), and have the potential to cause adverse effects in other ecologically important organisms. In six of nine TIEs, diazinon and/or chlorpyrifos were implicated as causes of observed toxicity, and these compounds were the most probable causes of toxicity in two of three TIEs. Every sample collected in the watershed that exhibited greater than 50% *C. dubia* mortality (n = 31) had sufficient diazinon and/or chlorpyrifos concentrations to account for the observed effects. The diazinon water quality criterion for the protection of freshwater aquatic life, 0.080 µg/L was exceeded in 15% of the main river samples. The USEPA CMC of 0.083 µg/L was exceeded in 8% of the main river samples, and measured chlorpyrifos concentrations were above the *C. dubia* LC_{50} in 16% of the main river samples. Toxicity tests and chemical analysis clearly identified the organophosphate pesticides chlorpyrifos and diazinon as pervasive in agricultural drains, and toxicity identification evaluations linked these compounds to toxicity in samples from a variety of sources (Hunt et al, 2002).

Macroinvertibrate communities have also been impacted from residual pesticides (Anderson et al, 2003). Macroinvertibrate community structure was moderately impacted downstream of an agricultural drain input, suggesting that pesticide pollution is the likely cause of laboratory-measured toxicity in the Salinas River samples. Toxicity to *C. dubia* and *H. azteca* occurred in samples that contained the greatest pesticide concentrations and these stations also had the greatest declines in macroinvertibrate abundances. It is noted that that toxicity may interact with other factors to impact the macroinvertibrate community in the system (Anderson et al, 2003).

Hyalella is a resident amphipod genus in the Salinas River and was clearly affected by the agricultural input when exposed in *situ* during a sediment toxicity study (Phillips et al, in press). Significant reductions in the abundance of benthic invertebrates, including *Hyalella* and daphnid species, at stations downstream from this drainage were noted. Toxicity identification evaluations indicated that organophosphate pesticides chlorpyrifos and diazinon caused toxicity to daphnids and that affects of suspended solids were negligible (Phillips et al, in press).

In a study of the impacts of agricultural drain water, the Salinas River water downstream of the agricultural drain was acutely toxic to cladocerans (*Ceriodaphnia dubia*), and toxicity to *C. dubia* was highly correlated with combined toxic units of chlorpyrifos and diazinon (Anderson et al, in press). Macroinvertibrate community structure was highly impacted downstream of the agricultural drain input, and a number of macroinvertibrate community metrics were negatively correlated with combined toxic units of chlorpyrifos and diazinon, as well as turbidity associated with drain water. The results of this study indicate that toxicity to *C. dubia* occurred in samples from stations where macroinvertibrate community structure was also impacted. Pesticide pollution is the likely cause of ecological damage in the Salinas River, and this factor may interact with other stresses associated with agricultural drain water to impact macroinvertibrate community in the system (Anderson et al, in press).

When the California Department of Pesticide Regulation conducted a study of four rivers, chlorpyrifos was detected during the first major runoff event of the rainy season along the Salinas River (Ganapathy et al, 1997). The enormous increase in rainfall and runoff may have washed chlorpyrifos-bound soil particles from fields into the river. Due to the fairly long field dissipation half-life of chlorpyrifos, ranging from 33 to 56 days and greater than 200 days (as cited in Ganapathy et al, 1997), and timing and distribution of the applications, it is likely that this first storm washed off chlorpyrifos residues from the applications made as early as fall (Ganapathy et al, 1997).

Objective

In light of the additive toxicity of chlorpyrifos and diazinon (Bailey et al, 1997), these studies reveal a need for reevaluation of regulatory practices of chlorpyrifos and diazinon in the Salinas River Watershed. Regulation of pesticide use when considering neighboring aquatic ecosystems requires an analysis of the linkage between chlorpyrifos and diazinon application data and later occurrence of pesticides in waterways.

The specific objectives of this paper are:

- Determine what proportion of pesticides applied to agricultural fields is transported to downstream waterways.
- Determine if the occurrence of high concentrations and/or loads in waterways is associated with application/irrigation runoff, or with precipitation.
- Determine if chlorpyrifos and diazinon concentrations in the sampled surface waters pose a threat to wildlife based on published CMC, CCC and LC_{50} values.

This study will be used by the Central Coast Watershed Studies (CCoWS) of the Watershed Institute at CSUMB as part of a larger study that was funded by a contract with the Department of Pesticide Regulation (DPR) of the California Environmental Protection Agency and was carried out in collaboration with the Central Coast Regional Water Quality Control Board (CCRWQCB). It is the CCRWQCB's responsibility to define and implement allowable Total Maximum Daily Loads (TMDLs) of pesticides in surface waters. CCoWS is providing technical assistance to the CCRWQCB by quantifying the distribution of chlorpyrifos and diazinon in impaired water bodies that are surrounded by intense agricultural production. The purpose of this study is to link this distribution of chlorpyrifos and diazinon in water bodies to the agricultural applications of these to pesticides in the upstream and surrounding watershed.

The concentrations of chlorpyrifos and diazinon in the water column and suspended sediments at 3 sites over a 6-month period (July – November, 2002) were measured under the supervision of Dr. Fred Watson and Don Kozlowski. Suspended sediment was sampled because diazinon and chlorpyrifos are associated with fine sediment particles, particularly those <60 micrometer, at specific concentrations that were much higher than those found for coarse sediment particles (URS, 1999).

Sampling was conducted during the non-winter irrigation season once monthly (6 dry weather events) and during the first winter storm of the wet season in 2002. Discharge measurements were taken with samples for the purpose of making load estimates. Pesticide analysis was done using an Enzyme Linked Immuno-Sorbent Assays (ELISA) procedure. Application data were obtained from the Monterey County Agricultural Commissioner.

METHODS

Site descriptions

Sites monitored for this study include three 303(d) listed water bodies and were predetermined by CCoWS. These three sites were selected from the nine sites monitored by CCoWS for the DPR. All three sites are on channelized ditches downstream of agricultural and urban land uses, lack riparian vegetation, and have a dominant substrate of silts and clays (Figure 2). None of the waterways sampled are natural waterways, but provide a source of water for birds and drain into natural waterways.

The Reclamation Ditch originates in the city of Salinas capturing the drainages of Gabilan, Natividad, and Alisal Creeks, flowing into the Tembladero Slough and finally into Moss Landing Harbor (Figure 2). The sampling site on the Reclamation Ditch is at San Jon Rd (REC-JON) and is approximately 5 km downstream from the city of Salinas. There is abundant riprap present on this reach of the ditch. This site is also a US Geological Survey gauging station, many discharge estimations for this site were taken from the USGS website. The upstream and surrounding land uses are row crop agriculture and urban communities.

The Blanco Drain was sampled at the Cooper Rd crossing (BLA-COO) (Figure3). This drain originates just south of the city of Salinas and flows north approximately parallel to the Salinas River before flowing into the upper most portion of the Salinas River Lagoon. The lower Salinas River Lagoon is part of the Salinas River National Wildlife Refuge estuarine area (Figure 1). This is one of the sampling sites from the State Mussel Watch project mentioned previously. The upstream and surrounding land use is predominantly tile drain row crop agriculture.

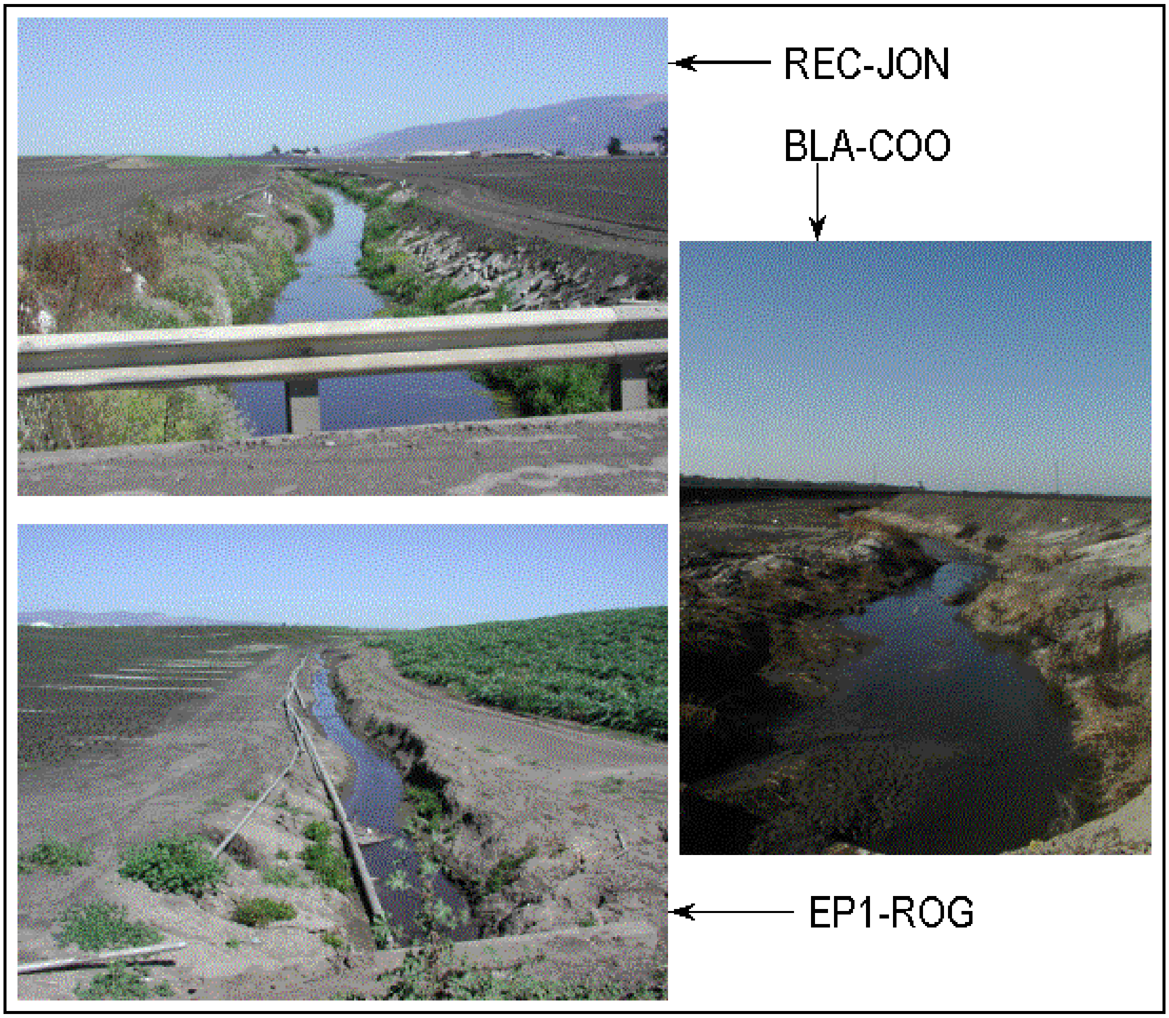

Figure 2 Sampled agricultural ditches in North Monterey County.

The Espinosa Slough drainage is northeast of the city of Salinas (Figure 3). The sampled tributary is channelized into a ditch approximately 1 to 2 meters wide, and contributes a lot of the water that feeds Espinosa Lake. The sampling site is located at the Rodger's Rd crossing immediately downstream of some greenhouses. The upstream and surrounding land use is predominantly row crop agriculture and greenhouses.

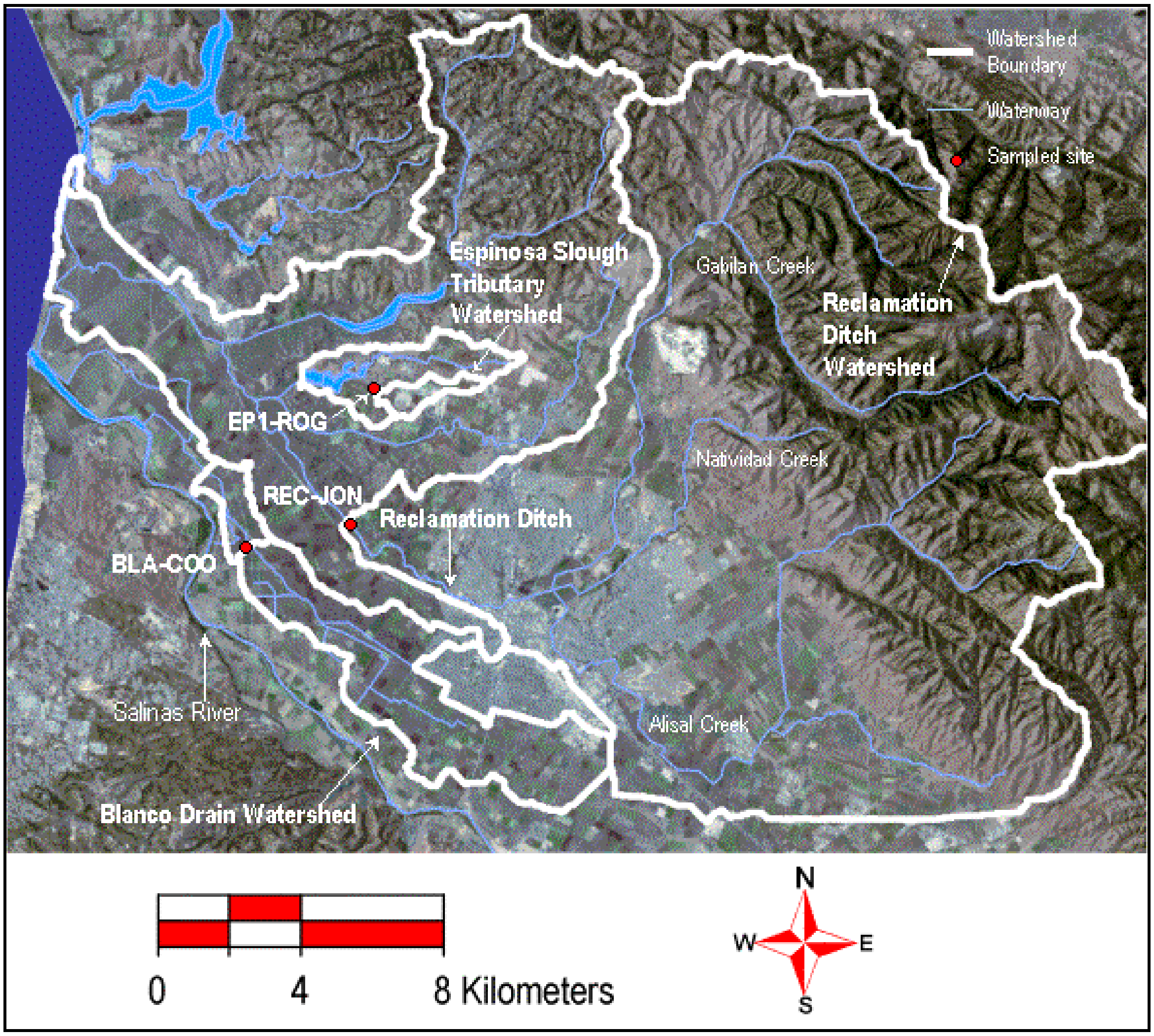

Figure 3 Map of sampled sites (A, B, and C) and their associated watershed boundaries (thick white lines). Not all waterways in the study area are displayed.

Drainage area delineations and application data

Agricultural pesticide application data from the Monterey County Agricultural Commissioner were received in the form of pounds of product applied to sections (square miles) of the townships (13, 14, and 15) and ranges (02, 03, and 04) of the study area. Data of pounds of product applied were converted into pounds active ingredient (lbs a.i.) by the DPR and Mark Angelo of the CCRWQCB. For the purpose of comparing these applications to pesticide loading rates in the waterways, applications were then converted to kg.

Subbasins (watershed drainage boundaries) above each sampling site were delineated by Fred Watson of CCoWS using Tarsier software (Watson and Rahman, 2003). To determine chlorpyrifos and diazinon use within individual subbasins during the sampling period, application data were incorporated into a geographic information system (GIS) coverage of the study area, and then township, range, and sections were segregated into those subbasins having known or defined boundaries (Figure 4). It was assumed that pesticides were applied uniformly across each square mile.

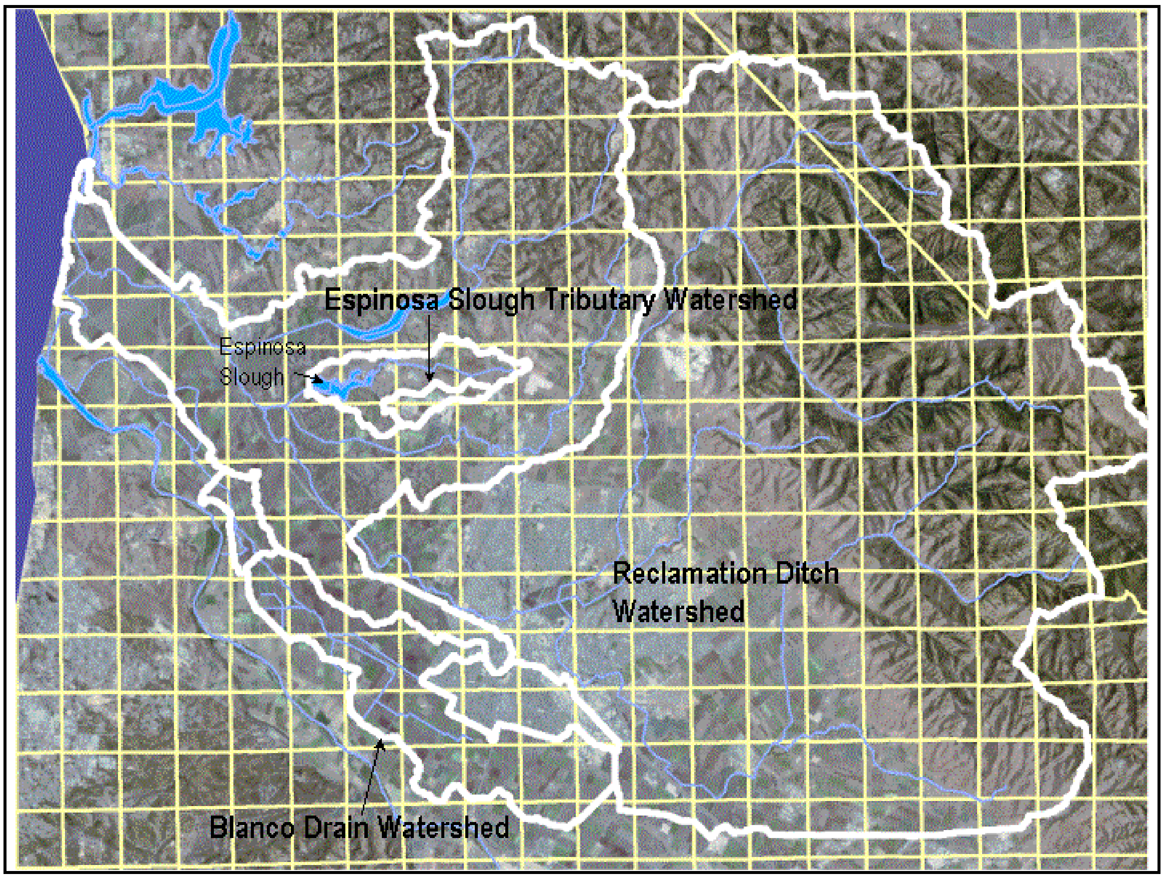

Figure 4 Watershed boundaries (thick white lines) overlaid onto sections (approximately square mile grid lines) of townships and ranges.

Applications in each subbasin were the sum of all applications in sections and portions of sections that were within each subbasin boundary. These data were considered on a daily and monthly basis, and were also separated into dry-weather and wet weather time periods as defined below.

Sampling design & methodology

Stream sampling took place during 5 dry-weather summer events (on July 8th, August 29th, September 13th and 25th, and October 22nd of 2002) and during the first rainstorm of the wet season (November 2002). This winter event consisted of a pre-storm sampling (November 6th), peak flow sampling (November 8th), and post storm sampling (November 11th). Precipitation data for this storm were obtained online from the California Data Exchange Center (CDEC, 2002). An average of precipitation from 2 rain gages located in Salinas and Castroville is presented for analysis.

Each visit to a site during a sampling event included collecting a stage reading, a discharge measurement, and sample collection. Two samples were collected in amber glass bottles and jars for pesticide analysis. A field-filtering unit (battery operated peristaltic pump and hose) was used to filter water samples at the site as well as collect suspended sediment on a 0.7-micron fiberglass filter (this suspended sediment was analyzed for chlorpyrifos and diazinon that was adsorbed to the sediment particles suspended in the water column) (Figure 5). A different hose was used for each site to avoid cross contamination. Field procedures for suspended sediment sample collection were adopted from a US Geologic Survey protocol for *in situ* filtration of samples for the determination of organic compounds (Sandstrom, 1995). A total of 8 water samples and 8 suspended sediment samples were collected at each site during every field visit (with the exception of a suspended sediment sample from BLA-COO on the 8th of July).

During each visit to a site, a depth-integrated sample (using a DH48) was also collected for suspended sediment concentration, turbidity, TDS, and transparency. These data are presented in table form in Appendix 2, Table 3. Suspended sediment concentrations were also used with pesticide concentrations from the filters to determine chlorpyrifos and diazinon concentrations on suspended particles in the water column.

The sampling events of July 8 and October 22, 2002 included depth profile measurements of pH, dissolved oxygen, temperature, and salinity using YSI sampling probes (YSI 556 Multi Probe System, YSI Incorporated). These data are presented in table form in Appendix 2, Table 4.

Figure 5 Don Kozlowski using the battery operated peristaltic pump to collected water and suspended sediment samples.

Laboratory analysis

Water samples were refrigerated and analyzed within 7 days after collection. Extraction of pesticides from suspended sediment samples was done with methanol. The method used was adapted from a sediment extraction procedure outlined by the State Water Resource Control Board in a document prepared for the Alameda County Flood Control and Water Conservation District (Katznelson, 1998). Wet sample filters were weighed before and after dehydration to obtain the dry weight of sediment that was extracted. After extraction, the samples were refrigerated and analyzed following water analysis (also within 7 days after collection).

Enzyme Linked Immuno-Sorbent Assays (ELISA) micro well test kits were purchased from Strategic Diagnostic (Figure 6). ELISA analysis was done following the same procedure outlined by the State Water Resource Control Board (Katznelson, 1998) and manufacturers instructions. Readings were compared to a 3-point standard curve, (for chlorpyrifos 50, 200, and 800 ng/L; for diazinon 25, 100, and 400 ng/L) using standards provided by the manufacturer. These standards served as a calibration curve for the test and were analyzed at the beginning and at the end of each ELISA run. To assess the accuracy of these readings, a correlation coefficient (R^2) was calculated for each curve. Precision was determined with two to three replicate measures of one sample and the three calibrators in each ELISA run by calculating the coefficient of variation (%CV). A summary of accuracy and precision data is displayed in Appendix 2, Table 2.

Figure 6 ELISA lab set up.

It should be noted that there are expected differences between sample concentrations obtained from the ELISA method and the standard, EPA certified GCMS 8141 method. A positive bias in the ELISA analyses relative to GC methods has been observed; therefore, ELISA data probably overestimate actual concentrations in the environment. It is stated that this observed bias in the

ELISA concentrations does not allow direct comparison to regulatory standards, and load calculations using the ELISA analysis would be similarly biased (Dileanis, 2002). The argument can be made however, that the GCMS method is negatively biased. The GCMS method screens for many analytes in a sample creating a lot of noise in the analysis that could interfere with readings of actual concentrations of individual analytes, whereas the ELISA method targets one specific analyte by an assimilated immune response in each micro well (Revital Katznelson, personal communication, 2002).

SSC, TDS, turbidity, and transparency were all analyzed by CCoWS lab protocols (Watson et al, 2002).

Calculations

Pesticide concentrations on suspended sediment particles were multiplied by the suspended sediment concentrations (obtained from depth integrated sampling) using the following equation:

$$C_{ss}\ (ng/L) = [SSC\ (mg/L) * E_{ss}\ (ng/kg)] / 10^6$$

Where C_{ss} is the pesticide concentration adhered to suspended sediment particles, SSC is the suspended sediment concentration, and E_{ss} is the ELISA reading or the amount of pesticide in the micro well.

Total pesticide concentrations are the pesticide concentrations on suspended sediment particles plus the pesticide concentration of the water samples:

$$C\ (ng/L) = C_{ss}\ (ng/L) + C_{h2o}\ (ng/L)$$

Where C is the total concentration, and C_{h2o} is the concentration in water samples. Maximum and minimum total concentrations and the standard deviation of each matrix of chlorpyrifos and diazinon are displayed for analysis and compared to CCC, CMC, and LD_{50} values.

Pesticide loads were calculated by multiplying the concentration times the discharge estimate taken with each sample:

$$L\ (ng/s) = Q\ (L/s) * C\ (ng/L)$$

Where L is the load, and Q is the discharge estimate. Loads were also calculated in grams per second for direct comparison to applications.

The loads for suspended sediment and water were calculated individually to evaluate the contribution of suspended sediment concentrations to the total load.

$$\%\ \text{Suspended sediment contribution} = (L_{ss} / L) * 100$$

Where L_{ss} is the load of pesticide being transported on suspended sediment particles.

Comparison of application data to in-stream load data

For comparison of loads to applications, the estimated loads moving through the waterways were multiplied by the number of days in the sampling interval. This calculation was made using the average of all estimated loads measured during the ambient monitoring and the average of all estimated loads measured during the storm event.

$$L_{ambient}\ (kg) = \bar{L}_{ambient}\ (g/s) / 10^3 * 86400\ (s/day) * 143\ days$$

$$L_{storm}\ (kg) = \bar{L}_{storm}\ (g/s) / 10^3 * 86400\ (s/day) * 20\ days$$

The ambient load accounts for applications between the 1st June and 22nd October, the storm load accounts for applications between the 23rd October and 11th November. These loads were then divided by the amount of pesticides applied (kg active ingredient) in the same time period calculated by the method explained above.

RESULTS

In total, 1,603 kg of chlorpyrifos were applied to fields in the three watersheds of the study area from June to November 2002. Most chlorpyrifos applications occurred in June and July. In total, 8,709 kg of diazinon were applied to fields in the study area from June through November 2002. Most diazinon applications occurred in June, July, and September. It is interesting that more of the less toxic and less persistent (in sediment/water systems, Table 1) chemical had been used.

This section is organized by watershed. After an overview of the November rainstorm, concentrations, applications, estimated loads, and then proportions of applications present in estimated loads are presented for an evaluation of each watershed.

Precipitation during November storm event

The storm event that was sampled 3 times (pre-storm, peak flow, and post storm) was the first flush of the season with the potential to wash or leach all chlorpyrifos and diazinon that had been accumulating on soil surfaces into the waterways. A total of 4.03 cm (1.59 in) of precipitation fell between North Salinas and Castroville from November 6th through 11th, 2002 (Figure 5). The maximum precipitation rate occurred from the 7th to the 8th.The rate of precipitation increased on the morning of the 7th, decreased, and then increased again on the morning of the 8th.

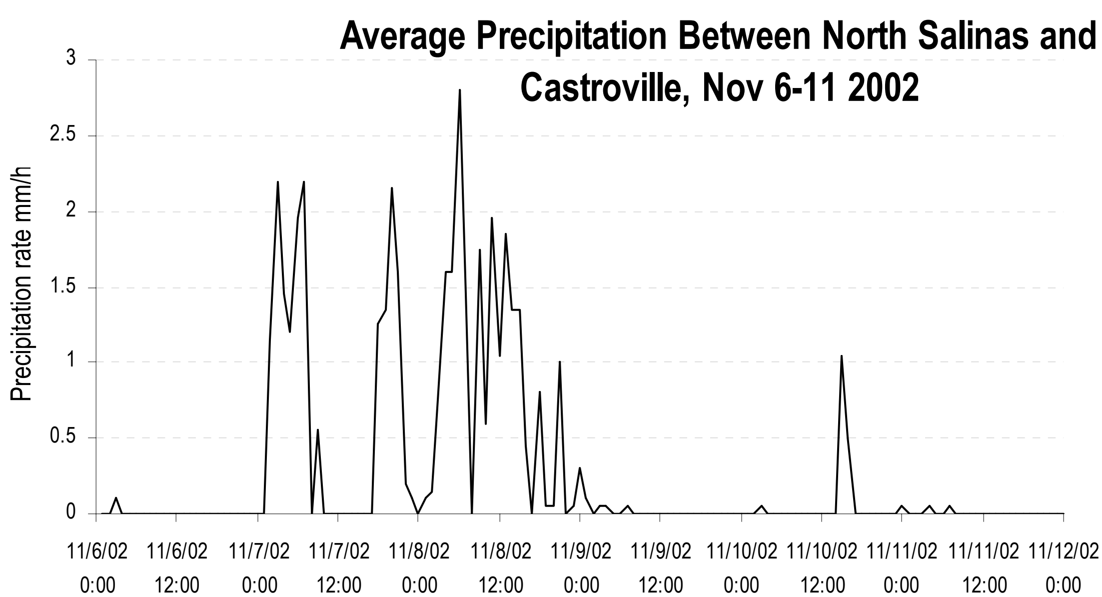

Figure 7. Average precipitation rate between North Salinas and Castroville. Data from California Data Exchange Center (CDEC, 2002).

Reclamation Ditch Watershed

The Reclamation Ditch is the largest of the 3 watersheds sampled (Figure 8).

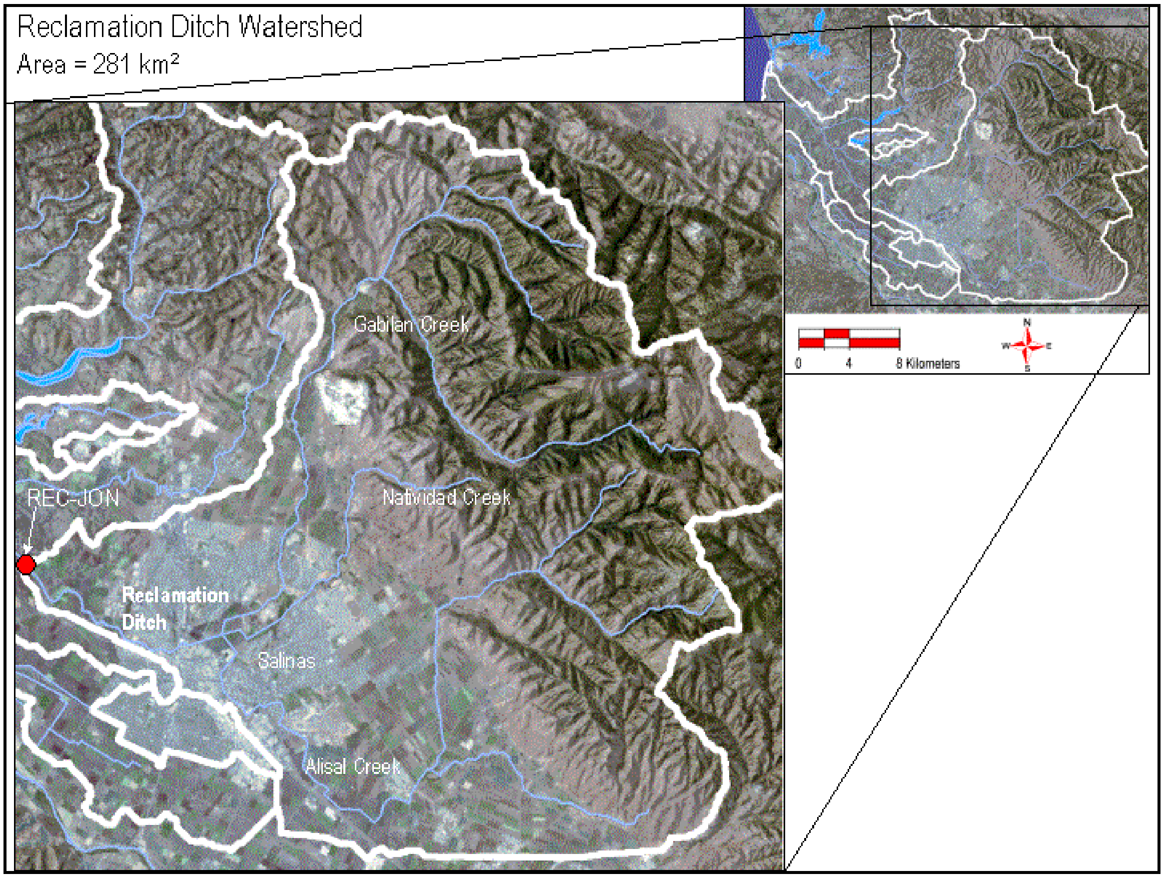

Figure 8 Reclamation Ditch Watershed and location of downstream sampling site REC-JON.

Water and suspended sediment concentrations are compared to CMC values for chlorpyrifos (20 ng/L) and diazinon (80 ng/L) and CCC values for chlorpyrifos (14 ng/L) and diazinon (50 ng/L) in Table 2. Comparisons are also made with the 96-hour LC_{50} value for Rainbow Trout: 3,000 ng/L for chlorpyrifos and 16,000 ng/L for diazinon.

Table 2. Concentrations of chlorpyrifos and diazinon at REC-JON.	**Max (ng/L)**	**Date**	**Min (ng/L)**	**Date**	**Average (ng/L)**	**Standard deviation (ng/L)**	**Samples exceeding CMC**	**Samples exceeding CCC**	**Samples exceeding LC50 for Rainbow Trout**
Total Chlorpirifos (ng/L)	3039	8-Nov	76	25-Sep	490	1030	100%	100%	13%
Total Diazinon (ng/L)	1639	13-Sep	103	6-Nov	596	486	100%	100%	0%
n = 8									

The maximum concentration of chlorpyrifos occurred in the peak storm sample corresponding to when the rate of precipitation was the highest (Figure 7). This is also the only sample that chlorpyrifos adsorbed to suspended sediment contributed more to the total concentration than chlorpyrifos dissolved in the water. The minimum diazinon concentration occurred in the pre-peak storm sample (Table 2). In all of the samples, diazinon dissolved in the water column was greater than diazinon adsorbed to suspended sediment. Of the 8 samples, the standard deviation of concentrations is larger than the average of these concentrations, indicating a large amount of variability in the concentration data. This variability carries over to load estimations.

The CMC and CCC for both chlorpyrifos and diazinon is exceeded in all samples collected, more than the recommendation of once every 3 years (USEPA, 1991; and see Table 2). Chlorpyrifos was present at concentrations exceeding the LC_{50} value for rainbow trout once, and diazinon was never observed at concentrations toxic to rainbow trout.

Overall, estimated summer chlorpyrifos loads at REC-JON follow the trend of applications in the Reclamation Ditch watershed, loads are higher when larger applications occur often, and loads are smaller with fewer applications (July through October Figure 9), though the highest estimated chlorpyrifos loads at REC-JON were during the storm and not during the time period of heavy application (Figure 9).

The same trend is present in estimated diazinon loads at REC-JON (Figure 10). Though applications were more intense during the ambient monitoring period, diazinon loads were greater during the storm than during the dry-weather sampling period.

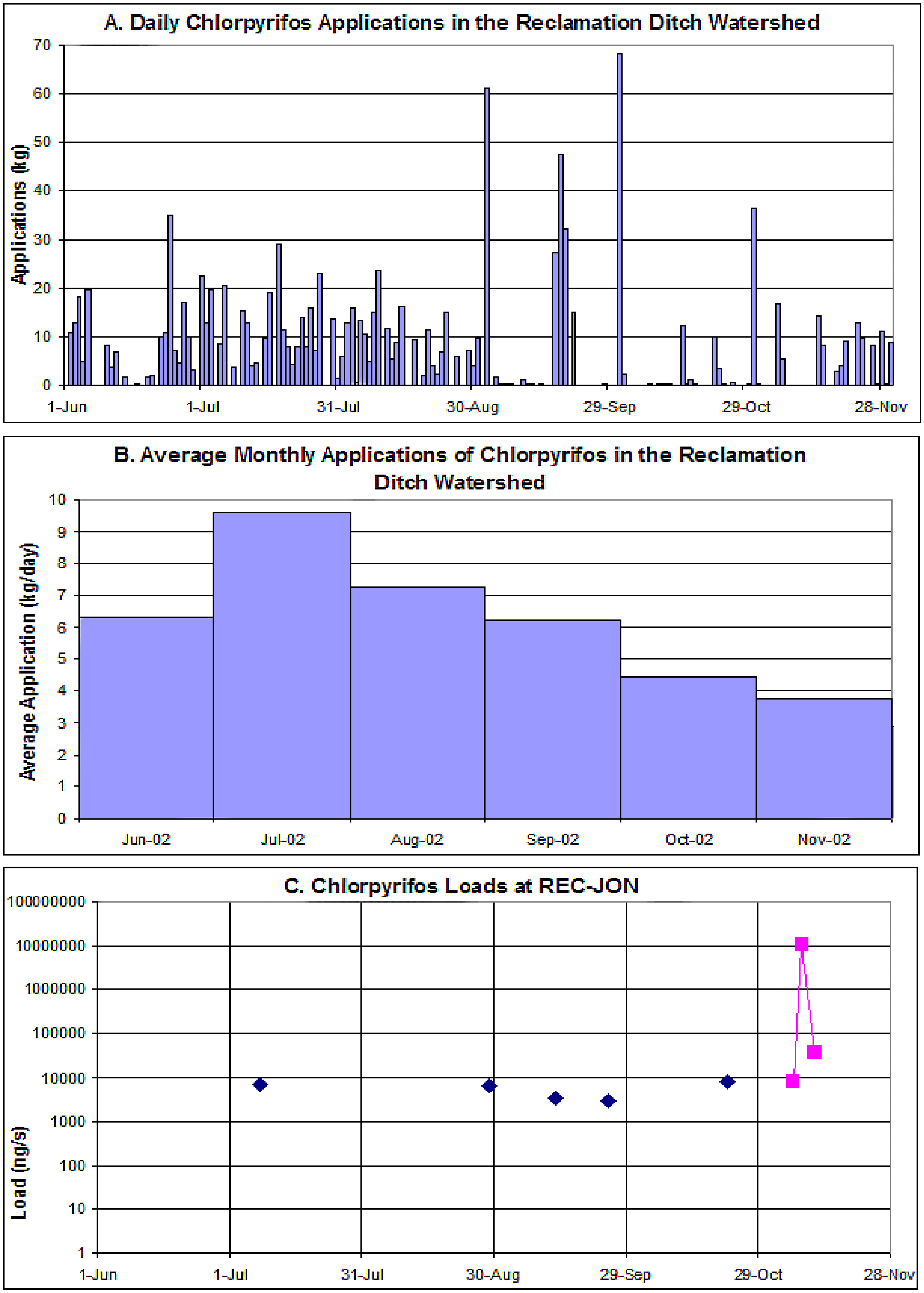

Figure 9. A. Daily applications and **B.** Average monthly applications per day of chlorpyrifos in the Reclamation Ditch Watershed from June to November 2002. **C.** Time series of chlorpyrifos loads observed at REC-JON on a log scale, ambient loads are displayed as instantaneous loads; storm loads are displayed as continuous loads.

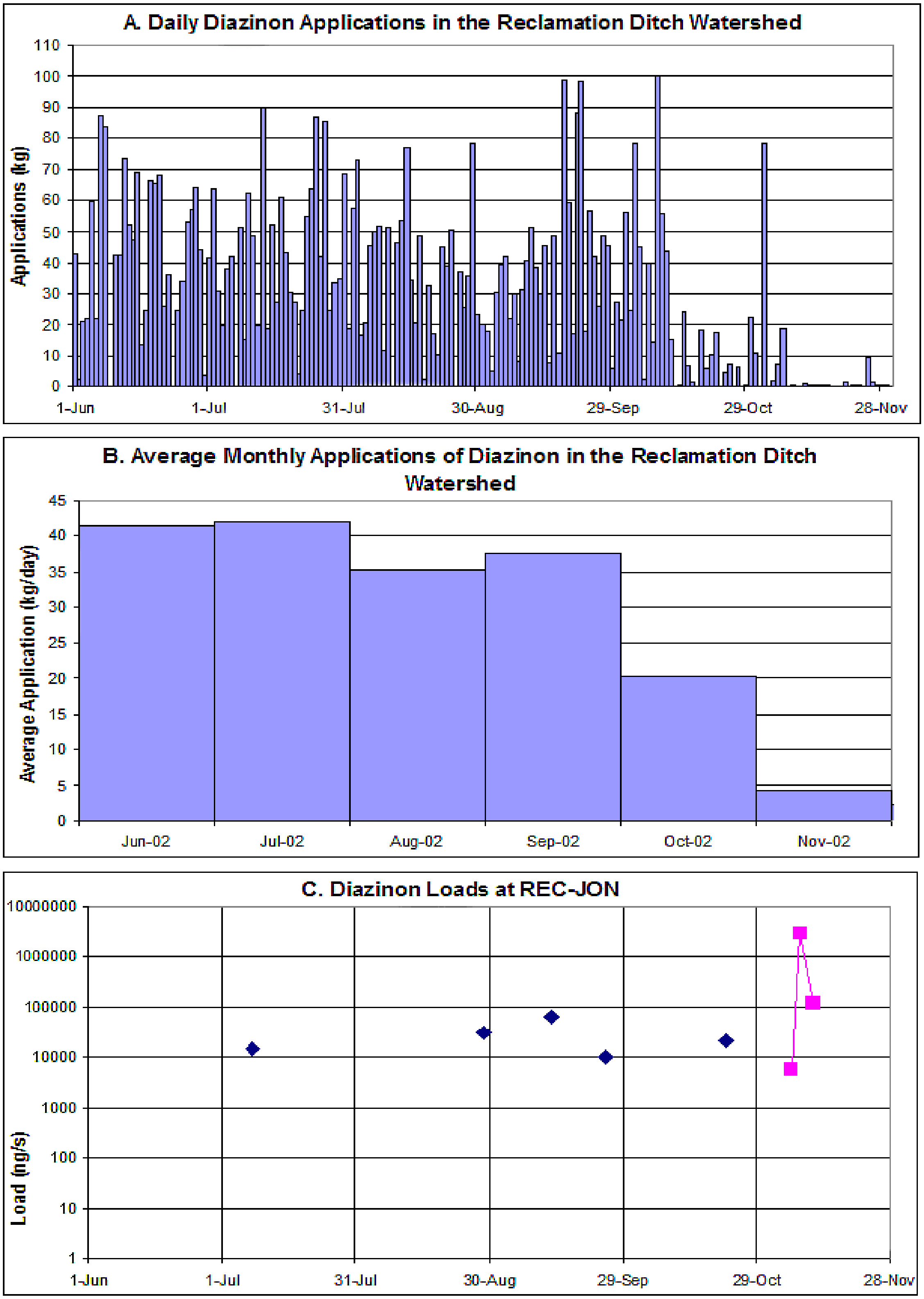

Figure 10. A. Daily applications and **B.** Average monthly applications per day of diazinon in the Reclamation Ditch Watershed from June to November 2002. **C.** Time series of diazinon loads observed at REC-JON on a log scale, ambient loads are displayed as instantaneous loads, storm loads are displayed as continuous loads.

Because the high variability between pesticide concentrations and thus loads, the comparison between applications and loads was grouped into the summer dry-weather time period and storm time period. Total applications in the time periods were evaluated with the average loads of each time period in Table 3.

Table 3. Summary of Chlorpyrifos and Diazinon applications in the Reclamation Ditch Watershed and estimated loads observed at REC-JON.

CHLORPYRIFOS				**Average of all estimated loads for time period between application dates (kg)**	**Estimated fraction of applications in average loads**
Time period	**# Of samples**	**Application dates**	**Applications (kg)**		
Ambient	5	1 June - 22 Oct	996	0.07	0.007%
Storm	3	23 Oct - 11 Nov	64	2.18	3.4%
DIAZINON					
Ambient	5	1 June - 22 Oct	5360	0.37	0.007%
Storm	3	23 Oct - 11 Nov	159	0.63	0.4%

In general, estimated proportions of transported pesticides during the ambient time period were much lower than during the storm (Table 3). This could be explained by less applications occurring during the storm time period, and/or by the fraction of the loads in the Reclamation Ditch that was sediment. The average sediment fraction of total estimated ambient loads was 28% for chlorpyrifos and 10% for diazinon; during the storm the average sediment fraction of total loads were greater: 41% for chlorpyrifos and 26% for diazinon. This is an indication that precipitation and runoff leached residual chlorpyrifos and diazinon that had been accumulating on the surfaces of the agricultural fields in the watershed into the Reclamation Ditch.

During the ambient time period, more diazinon was applied and higher diazinon loads (higher than chlorpyrifos loads) were estimated, though the estimated proportions of applications in loads is the same for both pesticides.

Blanco Drain Watershed

The Blanco Drain watershed is the second largest of the three watersheds sampled (Figure 11).

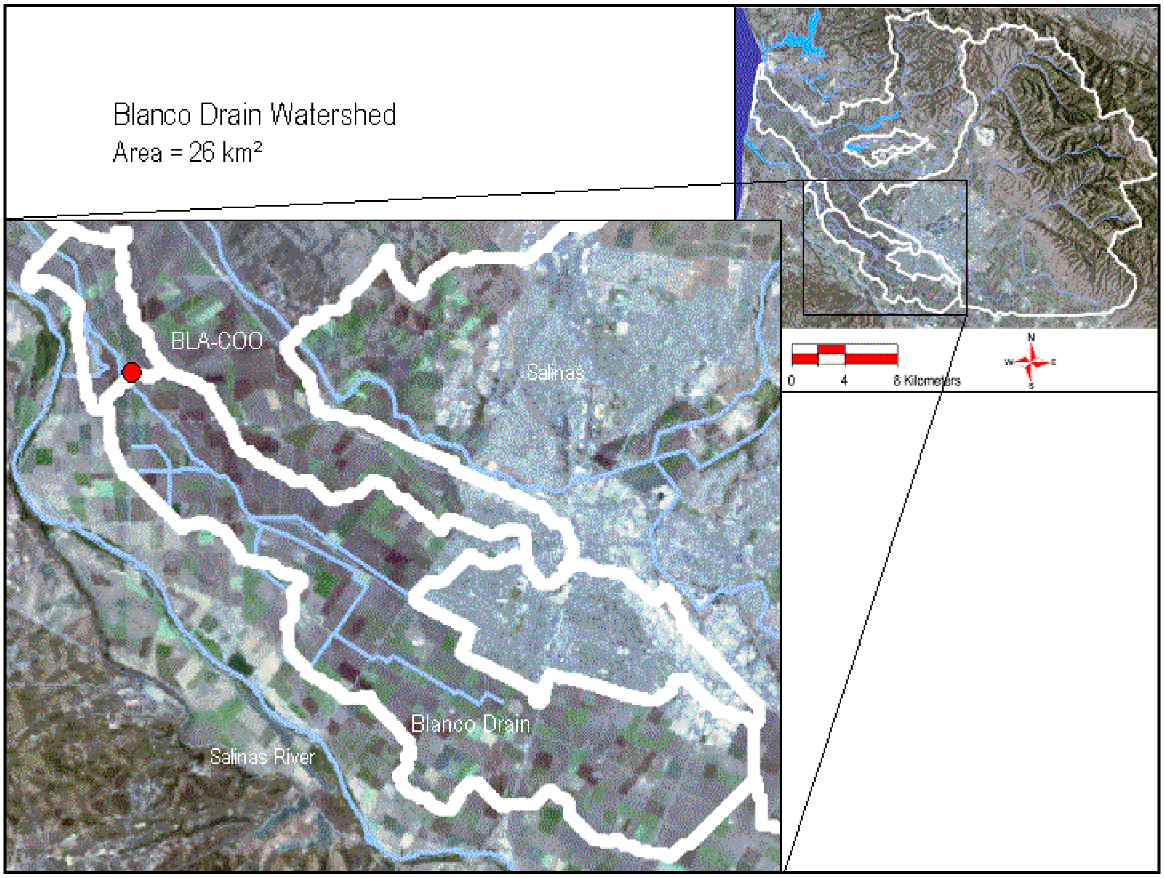

Figure 11 Blanco Drain watershed and location of downstream sampling site BLA-COO.

Water and suspended sediment concentrations were compared to the same CMC, CCC values and the same toxicity values for rainbow trout (Table 4).

Table 4. Concentrations of chlorpyrifos and diazinon at BLA-COO.	**Max (ng/L)**	**Date**	**Min (ng/L)**	**Date**	**Average (ng/L)**	**Standard deviation (ng/L)**	**Samples exceeding CMC**	**Samples exceeding CCC**	**Samples exceeding LC50 for Rainbow Trout**
Total Chlorpirifos (ng/L)	1172	8-Nov	51	25-Sep	206	391	100%	100%	0%
Total Diazinon (ng/L)	4352	8-Nov	72	8-Jul	691	1485	63%	100%	0%
n = 8									

Maximum concentrations occurred in the peak storm samples corresponding to when the rate of precipitation was the highest (Figure 5 and Table 4). In all of the samples, chlorpyrifos and diazinon dissolved in the water column contributed more to the total concentration than the amount adsorbed to suspended sediment. Of all the samples, the standard deviation of concentrations is larger than the average of these concentrations, indicating a large amount of variability in the concentration data. This variability carries over to load estimations.

Chlorpyrifos concentrations exceed the CMC and CCC in all of the samples collected. Diazinon concentrations exceed the CMC in more than half the samples and the CCC is exceeded on all of the samples. This is more than the recommendation of once every 3 years (table 4). Chlorpyrifos and diazinon was never present at concentrations exceeding the LC_{50} value for rainbow trout.

Overall, estimated summer chlorpyrifos loads at BLA-COO follow the trend of applications in the Blanco Drain watershed, loads are higher when larger applications occur often, and loads are smaller with fewer applications (July through October Figure 12), though the highest estimated chlorpyrifos loads at BLA-COO were during the storm and not during the time period of heavy application (Figure 12).

Estimated summer diazinon loads at BLA-COO peak on the 13th of September after a large application in the watershed at the beginning of September (Figure 13). Much more diazinon was moving through the sampling site during the peak of the storm than during the ambient sampling period (Figure 13C). This load peak during a time of little to no applications indicates that precipitation and runoff were leaching diazinon that had been accumulating on the surfaces of the fields in the watershed into the Blanco Drain.

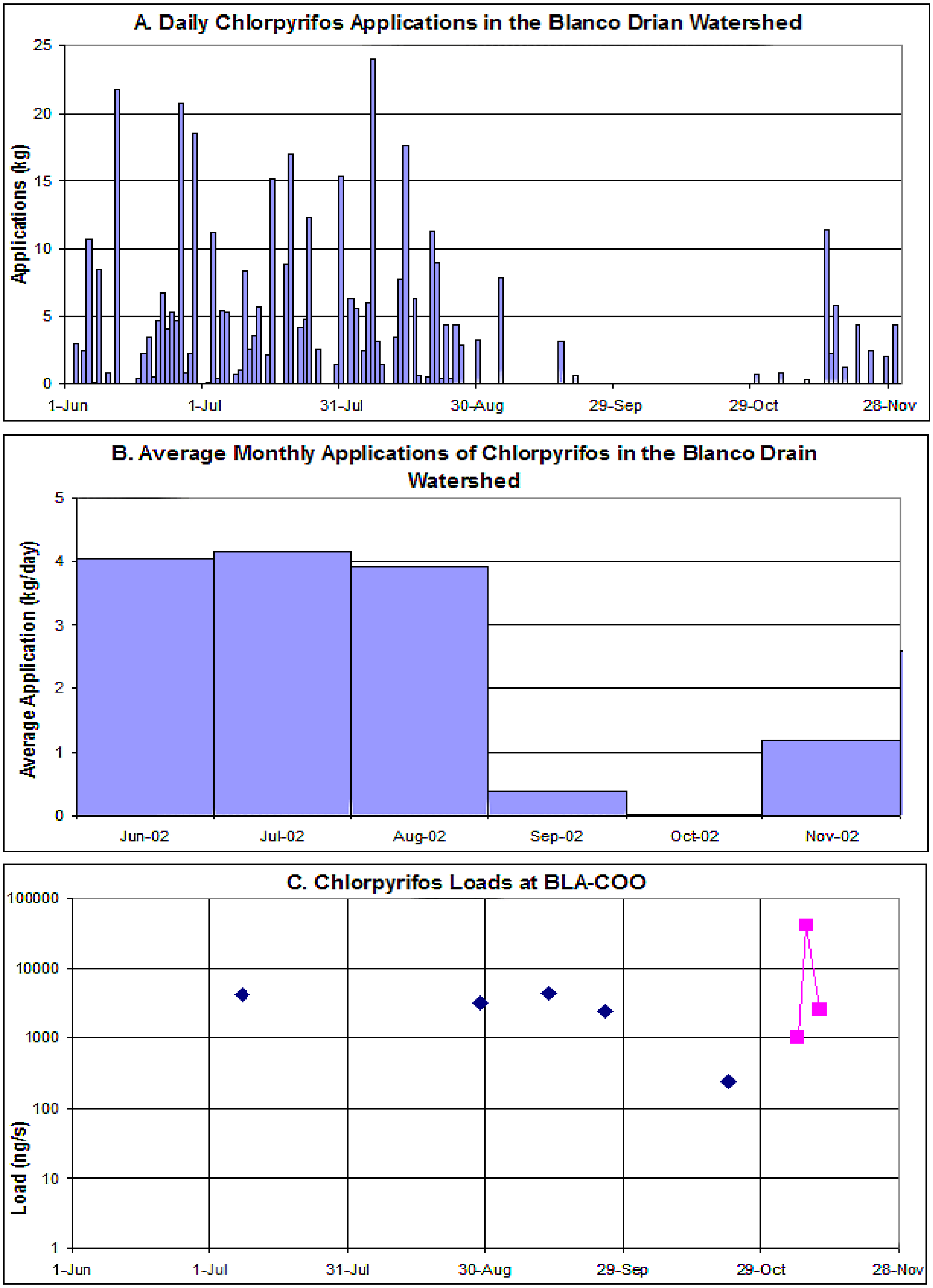

Figure 12 A. Daily applications and **B.** Average monthly applications per day of chlorpyrifos in the Blanco Drain Watershed from June to November 2002. **C.** Time series of chlorpyrifos loads observed at BLA-COO on a log scale, ambient loads are displayed as instantaneous loads, storm loads are displayed as continuous loads.

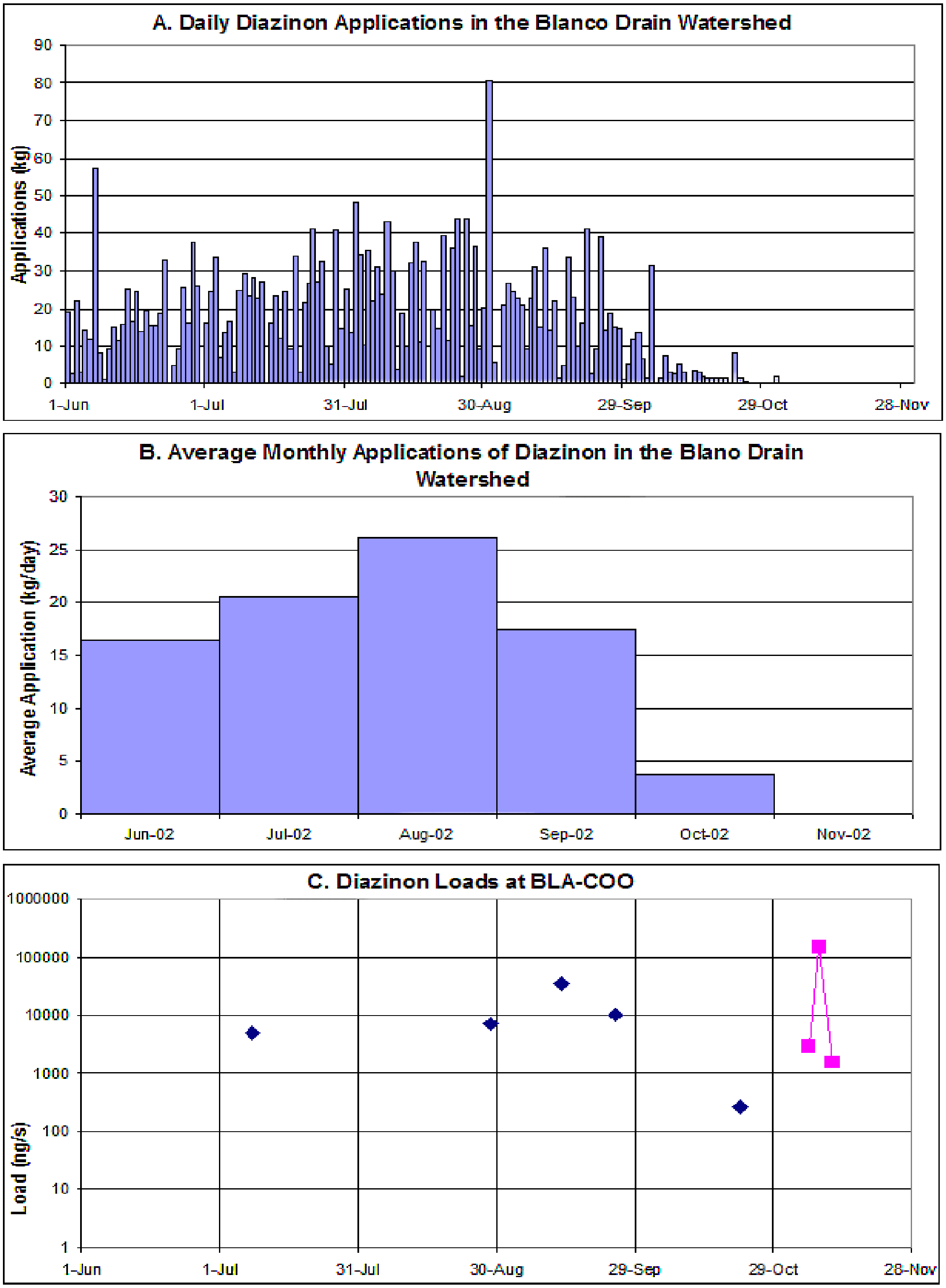

Figure 13 A. Daily applications and **B.** Average monthly applications per day of diazinon in the Blanco Drain Watershed from June to November 2002. **C.** Time series of diazinon loads observed at BLA-COO, ambient loads are displayed as instantaneous, storm loads are displayed as continuous.

Again, because the high variability between pesticide concentrations and thus loads, the comparison between applications and loads was grouped into the summer dry-weather time period and storm time period. Total applications in the time periods were evaluated average of the loads of each time period in Table 5.

Table 5. Summary of Chlorpyrifos and Diazinon applications in the Blanco Drain Watershed and estimated loads observed at BLA-COO.

CHLORPYRIFOS					
Time period	**# Of samples**	**Application dates**	**Applications (kg)**	**Average of all estimated loads for time period between application dates (kg)**	**Estimated fraction of applications in average loads**
Ambient	5	1 June - 22 Oct	383	0.05	0.013%
Storm	3	23 Oct - 11 Nov	2	0.01	0.5%
DIAZINON					
Ambient	5	1 June - 22 Oct	2561	0.17	0.007%
Storm	3	23 Oct - 11 Nov	12	0.03	0.3%

Estimated proportions of transported chlorpyrifos and diazinon during the ambient time period were much lower than during the storm. The average sediment fraction of total chlorpyrifos loads during the ambient time period was 2% and 6% during the storm. The average sediment fraction of total diazinon loads during the summer was 13% and 42% during the storm. Again, this is an indication that precipitation and runoff is washing residual chlorpyrifos and diazinon that has been accumulating on the surfaces of the agricultural fields in the watershed into the Blanco Drain.

Espinosa Slough Tributary Watershed

The Espinosa Slough watershed is the smallest of the sampled watersheds (Figure 14).

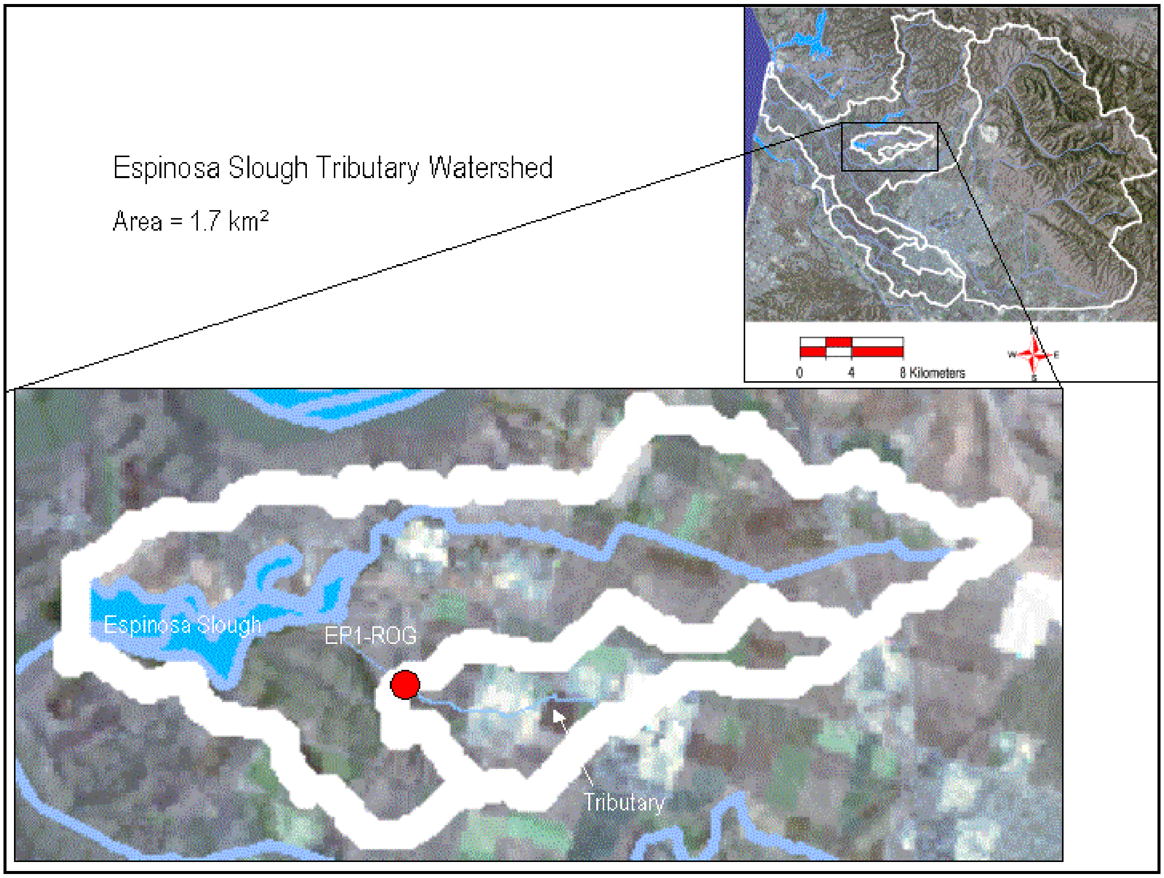

Figure 14 Espinosa Slough Tributary Watershed and location of downstream sampling site EP1-ROG.

Water and suspended sediment concentrations were compared to the same CMC, CCC values and the same toxicity values for rainbow trout (Table 6).

Table 6. Concentrations of chlorpyrifos and diazinon at EP1-ROG.	**Max (ng/L)**	**Date**	**Min (ng/L)**	**Date**	**Average (ng/L)**	**Standard deviation (ng/L)**	**Samples exceeding CMC**	**Samples exceeding CCC**	**Samples exceeding LC50 for Rainbow Trout**
Total Chlorpirifos (ng/L)	28467	13-Sep	225	29-Aug	5518	9401	100%	100%	50%
Total Diazinon (ng/L)	741794	8-Jul	4055	6-Nov	200	253241	100%	100%	88%
n = 8 for water samples; n = 7 for suspended sediment samples									

Maximum concentrations at EP1-ROG occurred in samples taken on the 13th of September (Table 6) corresponding to a large application in the beginning of that month (Figure 12A). Maximum diazinon concentrations occurred in the first sample collected from the site. Diazinon concentrations were the lowest in the pre-storm sample. Overall, more chlorpyrifos and diazinon were adsorbed to suspended sediment particles than was dissolved in the water. Of all the samples, the standard deviation of concentrations is larger than the average of these concentrations (with the exception of chlorpyrifos water concentrations, though the standard deviation is still high), indicating a large amount of variability in the concentration data. This variability carries over to load estimations.

Chlorpyrifos and diazinon concentrations exceed the CMC and CCC in all of the samples (table 6), more than the recommendation of once every 3 years (USEPA, 1991; and see Table 4). Chlorpyrifos and diazinon were present at concentrations exceeding the LC_{50} value for rainbow trout in at least half of the samples.

Chlorpyrifos and diazinon in-stream loads follow the same general trends at EP1-ROG. Estimated loads at EP1-ROG increase on the 13th of September corresponding to the large applications in the watershed (Figures 15A and 15C, 16A and 16C). Ambient loads increase again on the 22nd of October after a time period of few applications. Storm loads are not different from ambient loads even though few applications have occurred just prior to the storm (Figures 15 and 16).

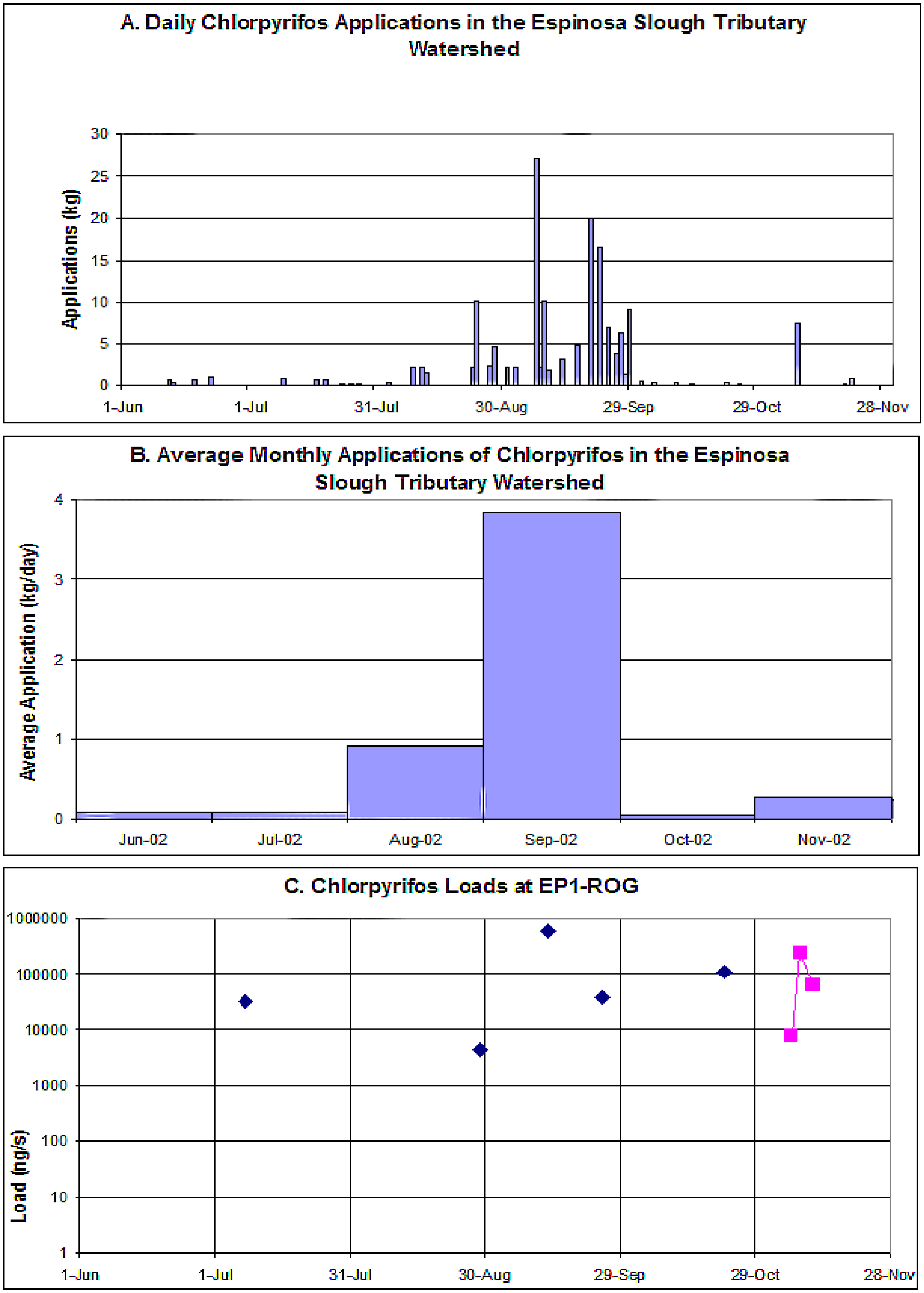

Figure 15 A. Daily applications and **B.** Average monthly applications per day of chlorpyrifos in the Espinosa Slough Tributary Watershed from June to November 2002. **C.** Time series of chlorpyrifos loads observed at EP1-ROG on a log scale, ambient loads are displayed as instantaneous loads, storm loads are displayed as continuous loads.

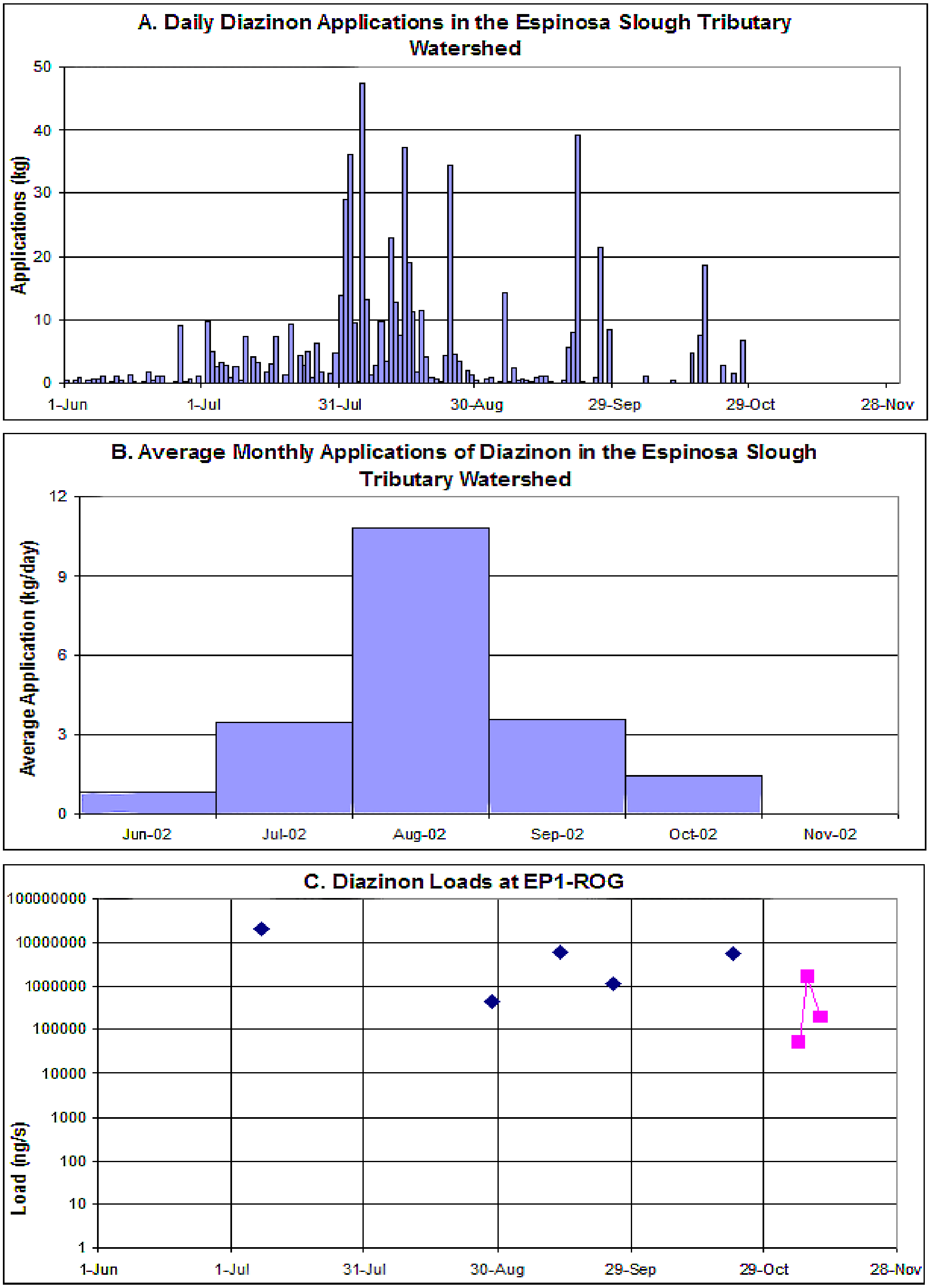

Figure 16 A. Daily applications and **B.** Average monthly applications per day of diazinon in the Espinosa Slough Tributary Watershed from June to November 2002**. C.** Time series of diazinon loads observed at EP1-ROG on a log scale, ambient loads are displayed as instantaneous loads, storm loads are displayed as continuous loads.

Again, because the high variability between pesticide concentrations and thus loads, the comparison between applications and loads was grouped into the summer dry-weather time period and storm time period. Total applications in the time periods were evaluated with the minimum, average, and maximum loads of each time period in Table 7.

Table 7. Summary of Chlorpyrifos and Diazinon applications in the Espinosa Slough Watershed and estimated loads observed at EP1-ROG.

CHLORPYRIFOS				**Average of all estimated loads for time period between application dates (kg)**	**Estimated fraction of applications in average loads**
Time period	**# Of samples**	**Application dates**	**Applications (kg)**		
Ambient	5	1 June - 22 Oct	150	2.06	1.4%
Storm	3	23 Oct - 11 Nov	8	0.1	0.8%
DIAZINON					
Ambient	5	1 June - 22 Oct	606	91.1	15.0%
Storm	3	23 Oct - 11 Nov	11	0.4	3.2%

The Espinosa tributary system exhibits behavior opposite to the Reclamation Ditch and Blanco Drain systems. More chlorpyrifos and diazinon was transported from agricultural fields to the tributary during the ambient sampling period than during the storm event (Table 7). This is contradictory to the idea that the first flush storm event washed chlorpyrifos off of agricultural fields and into the tributary. This could be due to greenhouse applications that are not influenced by precipitation and runoff. It could also be due to the small size of the watershed; there is less storage capacity for the sediment to settle out in.

Also, a greater fraction of the total estimated pesticide loads were transported on suspended sediment during the ambient sampling period than during the storm event, unlike REC-JON and BLA-COO. The average chlorpyrifos sediment fraction of total loads during the ambient time period was 82%, greater than 73% during the winter. The average diazinon sediment fraction of total loads during the ambient time period was 90%, greater than 56% during the storm.

DISCUSSION

Site comparisons

At REC-JON and BLA-COO maximum concentrations generally corresponded to the peak of the storm event (Tables 2 and 4), and at EP1-ROG maximum concentrations corresponded to peak in applications in the watershed (Table 6). The CMC and CCC for both chlorpyrifos and diazinon were exceeded at all 3 sampled sites (Tables 2, 4, and 6) with the exception of diazinon at BLA-COO where more than half of the samples exceeded the CMC value. The chlorpyrifos and diazinon 96-hour LC_{50} for rainbow trout was exceeded most often at EP1-ROG and as never exceeded at BLA-COO.

In general, total chlorpyrifos and total diazinon load estimations spike during the peak of the storm event (Figures 9C, 10C, 12C, 13C, 15C, and 16C). At REC-JON and BLA-COO, estimated loads of chlorpyrifos and diazinon followed the same trend as applications throughout the ambient monitoring period, though the largest in-stream loads occurred during the storm event (Figures 9, 10, 12, and 13). EP1-ROG exhibited different behavior. Both chlorpyrifos and diazinon loads in the tributary were high after large applications to the surrounding and upstream fields and greenhouses, though chlorpyrifos loads increased again in October after few applications and with no storm event (Figure 15). During the storm event at EP1-ROG, estimated chlorpyrifos and diazinon loads were less than loads during the ambient sampling period opposite to what was observed at REC-JON and BLA-COO.

In the Reclamation Ditch Watershed and in the Blanco Drain Watershed, estimated proportions of transported pesticides were greater during the storm than during the summer dry period (Tables 3 and 5). Loads were present during the storm event when the intensity of applications was less than during the ambient monitoring period. Also, at REC-JON and BLA-COO, the sediment fractions of total loads were greater during the storm event. These are indications that precipitation and runoff could have leached chlorpyrifos and diazinon that had been accumulating during the ambient time period on the surfaces of the surrounding and upstream agricultural fields into the waterways.

However, in the Espinosa Slough Tributary Watershed, more chlorpyrifos and diazinon were transported during the summer monitoring period than during the storm event (Table 7), and at EP1-ROG, the sediment fractions of total loads were greater during the ambient sampling period. This could be due to greenhouse applications immediately upstream of the sampling site that are not influenced by precipitation. At EP1-ROG suspended sediment accounted for more than half the load for both pesticides during both time periods and this site had greater suspended sediment concentrations. This could be due to less storage capacity for sediment to settle out in a smaller watershed.

Assumptions and limitations of data analysis

The proportions of applications of chlorpyrifos and diazinon being transported to downstream sampling sites is highly dependent on assumptions about the time period used to add up application data and average load data. Estimated applications of chlorpyrifos and diazinon from the entire month of June were considered in calculating summer application totals, though the first samples were taken on the 8th of July; 37 days after the first applications (that were considered in calculations). The time period of 37 days is longer than some of the published half-lives (Table 1), so including applications from June may result in underestimated proportions (percentages) of applications in loads.

This study was designed to determine the proportion of chlorpyrifos and diazinon applications that are present in downstream loads. Averaging the ambient loads is assuming a continuous loading rate over 4 months. If the primary goal was to provide a detailed analysis of the temporal and spatial dynamics of these two chemicals, the sampling regime of once monthly may have been too spread infrequent; pesticides may have been transported in runoff immediately after application and were missed at the sample site within the month, or maybe degraded before sampling occurred. If more samples were collected more frequently, there may not have been as much variability in the concentration data, and thus the load calculations.

Some of the lower published half-lives (Table 1) are much shorter than the time interval between sample collections. In the environment, pesticides degrade into a variety of other substances as a result of interactions with soil, water, sunlight, and oxygen. Pesticides are also degraded by living organisms. Soil microbes are responsible for catalyzing the breakdown of many pesticides (Kegley, 1999).

The spatial analysis was done under the assumption that chlorpyrifos and diazinon have been applied uniformly to the full square mile indicated in the county database. It is possible that applications were done on a site-specific or spot basis (possibly closer or farther away from agricultural drains). Application data also only includes what is reported to the County Ag Commissioner before application. There is the possibility of more or less than the reported amounts being applied at a time other than what was reported.

In the case of REC-JON, the watershed that drains a portion of runoff from the city of Salinas, residential users applying diazinon in accordance with label directions may contribute significantly to diazinon runoff in creeks (Scanlin et al, 1997). This study did not evaluate urban or residential sources of these pesticides. Because they are not reported or regulated like agricultural uses are, a similar analysis to this study is not possible for urban sources.

Chronic toxicity values (CCC) should be compared to an average in-stream concentration over 4 days. It may not be appropriate to compare CCC values to concentrations from samples taken once or twice a month. Collecting more samples would also help resolve some of the variability in the concentrations data.

Future studies should include a more comprehensive model to calculate pesticide applications and field amounts prior to sampling. This model should include estimates of pesticide decay rates, volatilization, and losses due to runoff, as well as estimates from non-agricultural sources.

CONCLUSIONS

Proportions of chlorpyrifos and diazinon applications in downstream waterways and timing of high in-stream loads

In the other studies that were sited in the introduction for chlorpyrifos and diazinon applications and downstream occurrence, the proportions of applications present in downstream waterways ranged from 0.04% to 0.49 %. The summer proportions estimated in this study are similar, most of which were less than 1% (Tables 3 and 5) with the exception of EP1-ROG (Table 7). Higher proportions of applications transported to downstream surface waters, higher in-stream storm loads, and high sediment contributions to total loads during the storm suggest that precipitation and runoff are leaching residual chlorpyrifos and diazinon from applications made during the ambient time period that had been accumulating on the surfaces of fields and into the ditches.

Espinosa Slough Tributary Watershed

Estimated proportions in the Espinosa Tributary Watershed were greater than the other watersheds (Table 7). Unlike the other two sites, the estimated proportions in the Espinosa Tributary Watershed were greater during the summer sampling period when most applications were being made. This could be due to greenhouse applications immediately upstream from the sampling site and/or irrigation events not quantified in this study. However, greenhouse applications may not account for higher sediment loads.

Greenhouse applications are different from field applications. All pesticide applications are required to be carried out according to label specifications, each product that contains a mixture of different compounds has different application directions depending on the form the pesticide are in (granular, liquid, etc), the crop the pesticide is applied to, timing of applications, and the area/perimeter of application. In general, pesticides used in greenhouses are in a liquid form and are applied by hand; pesticides used on row crop fields are in a granular form and are applied with a tractor at the time the seeds are planted (Patrick Brodrick with Pesticide Use Enforcement, personal communication, 2003). Also runoff/outputs from greenhouses are not influenced by precipitation like open fields are. Greenhouse effluents should be the subject of future research, and if found to be a significant source of pollution; pesticide application in greenhouses would potentially be a focus for regulation changes.

This sampling site also had the highest suspended sediment concentrations and the highest fraction of the total pesticide loads as sediment. It is the smallest watershed of this study and it is possible that there are different soil types on the fields in this watershed that influence runoff (Dubrovsky et al, 2000; Kegley, 1999). Scheduling and methods of irrigation is another factor to consider when identifying differences between runoff patterns in different watersheds.

Over spray could be another explanation for high in-stream loads at EP1-ROG. A study conducted on organophosphate pesticides including daizinon in Monterey and Fresno Counties (Scanlin et al, 1997) showed that regional aerial movement and deposition of organophosphate pesticides occurred in these counties during summer months. This explanation however, does not account for higher suspended sediment fractions of the total estimated loads during the summer months, and higher fractions overall compared to the other to sites.

Threat to wildlife

Regardless of increases, decreases, and variability in pesticide concentrations and estimated loads or the variability in applications, chlorpyrifos and diazinon are still present in the sampled surface waterways in concentrations that are known to be toxic to aquatic ecosystems due to a small proportion of pesticides applied for agricultural purposes. The data from this study indicates that chlorpyrifos and diazinon applications that are claimed to be in accordance with current regulations and label specifications yeild concentrations that are known to be toxic to wildlife. Though these sites are channelized ditches and not natural waterways, they are still places where birds frequent and they empty into National Wildlife Refuges and other natural waterways that provide aquatic habitat and are used by many organisms.

Regulation Agencies

The Regional Water Quality Control Board enforces clean water standards. One way to achieve clean water standards (not just for pesticides) is to limit, if not eliminate runoff from fields and greenhouses. It would be ecologically (though maybe not economically) beneficial to treat or clean runoff before it is discharged into surface waterways. The TMDL process can be used as a mechanism for locating potential sources of pollution. This should be followed by on site mitigation on individual fields.

Farmer education is a critical step to reducing toxic runoff from agricultural fields. The Natural Resources Conservation Service (NRCS) is continually conducting outreach in best management practices (BMPs), including runoff reduction methods on farmland. This service maintains resources to assist farmers with conservation efforts (NRCS, 2003).

Another option for meeting environmental objectives is regulating the use of lower amounts of chemicals that have been shown to cause toxicity, and enforcing application methods that contain applications to the application site. This responsibility would fall to the county Ag Commissioner, and would include more precautions than are specified on product labels. Also regulating the seasonal timing of application to give pesticicdes time to break down before adding more to the system.

The extreme measure to reduce the potential harmful impacts of these two pesticides to wildlife would be the removal of chlorpyrifos and diazinon from the list of registered pesticides. This is one of the California Department of Pesticide Regulation's strict oversights.

Future regulation of chlorpyrifos and diazinon and future studies

Production and formulation of diazinon is scheduled to phase out and end completely during 2003. Effective December 31, 2003, diazinon will no longer be available for use by homeowners for lawn and garden or indoor pest control. As of December 31, 2001 the USEPA has stopped the retail sale of chlorpyrifos to homeowners, limiting the use to certified, professional, or agricultural applicators (Zamora et al, 2003). In agriculture the use of chlorpyrifos is limited. Because chlorpyrifos and diazinon are included in many different products that have many uses, it is unlikely that they will be phased out of agricultural use (Patrick Brodrick with Pesticide Use Enforcement, personal communication, 2003) even though the Consumers Union has called on the EPA to completely phase out diazinon by 2004 (Landscape, 2000). If these two chemicals are ever phased out because of their potential hazards, other chemicals will be designed to take their place.

Transport processes should be fully evaluated for every chemical entering the environment if regulation of these chemicals is going to be effective at reducing the potential risks they pose to wildlife. This study only looked at two chemicals used in agriculture. Additive toxicity of many chemicals being applied to fields and transported through the environment should be considered for regulation. The most efficient method for determining the potential hazard of any agrochemical to an ecosystem is combining laboratory toxicity tests, chemical analysis, and bioassessments, with measures of relevant physical and abiotic factors to investigate potential ecological impacts in a river system receiving agricultural inputs (similar to Anderson et al, 2003), as well as linkages to applications with a focus on transport mechanisms.

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APPENDECIES

Appendix 1. Acute toxicity values.

Table 1. Acute toxicity values for Chlorpyrifos.			
Common name	**Scientific name**	**LD_{50} (mg/kg)/EC_{50} (µg/L)**	**Study time**
Estuarine mysid	Mysidopsis bahia	0.035 (0.029-0.043)*	96 hr
Sheepshead minnow	Cyprinodon variegatus	136 (113-153)*	96 hr
Longnose killfish	Fundulus similis	4.1 (2.8-6.9)*	96 hr
Atalnitic silverside	Menidia menidia	1.7 (1.4-2.0)*	96 hr
Striped mullet	Mugil cephalus	5.4 (4.0-6.9)*	96 hr
Ring-necked pheasant		8**	14 D
Red-winged blackbird		10**	14 D
Chukar		60**	14 D
California quail		70**	14 D
Mallard duck		80**	14 D
Bobwhite quail		**190****	14 D
Canada Goose		4,100**	14 D
Phytoplankton	**Isochrysis galbana**	140**	4 D
Phytoplankton	Thalassiosira sp.	150**	4 D
Phytoplankton	**Skeletonema costatum**	300**	4 D
Scud	Gammarus lacustris	0.1**	96 hr
Water flea	Daphnia magna	0.1**	48 hr
Water flea	Daphnia magna	1.7**	48 hr
Shrimp	Penaeus duorarum	2**	48 hr
Shrimp	Penaeus aztecus	0.2**	48 hr
Cutthroat trout		5**	96 hr
Bluegill sunfish		5.8**	96 hr
Bluegill sunfish		**8****	96 hr
Rainbow trout		7.1**	96 hr
Rainbow trout		15**	96 hr
Lake trout		70**	96 hr
Fathead minnow		**150****	96 hr
Striped bass		<1,000**	96 hr
Honeybee	Apis mellifera	0.1**	24 hr
Honeybee	Apis mellifera	**0.17****	96 hr
	Ceriodaphnia dubia	0.063 - 0.101***	24 hr
	Ceriodaphnia dubia	0.058 - 0.079***	48 hr
	Ceriodaphnia dubia	0.055***	96 hr
	Hyalella azteca	0.086****	10 D
	Ceriodaphnia dubia	20 ng/L*****	7 D
Bold values are geometric means of results from all available studies for that particular study time.			
*(Scimmel, 1983), **(USEPA, 1998), ***(Bailey et al, 1997), ****(Phipps et al, 1995), *****(as cited in Anderson et al, in press)			

Table 2. Acute toxicity values for Diazinon.			
Common name	**Scientific name**	**LD_{50} (mg/kg)/EC_{50} (µg/L)**	**Study time**
Fathead minnows	Pimephales promelas	7.8 (mg/L)*	96 Hr
Bluegills	Lepomis macrochirus	0.46 (mg/L)*	96 Hr
Brook trout	Salvelinus fontinalis	0.77 (mg/L)*	96 Hr
Flagfish	Jordanella floridae	1.6 (mg/L)*	96 Hr
	Ceriodaphnia dubia	0.26 - 0.58**	48 Hr
	Ceriodaphnia dubia	0.37 - 0.75**	24 Hr
	Ceriodaphnia dubia	0.26 - 0.58**	48 Hr
	Ceriodaphnia dubia	0.32**	96 Hr
	Ceriodaphnia dubia	0.35**	96 Hr
	Hyalella azteca	6.51***	10 D
	Ceriodaphnia dubia	110 (ng/L)****	7 D
Mallard duck		**2********	14 D
Ring-necked pheasant		4****	14 D
Canada Goose		6****	14 D
Water flea	Daphnia magna	**1********	48 hr
Water flea	Daphnia pulez	0.8****	48 hr
Shrimp	Penaeus aztecus	28****	48 hr
Scud	Gammarus fasciatus	0.2****	96 hr
Bluegill sunfish		**150********	96 hr
Bluegill sunfish		460****	96 hr
Rainbow trout		**580********	96 hr
Lake trout		600	96 hr
Brook trout		770	96 hr
Cutthroat trout		1,700	96 hr
Fathead minnow		7,800	96 hr
Honeybee	Apis mellifera	0.2	24 hr
Honeybee	Apis mellifera	**0.27**	48 hr
Bold values are geometric means of results from all available studies for that particular study time.			
*(Allison and Hermanutz, 1977), **(Bailey et al, 1997), ***(Phipps et al, 1995), ****(as cited in Anderson et al, in press), *****(Scimmel, 1983)			

Appendix 2. Raw data.

Table 1. Stage, discharge, and pesticide data for all 8 visits to each site.

Date/Time	Stage (m)	Q (M^3/S)	total SSC (mg/L)	Chlorp SS conc (ng/L)	Chlorp SS LOAD (µg/s)	Chlorp water conc (ng/L)	Chlorp Water LOAD (µg/s)	Total Chlorp conc (ng/L)	Total Chlorp LOAD (µg/s)	Sed fraction of total Chlorp LOAD	Diaz SS conc (ng/L)	Diaz SS LOAD (µg/s)	Diaz water conc (ng/L)	Diaz Water LOAD (µg/s)	Total Diaz conc (ng/L)	Total Diaz LOAD (µg/s)	Sed fraction of total Diaz LOAD
REC-JON																	
8-Jul-02	0.27	0.04	96.2	77.7	3.2	81.0	3.4	158.7	6.6	48.9%	105.4	4.4	248.3	10.4	1095870	14.8	29.8%
29-Aug-02	0.27	0.04	22.1	58.7	2.6	86.0	3.7	144.7	6.3	40.6%	30.5	1.3	697.0	30.3	1382304	31.6	4.2%
13-Sep-02	0.26	0.04	40.3	23.6	0.9	62.0	2.4	85.6	3.3	27.6%	19.1	0.7	1620.0	62.0	476291	62.7	1.2%
25-Sep-02	0.26	0.04	11.1	0.2	0.0	69.0	2.6	69.2	2.6	0.3%	8.8	0.3	262.0	10.0	792475	10.4	3.2%
22-Oct-02	0.26	0.05	22.3	17.2	0.9	110.5	5.5	127.7	6.3	13.5%	31.8	1.6	308.8	15.3	1428984	16.9	9.3%
6-Nov-02	0.21	0.06	37.1	335.3	19.0	101.0	5.7	436.3	24.7	76.9%	16.8	1.0	86.0	4.9	453898	5.8	16.4%
8-Nov-02	0.91	3.54	232.3	2889.5	10229	150.0	531.0	3039.5	10760	95.1%	324.4	1148.4	520.0	1840.8	1396848	2989.2	38.4%
11-Nov-02	0.34	0.24	85.6	6.1	1.5	148.0	35.4	154.1	36.9	3.9%	115.8	27.7	370.0	88.6	1352515	116.3	23.8%
BLA-COO																	
8-Jul-02	0.57	0.07	107.6	0.0	0.0	63.0	4.2	63.0	4.2	0.0%	0.0	0.0	71.5	4.8	71.5	4.8	0.0%
29-Aug-02	0.48	0.05	23.1	2.5	0.1	58.0	3.1	60.5	3.3	4.1%	34.0	1.8	100.0	5.4	134.0	7.2	25.4%
13-Sep-02	0.36	0.08	63.9	1.5	0.1	55.0	4.2	56.5	4.3	2.7%	7.6	0.6	443.8	34.2	451.3	34.7	1.7%
25-Sep-02	0.34	0.05	81.7	0.0	0.0	51.0	2.4	51.0	2.4	0.0%	16.1	0.8	202.0	9.6	218.1	10.4	7.4%
22-Oct-02	0.29	0.06	45.1	2.4	0.1	61.0	3.7	63.4	3.9	3.8%	23.7	1.5	50.0	3.1	73.7	4.5	32.2%
6-Nov-02	0.23	0.02	43.9	5.6	0.1	45.0	0.9	50.6	1.0	11.1%	146.4	2.9	0.0	0.0	146.4	2.9	100%
8-Nov-02	0.30	0.03	40.7	30.1	1.0	1142.0	39.8	1172.1	40.8	2.6%	15.7	0.5	4343.5	151.3	4359.2	151.8	0.4%
11-Nov-02	0.23	0.02	7.0	4.4	0.1	123.0	2.5	127.4	2.5	3.5%	20.2	0.4	58.0	1.2	78.2	1.6	25.8%
EP1-ROG																	
8-Jul-02	0.47	0.03	1076.1	1029.7	28.2	119.0	3.3	1148.7	31.5	89.6%	674559	18483	67235	1842.2	741794	20325	90.9%
29-Aug-02	0.27	0.02	83.3	93.3	1.8	132.0	2.5	225.3	4.3	41.4%	19535.6	369.2	3605.5	68.1	23141.1	437.4	84.4%
13-Sep-02	NC	0.02	410.4	27618.1	559.3	849.0	17.2	28467.1	576.5	97.0%	279476.9	5659.4	12419.0	251.5	291895.9	5910.9	95.7%
25-Sep-02	NC	0.01	83.6	2869.7	32.6	386.0	4.4	3255.7	37.0	88.1%	77492.3	881.1	17829.5	202.7	95321.8	1083.8	81.3%
22-Oct-02	0.30	0.02	375.6	4052.6	99.7	335.5	8.3	4388.1	108.0	92.4%	220779.8	5432.3	8446.3	207.8	229226.1	5640.1	96.3%
6-Nov-02	0.30	0.01	378.7	271.6	3.3	347.0	4.3	618.6	7.6	43.9%	1190.0	14.6	2864.5	35.2	4054.5	49.9	29.4%
8-Nov-02	0.48	0.12	1002.9	1773.0	211.9	230.0	27.5	2003.0	239.4	88.5%	9842.4	1176.2	2957.5	353.4	12799.9	1529.6	76.9%
11-Nov-02	0.30	0.02	213.1	3583.1	54.2	497.0	7.5	4080.1	61.7	87.8%	8124.7	122.8	4735.5	71.6	12860.2	194.4	63.2%

Table 2. Accuracy and precision of all ELISA analysis.	Chlorpyrifos	Diazinon
# Of calibrator pairs	108	140
Mean CV per calibrator pair (standard deviation)	6.77% (9.28%)	3.57% (3.98%)
Max CV	38.24%	23.97%
# Of calibrator pairs with a CV > 15%	8	1
Mean R^2 for calibration curve (standard deviation)	0.95	0.96
Minimum R^2	0.60	0.84

Table 3. Suspended sediment concentrations, TDS, transparency, and turbidity from all sampled sites.

Site code	**Date/Time**	**SSC (<=63um) (ng/L)**	**SSC (>63um) (ng/L)**	**TDS (us)**	**Transparency (cm)**	**Turbidity (NTU)**
BLA-COO	8-Jul-02	107.61	0.00	2.95	14.5	NC
BLA-COO	29-Aug-02	23.14	0.00	2940	20.8	2.73
BLA-COO	13-Sep-02	63.87	0.00	3000	21.3	5.73
BLA-COO	25-Sep-02	81.69	0.00	3210	29.6	2.36
BLA-COO	22-Oct-02	45.06	0.00	3440	29.5	4.14
BLA-COO	6-Nov-02	43.87	0.00	OR	29.2	9.47
BLA-COO	8-Nov-02	40.68	0.00	2710	9.1	64.3
BLA-COO	11-Nov-02	7.00	0.00	3170	21.8	9.4
EP1-ROG	8-Jul-02	671.59	404.48	1636	5.2	NC
EP1-ROG	29-Aug-02	83.25	0.00	1518	9.4	108
EP1-ROG	13-Sep-02	250.64	159.72	2280	7.3	152
EP1-ROG	25-Sep-02	69.63	13.93	1320	18.8	47.9
EP1-ROG	22-Oct-02	353.64	21.95	1339	4.1	257
EP1-ROG	6-Nov-02	281.17	97.50	3060	14.2	170
EP1-ROG	8-Nov-02	739.37	263.49	973	2.2	517
EP1-ROG	11-Nov-02	192.56	20.53	1674	7.5	114
REC-JON	8-Jul-02	96.20	0.00	1852	18.5	NC
REC-JON	29-Aug-02	22.10	0.00	1596	20.8	7.78
REC-JON	13-Sep-02	40.27	0.00	1685	24.3	4.63
REC-JON	25-Sep-02	11.10	0.00	1511	29.1	6.64
REC-JON	22-Oct-02	22.28	0.00	1852	26.1	13.5
REC-JON	6-Nov-02	37.07	0.00	1620	27.2	17.4
REC-JON	8-Nov-02	232.32	0.00	260	3	273
REC-JON	11-Nov-02	85.62	0.00	551	20	43

Table 4. Depth profiles of YSI measurements of temperature, pH, dissolved oxygen, salinity, and TDS from July 8 and October 22, 2002

Site	Date	Depth (m)	Temp C	pH	DO (mg/L)	DO %	Salinity (µs)
BLA-COO	08-Jul-02	0.0	17.90	7.81	6.09	64.7	1.37
BLA-COO	08-Jul-02	0.5	17.72	7.77	5.77	61.1	1.37
BLA-COO	22-Oct-02	0.0	14.13	7.81	5.41	53.1	1.44
EP1-ROG	08-Jul-02	0.0	28.36	8.31	6.90	89.1	0.71
EP1-ROG	22-Oct-02	0.0	17.71	8.28	8.66	91.3	0.53
EPL-EPL	08-Jul-02	0.0	29.41	9.79	21.17	281.4	2.79
EPL-EPL	23-Oct-02	0.0	14.97	8.54	12.98	130.6	2.43
EPL-EPL	23-Oct-02	0.5	15.00	8.54	11.07	111.4	2.43
REC-JON	08-Jul-02	0.0	21.84	9.15	17.32	198.2	0.68
REC-JON	22-Oct-02	0.0	14.52	7.97	5.47	53.9	0.72