Probabilistic Estimation of Dissolved Phase Pyrethroid Concentrations from Whole Water Analytical Data

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ABSTRACT

This report describes a Monte Carlo procedure for estimating synthetic pyrethroid dissolved phase concentrations from whole surface water sample chemical analytical data. Whole water samples are unfiltered water samples that contain suspended sediment. The portion of pyrethroid that is actually dissolved - as opposed to that which is sorbed to suspended sediment - has the greatest bioavailability, and is considered to be primarily responsible for aquatic toxicity in short-term acute exposures. In contrast, the sediment-sorbed fraction is thought to display lower short-term bioavailability. The procedure described in this report provides an estimate of the expected range of dissolved-phase pyrethroid concentration in a sample based on (a) whole water analytical pyrethroid concentration in the sample, (b) measured suspended sediment in the sample, (c) the distribution of organic-carbon normalized soil partition coefficients (K_{OC}) for specific pyrethroids, and (d) the distribution of suspended sediment organic carbon data from Central Valley agriculturally-dominated tributaries. Knowledge of dissolved concentration allows a screening level, or qualitative comparison of monitoring data to acute aquatic toxicity laboratory data obtained in sediment free water. While this report focuses on water samples, the calculation procedure is applicable to bed sediment pore water given appropriate input data. Several standard assumptions about sorption are part of the calculation procedure, including sorption reversibility, rapid attainment of equilibrium, linearity, and the dominance of solid-phase organic carbon as the locus for sorption. While these assumptions are commonly utilized in transport models and environmental risk assessments, a discussion of their potential significance is provided. Finally, examples of model applications based on recent monitoring data are included.

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INTRODUCTION

The Department of Pesticide Regulation's (DPR) Environmental Monitoring Branch Surface Water Protection Program recently conducted monitoring studies for several synthetic pyrethroids (Bacey, 2002; Bacey et al., 2003; Gill, 2002) and further studies are underway (Kelley, 2003). The pyrethroid analytes in DPR's studies are those with the highest reported agricultural and commercial structural uses in California: bifenthrin, cypermethrin, cyfluthrin, λ-cyhalothrin, esfenvalerate, and permethrin (Figure 1). Two primary reasons for conducting surface water studies of pyrethroids are because of (1) their high aquatic toxicities observed in laboratory studies (e.g., Solomon et al., 2001), and (2) similarities of their uses to those of the organophosphate (OP) insecticides diazinon and chlorpyrifos. The two OPs have been detected in California surface water at levels that exceed criteria established to protect aquatic life (Spurlock, 2001).

Pyrethroid hydrophobicity

Although synthetic pyrethroids share some of the same uses as certain OPs (e.g. dormant season winter orchard applications), they also possess physicochemical properties that mitigate their aquatic toxicity in the environment relative to toxic concentrations measured in typical laboratory tests. Pyrethroids have high molecular weights, are nonionic in neutral solution, and so are extremely hydrophobic. Octanol-water partition coefficients (K_{OW}) on the order of 10^6 and water solubilities in the low ug/L range are typical (Table 1). These properties are comparable in magnitude to those of other well-known extremely hydrophobic chemicals such as DDT, hexachlorobenzene, and various poly-chlorinated biphenyls.

TABLE 1. Water solubility, log octanol/water partition coefficient (K_{OW}) (Laskowski, 2002).

CHEMICAL	solubility ug L^{-1} (ppb)	log_{10} K_{OW}
bifenthrin	0.014	6.4
cyfluthrin	2.3	6.0
cypermethrin	4	6.5
λ - cyhalothrin	5	7.0
esfenvalerate	6	5.6
permethrin	5.5	6.1

Figure 1. Structures of 6 synthetic pyrethroids

	R₁	R₂	R₃		
	CCl_2	CN	F	cyfluthrin	434 daltons
	CCl_2	CN	H	cypermethrin	416 daltons
	$CClCF_3$	CN	H	λ-cyhalothrin	450 daltons
	CCl_2	H	H	permethrin	391 daltons

fenvalerate   420 daltons

bifenthrin   423 daltons
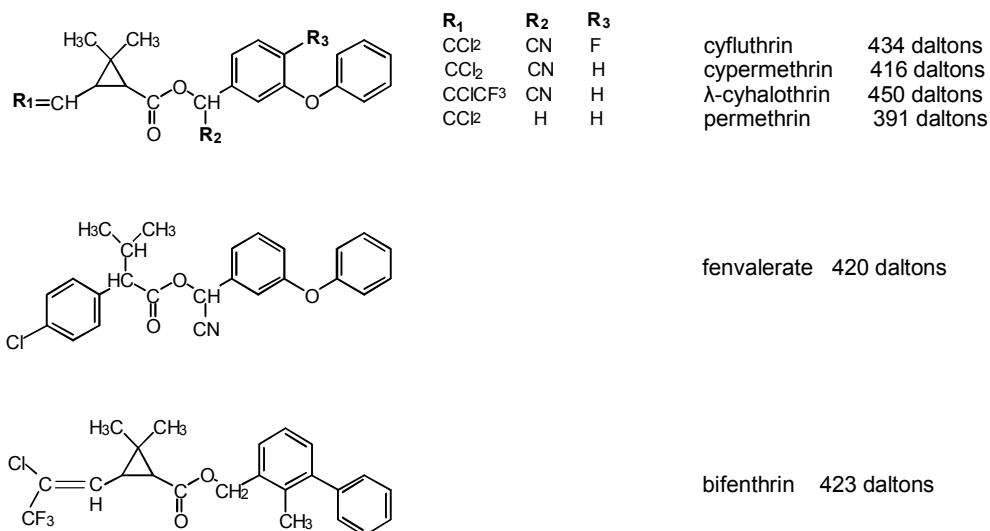
One consequence of the extreme hydrophobicity of synthetic pyrethroids is that they display a high degree of sorption to many materials, including sediment, walls of sampling containers and other materials that a water sample may contact (e.g., filtration apparatus). DPR's pyrethroid surface water monitoring studies therefore utilize grab sampling techniques, where water samples are collected directly into glass sampling containers. Liquid-liquid extraction is performed directly on the unfiltered samples (water + suspended sediment), and the sample container itself is rinsed with extracting solvent to remove any pyrethroid sorbed to the container walls. Consequently, DPR's analytical results are "whole-water" results; the reported concentrations include both dissolved and sediment-bound pyrethroid residues.

Bioavailability, exposure, toxicity

While there have been some pyrethroid detections in DPR's surface water studies, their significance to aquatic life is difficult to assess. On the basis of laboratory acute aquatic

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toxicity data pyrethroids are very toxic. But those data are typically obtained in aqueous systems with no sediment. Actual surface water samples contain suspended sediments that reduce bioavailability of the hydrophobic pyrethroids - hence their toxicity - relative to the pure water case.

The "equilibrium partitioning" (EqP) approach is commonly used to describe reduced bioavailability of hydrophobic organic compounds in sediment/water systems (Di Toro et al., 1991; Wenning and Ingersoll, 2002). EqP assumes that an organism's exposure to a hydrophobic contaminant in a sediment/water system depends on the contaminant's chemical activity. No explicit assumptions about exposure route are required. At equilibrium, a contaminant's activity in all phases is the same (e.g. sorbed, dissolved, and in biota). Further, the activities of hydrophobic contaminants are proportional to their concentrations. Therefore - at equilibrium - effects on aquatic organisms in sediment/water systems are expected when contaminant activity (i.e. concentration) in the dissolved phase is equivalent to the effect activity (concentration) determined in water-only systems.

A subtly different conceptual approach that leads to similar conclusions was employed in a recent cotton pyrethroid risk assessment (Solomon et al., 2001; Giddings et al., 2001; Hendley et al., 2001; Travis and Hendley, 2001; Maund et al, 2001). In their studies it was explicitly assumed that only the dissolved fraction of pyrethroid in the water column is bioavailable (Travis and Hendley, 2001; Maund et al., 2001). Consequently, modeled dissolved pyrethroid water column concentrations were compared directly to laboratory measured acute toxicities for water column organisms in that risk assessment. Similarly, modeled pore water concentrations in sediment were compared to acute toxicities for sediment-dwelling organisms.

The purpose here is to develop a method for conducting screening level evaluations of pyrethroid/surface water samples because DPR currently has no way to evaluate pyrethroid analytical results. Similar to the approaches discussed above, it is assumed

here that toxicity may occur when estimated dissolved phase concentrations approximate effect concentrations measured in water-only systems. However, there is uncertainty about whether only the dissolved phase is truly bioavailable. Therefore future studies to validate this model for pyrethroids in California sediment are highly recommended. These validation studies should include comparison of measured and predicted pyrethroid aquatic and sediment toxicities in both spiked and environmental samples.

MODEL FORMULATION
Assuming linear equilibrium reversible sorption

$$C_S = K_d \; \rho \; C_{Aq} \; 10^{-3} \qquad\qquad [1]$$

where C_S = sorbed phase concentration (whole water basis, ug pyrethroid/L), K_d is the sorption distribution constant (ml/gm sediment), ρ is the sediment concentration (g/L), and C_{Aq} is the "free" aqueous, or dissolved phase concentration (ug/L). Assuming humic, or organic carbon, dominated sorption

$$K_d = f_{OC} \; K_{OC} \qquad\qquad [2]$$

where f_{OC} is the sediment organic carbon content (g OC/g sediment) and K_{OC} is the organic carbon normalized sorption coefficient for the pyrethroid [ml/(g OC)]. The analytical whole water pyrethroid concentration C_T (ug/L) obtained from laboratory results is comprised of sorbed pyrethroid [C_S, (ug sorbed pyrethroid) L^{-1}] and dissolved pyrethroid [C_{Aq}, (ug dissolved pyrethroid) L^{-1}]:

$$C_T = C_S + C_{Aq} \qquad\qquad [3]$$

Combining [1] and [2], substituting into [3] and rearranging yields

$$C_{Aq} = \frac{C_T}{\left[1 + K_{OC} \, f_{OC} \, \rho \, 10^{-3}\right]} \qquad\qquad [4]$$

In any particular sample C_T and ρ are measured, so knowledge of K_{OC} and f_{OC} are required to obtain an estimate of the dissolved pyrethroid concentration C_{Aq}.

Monte Carlo analysis is a method of estimating the probability distribution of a model output variable given the distributions of input variables. The method involves repetitive model calculations in which each calculation is conducted using input variables randomly selected from their respective probability distributions. The aggregate output data is then assumed to estimate the probability distribution of the output variable. In this case, the variables K_{OC} and f_{OC} are considered random variables due to natural variability and/or uncertainty in their values. When their probability distributions are known, equation [4] provides a model that allows estimation of the distribution of C_{Aq} using Monte Carlo techniques. This report describes the procedure. The resultant distribution of C_{Aq} embraces variability, uncertainty, and experimental error associated with K_{OC} and f_{OC}. While pyrethroids are the focus of this paper, the method is generally applicable to other hydrophobic nonionic organic compounds whose sorption is dominated by humic materials.

Pyrethroid sorption - K_{OC} data distributions
Several sources of data were examined in the search for reliable pyrethroid sorption data. These included DPR's pesticide chemistry database (Kollman and Segawa,1995), DPR's Registration Branch Library of registrant data submissions, and the USDA-ARS pesticide properties database (USDA-ARS, 2003). Most of the available data from these sources were obviously unreliable. Reported K_{OC}s were commonly far below those expected based on solubility and K_{OW}, there was extreme and unexplainable data variability both within and between the individual pyrethroids, and there were significant deficiencies in most of the actual studies examined. The deficiencies in the older DPR registration studies included failure to report the actual study data, no reported quality control/quality assurance data, reported equilibrium pyrethroid concentrations in the test systems at levels that were 2 – 3 orders of magnitude greater than solubility, and use of surfactants or high levels of cosolvent in test systems to achieve dissolved concentrations high enough to measure. In short, many data – especially from older

studies in the 1970s or early 1980s - were obtained using insensitive analytical techniques and/or inappropriate experimental procedures.

Laskowski (2002) recently conducted a detailed review of pyrethroid environmental fate studies. Most of the soil sorption studies reviewed were relatively recent, and all were conducted by member companies of the Pyrethroid Working Group in support of U.S. or European pesticide registration. None of these data were previously available in the public domain. Laskowski (2002) included a critical evaluation of experimental study methodologies, and developed a rating system (scale 1 – 10) to distinguish between low and high confidence data, respectively.

bifenthrin, cyfluthrin, cypermethrin, λ-cyhalothrin, permethrin   With the exception of bifenthrin, only experimental sorption data from Laskowski (2002) with ratings of 5 or greater were considered acceptable for the purposes of this study. Bifenthrin was excepted from this condition because the only available sorption data had a rating of 3. Sorption data with ratings of 5 or greater were available for cyfluthrin, cypermethrin, λ-cyhalothrin, and permethrin, and the K_{OC} data for these four were log-normally distributed (Figure 2). "Best-fit" distributions were estimated using *Crystal Ball 2000* standard edition (Decisioneering, 2000), and these served as the log K_{OC} sampling distributions for these four pyrethroids during the Monte Carlo simulations (Table 2). In the case of bifenthrin, the lowest and highest reported bifenthrin log K_{OC} values of 5.06 and 5.95 (K_{OC} =116,000 and 888,000, respectively, Laskowski, 2002) were assumed to represent the lower and upper bounds of a uniform log K_{OC} distribution in the simulations.

esfenvalerate   Laskowski (2002) reported no available esfenvalerate or fenvalerate sorption data. Consequently various methods for estimating esfenvalerate K_{OC} were evaluated. These included several well-known linear free energy relationships (LFER) that relate octanol/water partition coefficient (K_{OW}) and K_{OC} (Lyman, 1990; Seth et al., 1999; Xia and Pignatello, 2001), and a fragment contribution method based in

part on molecular topology as described by first-order molecular connectivity indices (Meylan et al., 1992). The latter estimates were calculated using the *pckocwin* module of the program "Estimation Programs Interface for Windows" (EPI ver. 3.10), developed by Syracuse Research Corp. for USEPA OPPT (2000).

TABLE 2. Parameters for pyrethroid **log** K_{OC} sampling distributions. Cyfluthrin, cypermethrin, λ - cyhalothrin, permethrin derived from combined sorption *and* desorption data. For esfenvalerate and bifenthrin see text discussion.

Chemical	distribution	mean, μ	standard deviation, σ
cyfluthrin	normal	5.07	0.1381
cypermethrin	normal	5.46	0.2278
esfenvalerate	normal	5.64 (est.)	0.2159 (est.)
λ - cyhalothrin	normal	5.48	0.2586
permethrin	normal	5.40	0.2389
bifenthrin	uniform: range 5.06 - 5.95		

Figure 2. Experimental cyfluthrin, cypermethrin, λ-cyhalothrin and permethrin K_{OC} data selected for use in the Monte Carlo simulations. Includes only data with experimental rating equal to or greater than *5* Laskowski (2002). These plots describe the distribution of the K_{OC} data. The y-axis reports the cumulative probability for any given value of K_{OC} on the x-axis, where the cumulative probability represents the fraction of the population with K_{OC} less than or equal to the given K_{OC}. These probability plots are essentially linear using a logarithmic K_{OC} axis, indicating that K_{OC} for each of these 4 pyrethroids is a log-normally distributed variable.
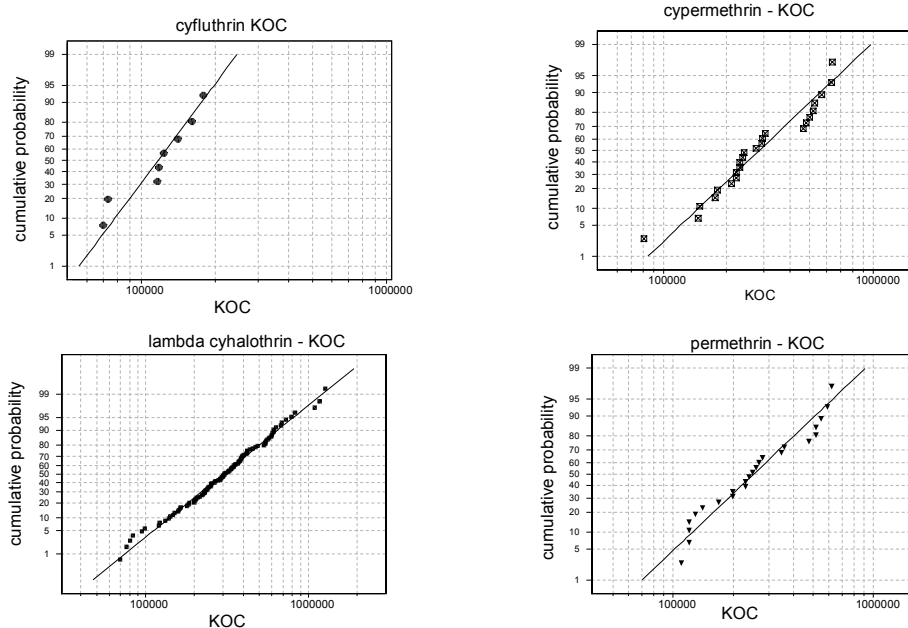
Figure 3. Comparison of estimated and measured log K_{OC} data for 4 pyrethroids. Estimated values obtained using various K_{OW}-K_{OC} LEFRs and a fragment contribution method (Meylan et al., 1992) calculated by program "pckocwin". Each "box" in the box plots spans the interquartile range (25th to 75th percentile) of the data group. The center line is the median for the group.
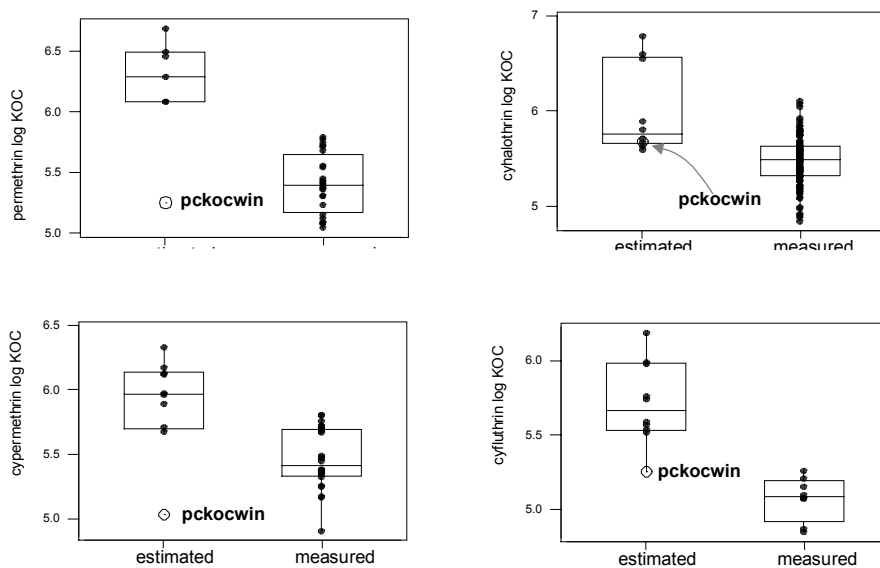
The fragment contribution method has been reported to outperform LFER estimates of K_{OC} based on water solubility or K_{OW} (Meylan et al., 1992). The ability of these estimation methods to predict pyrethroid sorption coefficients was tested by comparing K_{OC} predictions to the highest quality experimental K_{OC} data for cyfluthrin, λ-cyhalothrin, cypermethrin, and permethrin. In general, the LFER estimation methods consistently yielded predictions that were much higher than measured values (Figure 3). In contrast, the *pckocwin* estimates were comparable to the measured data. Based on the general agreement between the *pckocwin* estimates and measured data for cyfluthrin, λ-cyhalothrin, cypermethrin, and permethrin, the mean esfenvalerate log K_{OC} here was assumed equal to the log of the *pckocwin* estimate of 437,000 (i.e., log K_{OC}=5.64). This value is comparable to the recent single esfenvalerate K_{OC} value reported in the manufacturer's product technical bulletin of 252,000 (E.I. duPont de Nemours and Company, 2002). Further, esfenvalerate's log K_{OC} was assumed normally-distributed similar to the other four pyrethroids (Figure 2), with a variance assumed equal to that of the mean variance of cyfluthrin, λ-cyhalothrin, cypermethrin, and permethrin's log K_{OC}. The latter assumption was based on the observed homogeniety of log K_{OC} variances of the four pyrethroids with reliable data (Figure 4). In

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summary, the esfenvalerate log K_{OC} was taken as normally distributed with mean μ = 5.64 and variance σ = 0.2159 (Table 2); this sampling distribution was used in the esfenvalerate Monte Carlo simulations.

Although the cyfluthrin, λ-cyhalothrin, cypermethrin, and permethrin K_{OC} data have been vetted, the range of variation is greater than typically observed for other K_{OC} data. Reported K_{OC} values typically vary by a factor of about 2 – 3 (Lyman, 1990; Rutherford et al., 1992). K_{OC} determinations for extremely hydrophobic chemicals are prone to error because they tend to adsorb to laboratory glassware, and because the dissolved portion is a small fraction of total sorbate in the test system. It is apparent that K_{OC} variability for such pesticides includes both natural sorbent-to-sorbent variation and experimental error. While a potential mineral contribution to sorption may contribute to variability in K_{OC} among sorbents, there is little, if any, available data demonstrating a significant mineral contribution to pyrethroid sorption in natural sorbents. Consequently the presumption here is that the dominant pyrethroid sorption mechanism in surface water is similar to other extremely hydrophobic chemicals: partitioning between the solution phase and humic materials associated with suspended sediment.

Figure 4. Homogeniety of log K_{OC} variance for cyfluthrin, cypermethrin, λ-cyhalothrin and permethrin.
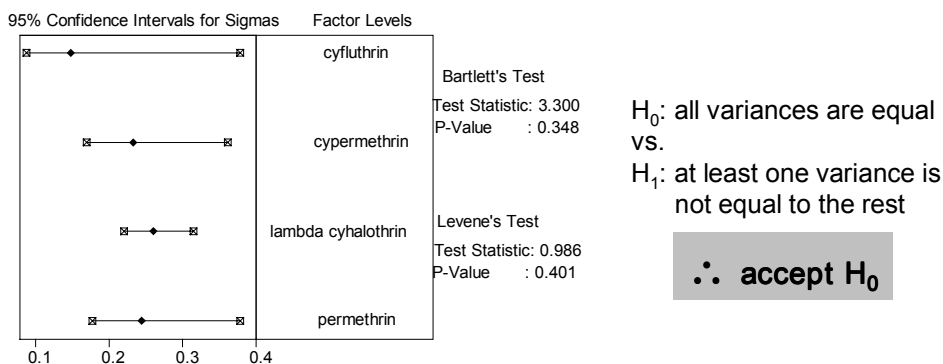
Assumptions about sorption

Hysteretic, or nonsingular sorption, occurs when the sorption isotherm is not single-valued. That is, if different partition coefficients are obtained depending on whether equilibrium is approached via solute uptake by the sorbent (sorption) as opposed to release of sorbed solute from the sorbent (desorption). While hysteresis may arise from experimental artifacts such as failure to reach desorptive equilibrium, the thermodynamic basis for sorption hysteresis in certain microporous systems is well documented (Hiemenz, 1986). Similar mechanisms may be applicable to sorption in polymeric soil humic materials (Xia and Pignatello, 2001). Equation 4 assumes a reversible (non-hysteretic) sorption isotherm, and severe deviations could be a source of significant error. An analysis of variance (ANOVA) to test for differences between the laboratory short-term mean sorption and desorption log K_{OC}s indicated no evidence that sorption was hysteretic for any of the four pyrethroids (Figure 5). Consequently the desorption and sorption K_{OC} data for each pyrethroid were lumped together; nearly half the log K_{OC} data in Figure 2 are from desorption experiments (Appendix 1).

Figure 5. Two-way ANOVA to test effect of chemical and type (desorption or sorption) on log K_{OC}

```
General Linear Model - Analysis of Variance for logKOC, using Adjusted SS for Tests
Factor      Type Levels Values
chem        fixed     4 cyfluthrin, cypermethrin, lambda cyhalothrin, permethrin
type        fixed     2 adsorption desorption


Source        DF     Seq SS     Adj SS     Adj MS       F       P
chem           3    1.30138    1.28034    0.42678    6.73   0.000
type           1    0.06257    0.02114    0.02114    0.33   0.565
chem*type      3    0.00679    0.00679    0.00226    0.04   0.991
Error        148    9.38700    9.38700    0.06343
Total        155   10.75774
```

Conclude:
1. mean log KOCs are not equal among the 4 pyrethroids
2. no evidence that mean desorption and sorption log KOCs are different

Pesticide sorption is sometimes nonlinear, where sorption partition coefficients vary with concentration (e.g., Spurlock et al., 1995). The empirical Freundlich sorption isotherm is usually used to describe a nonlinear equilibrium relationship between S and C_{Aq}.

$$S = K_f \, C_{Aq}^N \qquad\qquad [5]$$

where S is the sorbed concentration (mass sorbed/gm sediment), K_f is the nonlinear Freundlich partition coefficient (analogous to the linear partition coefficient K_d in Eq. 1), and the exponent N indicates the degree of nonlinearity. In Eq. 1, S is proportional to C_S under conditions of dilute sediment concentration. When N is equal to 1, K_f and K_d are essentially equivalent and sorption is linear. Laskowski (2002) reported "reliable" (experimental rating ≥ 5) Freundlich sorption data for 13 pyrethroid/soil combinations. Values for the Freundlich exponent N ranged from 0.8 to 1.2, with most values clustered around unity. The mean value of N for these isotherms was 0.97, and the 95% confidence interval for the mean included unity [0.91,1.03]. The data indicate that the existing pyrethroid sorption data are adequately described by linear isotherms.

An additional model assumption is the rapid attainment of sorption/desorption equilibrium between sediment and soil. Some experimental data in the literature demonstrate the presence of a slow sorption mechanism(s) that may progress over characteristic time frames ranging up to a year or more (Pignatello and Xiang, 1996). Typically, the kinetically limited fraction may account for 10 - 50 per cent or more of the total sorbed chemical after many months. In general, our current knowledge of long-term sorptive rates and mechanisms is poor. When pyrethroid applications are soon followed by a rainfall or irrigation runoff event, neither sorptive uptake by field soil nor subsequent desorptive release from entrained soil (sediment) in runoff may be at "true" thermodynamic equilibrium. Consequently the net effect of sorption kinetics on model predictions here is unclear, and so adds uncertainty to the predictions.

Sediment organic carbon content distribution

The United States Geological Survey (USGS) collected both suspended sediment (SS, USGS method 80154) and particulate organic carbon (POC, USGS method 689) data as part of the San Joaquin Valley/Tulare Lake Basin study unit and Sacramento Valley study unit National Water Quality Assessment Program (NAWQA) sampling in the years 1992 - 1998 (data available online at http://ca.water.usgs.gov/sanj_nawqa/, verified September 12, 2003). The ratio [POC/SS] provides an estimate of suspended sediment organic carbon (f_{OC}) content, and these estimates compare favorably to direct f_{OC} measurements in San Joaquin River basin surface water suspended sediments (Kratzer, 2003). Here, data from 6 tributary sites (Table 3) - as opposed to rivers - were used to estimate the sampling distributions of f_{OC} in California Central Valley agriculturally dominated tributaries (Figure 6). Harding Drain (also known as Turlock Irrigation District drain #5) was excluded because it receives discharges from dairies, feedlots, a waste water treatment plant, and a rendering plant which contribute to a high organic carbon load in the water body (Ross et al., 1999; Ross et al., 2000). At values of f_{OC} less than about 0.002 to 0.003, mineral contributions to sorption become increasingly important and the assumption of organic carbon-based sorption may no longer be valid (DiToro et al., 1990; Rutherford et al., 1992; Spurlock and Biggar, 1992). Only a few percent of the data were below this range.

TABLE 3. Suspended sediment organic carbon fraction in six Sacramento/San Joaquin Valley agriculturally-dominated tributaries.

Site	Basin	N	mean (f_{OC})	SD (f_{OC})
Colusa Basin Drain	Sacramento	28	0.011	0.006
Mud Slough	San Joaquin	18	0.034	0.014
Orestimba Creek (River road)	San Joaquin	90	0.019	0.029
Sacramento Slough	Sacramento	22	0.022	0.040
Salt Slough	San Joaquin	33	0.018	0.010
Spanish Grant Drain	San Joaquin	19	0.032	0.032
Grand Total		210	0.021	0.026

Figure 6. (a) Histogram and (b) cumulative distribution of suspended sediment organic carbon (f_{OC}) in six California Central Valley agriculturally dominated tributaries. f_{OC} calculated as (particulate organic carbon/suspended sediment). Data from USGS San Joaquin and Sacramento National Water Quality Assessment Studies. N = 210.
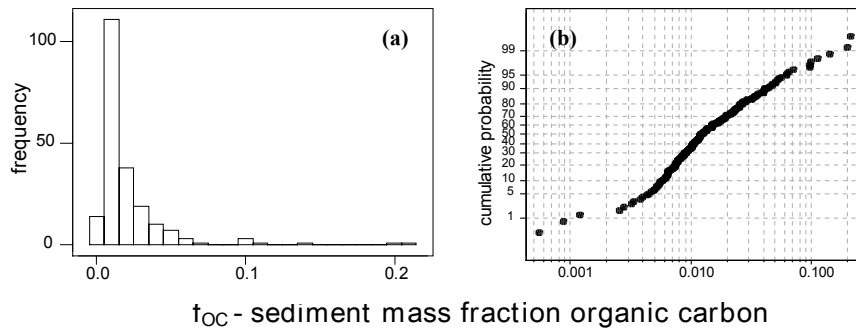
A two-way ANOVA (not shown) on the transformed f_{OC} data indicated no significant difference between tributary f_{OC} collected during rainy periods as opposed to drier periods (p=0.47) or between the San Joaquin and Sacramento River basins (p=0.12). The f_{OC} data were transformed using the arcsin-square root to stabilize group variances. For the purposes of the ANOVA, rainy periods were classified as those days where the sum of rainfall at any one of three stations in the respective basin exceeded 0.3 inches on the sampling day and two prior days. These results indicate that f_{OC} in rainfall runoff suspended sediment is comparable to suspended sediment f_{OC} during the drier portions of the year.

POC and SS were modestly log-log correlated, indicating higher POC loads were associated with higher sediment loads (Figure 7a). However, the slope of the relationship was <1, indicating that increases in POC were not commensurate with those in SS. Consequently, f_{OC} was lower in high SS water samples than in low SS samples (Figure 7b). This probably reflects the combined effect of the known general inverse correlation between sediment grain size and organic carbon content (Nowell et al., 1999), and the lower mass fraction of sediment fines during high flow, high suspended sediment runoff events. Based on the emiprical relationship between SS and f_{OC} in Figure 7B, different f_{OC} sampling distributions were developed for the Monte

Carlo simulations here based on SS content. The 210 f_{OC} data were ranked in ascending order of SS and then divided into 5 separate groups with approximately equal numbers of members: 0 - 47 mg/L SS, 48 - 70 mg/L SS, 71-125 mg/L SS, 126-226 mg/L SS, and 227-1700 mg/L SS (Figure 8). The f_{OC} sampling distribution for a particular simulation was then chosen based on the SS concentration of the sample.

Figure 7. (a) observed log-log relationship between POC and SS data, (b) log-log relationship between f_{OC} and SS. SS and POC data from USGS San Joaquin and Sacramento National Water Quality Assessment Studies.
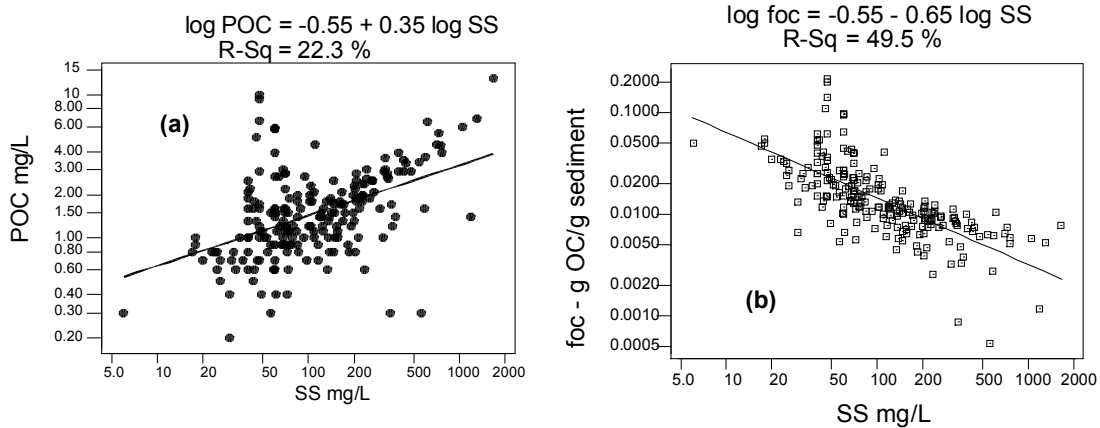
Figure 8. Cumulative distributions of f_{OC} in the 5 suspended sediment (SS) classes.
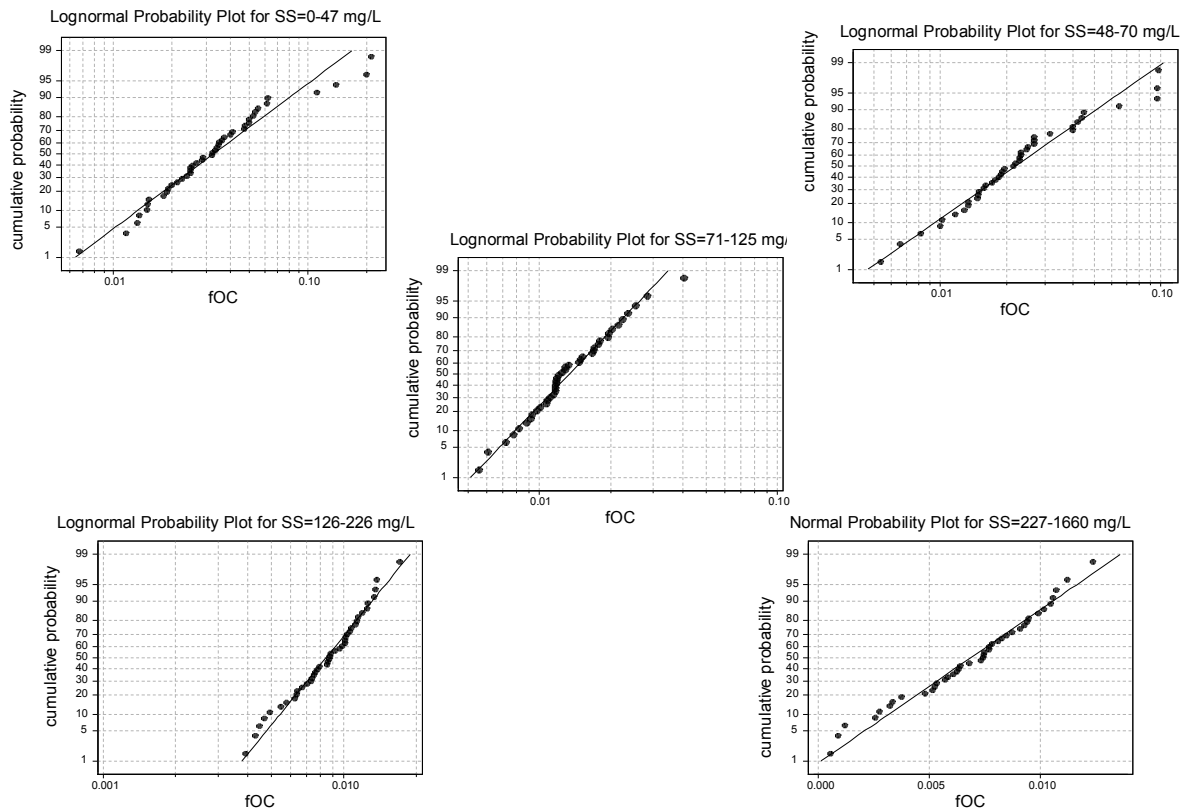
APPLICATION OF THE MODEL

Wadsworth Canal, Butte County, February 15-16, 2003.

DPR personnel sampled Wadsworth Canal for pyrethroids, organophosphates, and herbicides several times during a February 2003 rain runoff event (Bacey et al., 2003). Permethrin was detected in a single sample at a concentration of 0.094 ug L^{-1}; SS was determined at 3114 mg L^{-1} in a companion sample collected at the same time (0230 hours, 2/16/2003). The sample SS was greater than the highest SS concentration of the 227-1700 mg L^{-1} SS group in Figure 8. However, this f_{OC} sampling distribution was used in the absence of any other data. The distribution of dissolved permethrin concentrations in Figure 9 is based on 2500 Monte Carlo simulations of Eq. 4. with inputs consisting of random samples from permethrin log K_{OC} sampling distribution (Table 2) and the f_{OC} sampling distribution (Figure 8e). The Monte Carlo simulation was conducted using Crystal Ball 2000 (Decisioneering, Inc., 2000).

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The *mysidopsis bahia* 96-hour LC_{50} (Table 4) was exceeded by approximately 9 percent of the dissolved concentration estimates for this single grab freshwater sample (Figure 9). Saltwater arthropods are generally more susceptible to pyrethroids than freshwater arthropods, and *m. bahia* is among the most sensitive of saltwater arthropods (Solomon et al., 2001). In other comparisons with aquatic toxicity data, few of the estimates for this particular sample exceeded freshwater acute toxicities (e.g., Table 4).

TABLE 4. Selected acute toxicity data for permethrin.

Chemical	organism	LC50 - ug L^{-1}	exceedance probability[C]
permethrin	daphnia magna[1,A]	0.075	< 0.01
permethrin	mysidopsis bahia[2,B]	0.033	0.09
permethrin	ceriodaphnia dubia[3,A]	0.55	0.00

1 DPR Ecotoxicity database; **2** USEPA Pesticide Ecotoxicity database; **3** Mokrey and Hoagland, 1991.
A - freshwater organism
B - saltwater organism
C - probability that a randomly selected permethrin dissolved concentration estimate exceeds the listed LC_{50} value.

The tails of the estimated dissolved concentration distribution are the least likely values within the distribution. They are calculated based on the most extreme values of input variables. They may also reflect the generally poorer fit of the sampling distribution to the highest and lowest input data values. Typically the largest deviations of input data from fitted distributions occur near the tails of the distributions. The convention used here is to report the median estimated dissolved concentration (50th percentile) as a measure of central tendency, and the 10th and 90th percentiles as a measure of the probable range of the distribution of estimates. Under these assumptions, the "best" point estimate of permethrin dissolved concentration in this sample is 0.015 ug/L, with a range of most probable values of 0.007 to 0.032 ug/L.

Figure 9. Estimated <u>dissolved phase</u> permethrin concentrations for Wadsworth Canal sample collected 02:30 hours 02/16/03 (Bacey et al., 2003) (a) cumulative probability plot, (b) percentiles, (c) histogram/probability plot.
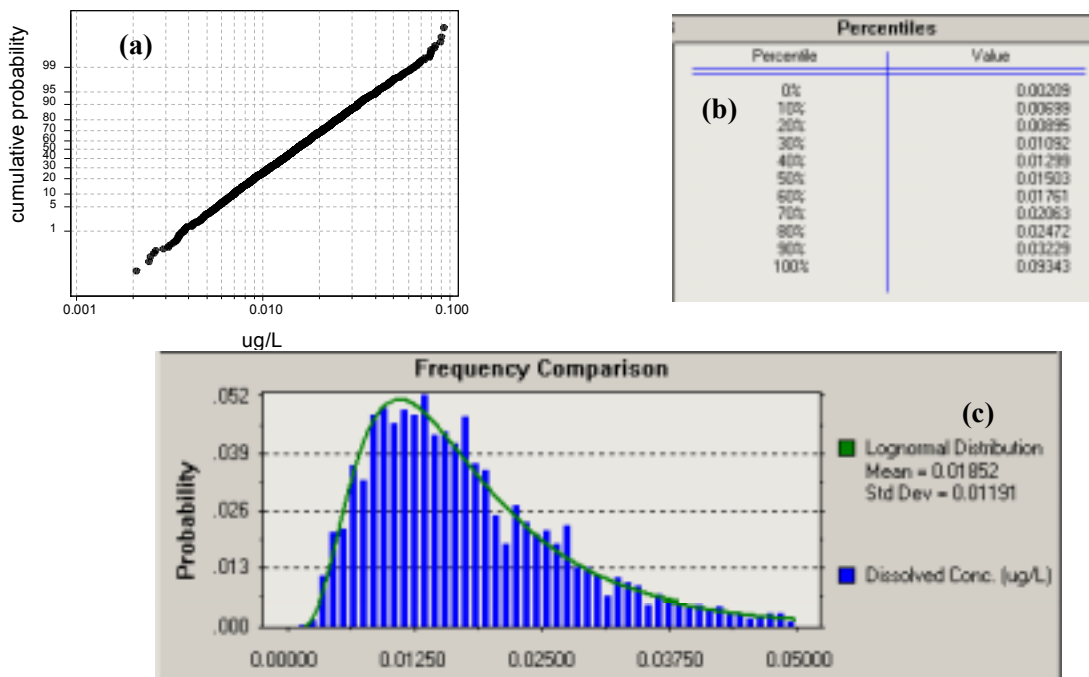
Del Puerto Creek, Stanisluas County, March 15, 2003.

In the second sampling event in the study of Bacey et al. (2003), samples were collected from Del Puerto Creek during a rain runoff event on March 15, 2003. Esfenvalerate was detected in several of the samples along with a number of OPs and herbicides (Table 5). Figure 10 illustrates the effect of SS on C_{Aq}, where the range of estimated C_{Aq} in the first sample is actually lower than that in samples with lower C_T (e.g., trace detections). The median estimated esfenvalerate dissolved concentrations were < 0.02 ug L^{-1}, less than all esfenvalerate freshwater aquatic toxicities that were examined. However, Table 5 also demonstrates the reality of runoff samples in agricultural areas: multiple contaminants are usually present. The approach discussed here does not address multiple toxicants. All of the six samples collected at Del Puerto Creek for toxicity testing displayed significant toxicity to *Ceriodaphnia dubia* in bioassays. While the levels of the OPs diazinon and chlorpyrifos were high enough to

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cause the observed toxicity in nearly all the samples, any potential contribution of esfenvalerate to *C. dubia* acute toxicity is indeterminate. This is partially due to a lack of *C. dubia* LC_{50} data for esfenvalerate, and also due to a lack of knowledge concerning toxicological interactions between the suite of contaminants present in the water.

TABLE 5. Selected monitoring data for Del Puerto Creek, March 15, 2003 (Bacey et al., 2003). Concentrations in ug/L [A]

SAMPLING TIME	9:20	10:20	11:20	12:20	13:20	14:20
Esfenvalerate	0.062	0.093	0.087	0.057	*trace*	*trace*
Chlorpyrifos	**ND**	0.0594	0.233	0.169	0.104	0.115
Diazinon	0.0826	0.096	0.119	0.109	0.111	0.0924
Dimethoate	**ND**	*trace*	*trace*	0.201	0.302	0.25
Ethoprop	*trace*	*trace*	*trace*	**ND**	**ND**	**ND**
Methyl Parathion	*trace*	*trace*	*trace*	*trace*	**ND**	**ND**
Simazine	2.281	1.943	3.787	1.155	0.404	0.243
Diuron	2.819	4.184	4.288	5.516	5.524	5.94
Hexazinone	0.09	0.316	3.564	1.032	0.382	0.288
Norflurazon	1.387	2.021	3.034	3.536	1.51	1.143
Metribuzin	0.142	**ND**	**ND**	**ND**	**ND**	**ND**
ACET[B]	0.112	0.08	0.147	**ND**	**ND**	**ND**
Bromacil	**ND**	0.246	0.463	**ND**	**ND**	**ND**
Sediment (g/L)	**2.709**	**1.476**	**1.217**	**0.728**	**0.558**	**0.452**

[A] A trace detection is a detection where the analyte concentration is between the method detection limit and the reporting limit, where the detection is due to the analyte in the chemist's best professional judgement. The method detection limit for the trace detections above was 0.028 ug/L, and the reporting limit was 0.05 ug/L. **ND** = not detected.

[B] 2-amino-4-chloro-6-ethylamino-*s*-triazine, a a chlorotriazine herbicide degradate

Pyrethroid comparison   Figure 11 illustrates cyfluthrin, esfenvalerate, cypermethrin, cyhalothrin, permethrin, and bifenthrin dissolved concentration estimates under a theoretical scenario of 0.1 ug L^{-1} whole water pyrethroid concentration and SS = 1 g L^{-1}. Estimates for cyfluthrin were substantially higher than the others, while esfenvalerate estimates were the lowest. The largest source of variation in the estimates of dissolved concentration for all pyrethroids was uncertainty/variability in K_{OC}. As determined by the Monte Carlo software (Decisioneering, 2000) the proportion of variance in dissolved concentration accounted for by K_{OC} (as opposed to f_{OC}) ranged from 56 percent (esfenvalerate) to 68 percent (bifenthrin).

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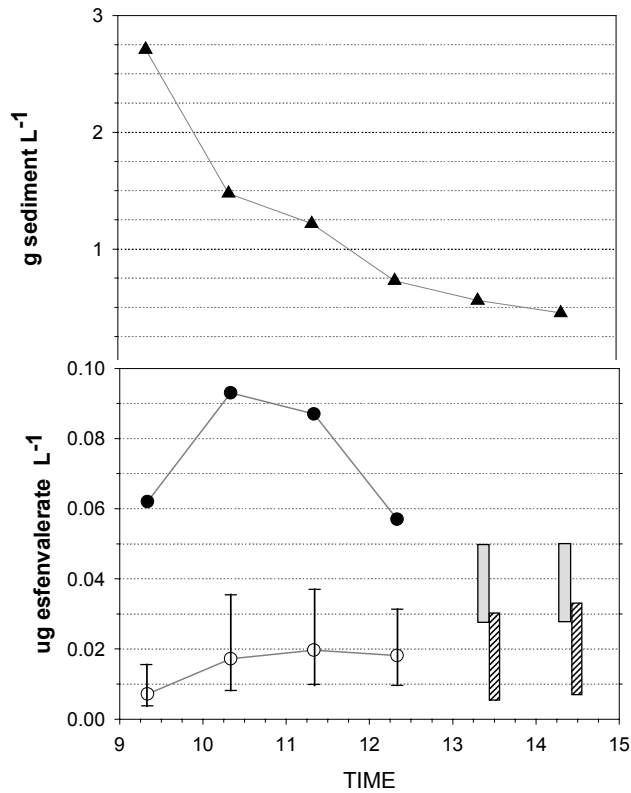
Figure 10. Esfenvalerate dissolved concentration estimates: March 15, 2003, Del Puerto Creek, Stanislaus County (Bacey et al., 2003)

Legend:
▲ suspended sediment g/L
● measured total esfenvalerate ug/L
○ predicted dissolved esfenvalerate ug/L
Error bars are 10th/90th centiles

Range of analytical concentration for a *trace* detection

Range of estimated dissolved concentrations for the *trace* detection [A]
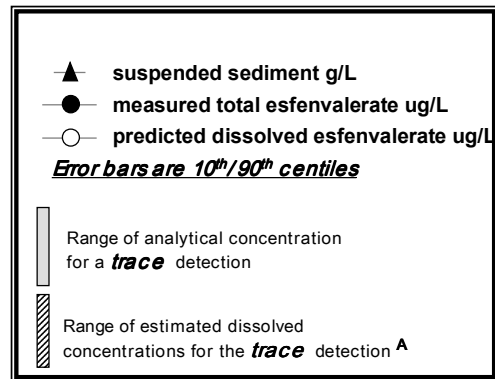
[A] Range for "trace" detection dissolved concentration estimate calculated as 10th percentile of reporting limit (0.028 yg/L) and 90th percentile of detection limit (0.05 ug/L). For definition of trace detection see footnote, Table 5.

Figure 11. Comparison of dissolved concentration estimates for six pyrethroids under hypothetical condition of 1 g L^{-1} suspended sediment and 0.1 ug L^{-1} pyrethroid whole water concentration.

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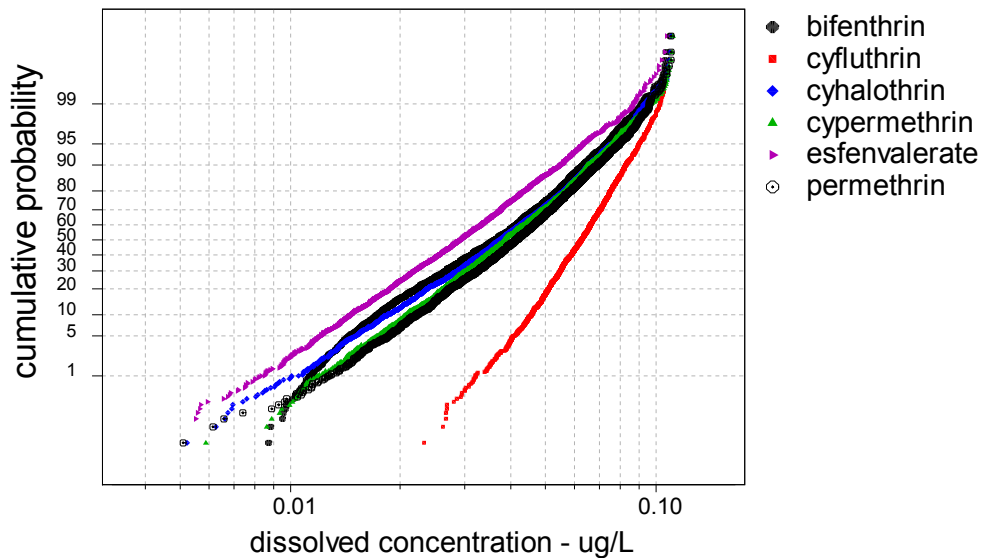
DISCUSSION

The calculated results obtained from the relatively simple method developed here should provide more realistic estimates of potential pyrethroid impacts in California than those based on modeling risk assessments (e.g., Maund et al., 2001) because dissolved concentration estimates here are derived from actual measured pyrethroid and suspended sediment data as opposed to non-measurement-based modeling efforts. Nonetheless, any comparisons between estimated dissolved concentrations from this method and actual acute toxicity data are probably best considered screening level comparisons for several reasons.

1. The calculations assume sorption reversibility, rapid attainment of equilibrium, sorption linearity, and organic carbon-based sorption. While these are common assumptions, and most are supported by available data, the lack of pyrethroid sorption kinetic data is a source of uncertainty in the calculations.

2. The dissolved concentration estimates are for a sample taken at a single point in time. Although "symptoms of poisoning appear rapidly in all pyrethroids", and "uptake and expression of toxicity in aquatic organisms is rapid" (Solomon et al., 2001), exposure duration should formally be considered in quantitative comparisons to 48 hour or 96 hour LC_{50} data. Closely-spaced time series sampling data can mitigate this source of uncertainty when available.

3. The assumption that exposure is only due to the free dissolved fraction may break down in certain cases, e.g. longer term chronic exposures in bed sediments.

4. The simplified method described here neglects the influence of dissolved organic matter (DOC). Although the effect is poorly understood, DOC does affect sorption and bioavailability of hydrophobic chemicals (Suffet et al., 1994), including synthetic pyrethroids (Day, 1991).

These uncertainties should be addressed in future studies designed to statistically compare predicted and measured pyrethroid toxicities in surface water and bed sediment samples.

CONCLUSION

A method was developed for estimating dissolved phase pyrethroid concentrations in whole water samples. The method is generally similar to approaches taken in a recent aquatic risk assessment for the pyrethroids, and to the approach proposed for establishment of sediment quality criteria by USEPA. The calculations here are based on actual measured data as opposed to modeled simulations of runoff concentration. The Monte Carlo approach utilized here yields a distribution of estimated pyrethroid dissolved phase concentrations based on repetitive calculations of organic carbon-based pyrethroid-suspended sediment sorption equilibria. The output distribution of dissolved phase concentration reflects (1) variability in the suspended sediment organic carbon fraction of California Central Valley agriculturally dominated tributaries, and (2) both uncertainty and variability in individual pyrethroid organic carbon-based sorption coefficients K_{OC}. The intended use of the model is to allow screening-level comparisons between dissolved phase pyrethroid concentrations and laboratory toxicity data to determine if samples may be toxic to aquatic life. A validation based on comparison of predicted and actual measured toxicities in sediment-water suspensions is needed.

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APPENDIX I. K_{OC} DATA USED IN MONTE CARLO SIMULATIONS

All KOC data from Laskowski (2002), experimental rating ≥ 5

chem	KOC	logKOC	type
cyfluthrin	69900	4.844	desorption
cyfluthrin	117000	5.068	desorption
cyfluthrin	141000	5.149	desorption
cyfluthrin	161000	5.207	desorption
cyfluthrin	73500	4.866	sorption
cyfluthrin	118000	5.072	sorption
cyfluthrin	180000	5.255	sorption
cyfluthrin	124000	5.093	sorption
cypermethrin	480000	5.681	desorption
cypermethrin	231000	5.364	desorption
cypermethrin	298000	5.474	desorption
cypermethrin	239000	5.378	desorption
cypermethrin	569000	5.755	desorption
cypermethrin	242000	5.384	desorption
cypermethrin	278000	5.444	desorption
cypermethrin	639000	5.806	desorption
cypermethrin	80300	4.905	desorption
cypermethrin	306000	5.486	desorption
cypermethrin	177000	5.248	desorption
cypermethrin	638000	5.805	desorption
cypermethrin	526000	5.721	sorption
cypermethrin	180000	5.255	sorption
cypermethrin	223000	5.348	sorption
cypermethrin	149000	5.173	sorption
cypermethrin	518000	5.714	sorption
cypermethrin	211000	5.324	sorption
cypermethrin	498000	5.697	sorption
cypermethrin	223000	5.348	sorption
cypermethrin	232000	5.365	sorption
cypermethrin	295000	5.470	sorption
cypermethrin	147000	5.167	sorption
cypermethrin	466000	5.668	sorption
λ – cyhalothrin	140000	5.146	desorption
λ – cyhalothrin	299000	5.476	desorption
λ – cyhalothrin	620000	5.792	desorption
λ – cyhalothrin	121000	5.083	desorption
λ – cyhalothrin	425000	5.628	desorption
λ – cyhalothrin	247000	5.393	desorption
λ – cyhalothrin	186000	5.270	desorption

chem	KOC	logKOC	type
λ – cyhalothrin	593000	5.773	desorption
λ – cyhalothrin	423000	5.626	desorption
λ – cyhalothrin	390000	5.591	desorption
λ – cyhalothrin	374000	5.573	desorption
λ – cyhalothrin	370000	5.568	desorption
λ – cyhalothrin	602000	5.780	desorption
λ – cyhalothrin	148000	5.170	desorption
λ – cyhalothrin	490000	5.690	desorption
λ – cyhalothrin	341000	5.533	desorption
λ – cyhalothrin	98800	4.995	desorption
λ – cyhalothrin	417000	5.620	desorption
λ – cyhalothrin	253000	5.403	desorption
λ – cyhalothrin	226000	5.354	desorption
λ – cyhalothrin	184000	5.265	desorption
λ – cyhalothrin	684000	5.835	desorption
λ – cyhalothrin	271000	5.433	desorption
λ – cyhalothrin	1100000	6.041	desorption
λ – cyhalothrin	690000	5.839	desorption
λ – cyhalothrin	181000	5.258	desorption
λ – cyhalothrin	403000	5.605	desorption
λ – cyhalothrin	348000	5.542	desorption
λ – cyhalothrin	253000	5.403	desorption
λ – cyhalothrin	76400	4.883	desorption
λ – cyhalothrin	1190000	6.076	desorption
λ – cyhalothrin	151000	5.179	desorption
λ – cyhalothrin	232000	5.365	desorption
λ – cyhalothrin	442000	5.645	desorption
λ – cyhalothrin	550000	5.740	desorption
λ – cyhalothrin	350000	5.544	desorption
λ – cyhalothrin	238000	5.377	desorption
λ – cyhalothrin	477000	5.679	desorption
λ – cyhalothrin	380000	5.580	desorption
λ – cyhalothrin	123000	5.090	desorption
λ – cyhalothrin	383000	5.583	desorption
λ – cyhalothrin	199000	5.299	desorption
λ – cyhalothrin	1280000	6.107	desorption
λ – cyhalothrin	551000	5.741	desorption
λ – cyhalothrin	268000	5.428	desorption
λ – cyhalothrin	322000	5.508	desorption
λ – cyhalothrin	203000	5.307	desorption
λ – cyhalothrin	80700	4.907	desorption

chem	KOC	logKOC	type
λ – cyhalothrin	344000	5.537	desorption
λ – cyhalothrin	579000	5.763	desorption
λ – cyhalothrin	224000	5.350	sorption
λ – cyhalothrin	386000	5.587	sorption
λ – cyhalothrin	457000	5.660	sorption
λ – cyhalothrin	83800	4.923	sorption
λ – cyhalothrin	243000	5.386	sorption
λ – cyhalothrin	231000	5.364	sorption
λ – cyhalothrin	301000	5.479	sorption
λ – cyhalothrin	307000	5.487	sorption
λ – cyhalothrin	640000	5.806	sorption
λ – cyhalothrin	230000	5.362	sorption
λ – cyhalothrin	328000	5.516	sorption
λ – cyhalothrin	619000	5.792	sorption
λ – cyhalothrin	360000	5.556	sorption
λ – cyhalothrin	734000	5.866	sorption
λ – cyhalothrin	164000	5.215	sorption
λ – cyhalothrin	336000	5.526	sorption
λ – cyhalothrin	242000	5.384	sorption
λ – cyhalothrin	142000	5.152	sorption
λ – cyhalothrin	205000	5.312	sorption
λ – cyhalothrin	289000	5.461	sorption
λ – cyhalothrin	166000	5.220	sorption
λ – cyhalothrin	391000	5.592	sorption
λ – cyhalothrin	199000	5.299	sorption
λ – cyhalothrin	797000	5.901	sorption
λ – cyhalothrin	358000	5.554	sorption
λ – cyhalothrin	394000	5.595	sorption
λ – cyhalothrin	325000	5.512	sorption
λ – cyhalothrin	539000	5.732	sorption
λ – cyhalothrin	307000	5.487	sorption
λ – cyhalothrin	161000	5.207	sorption
λ – cyhalothrin	255000	5.407	sorption
λ – cyhalothrin	312000	5.494	sorption
λ – cyhalothrin	234000	5.369	sorption
λ – cyhalothrin	555000	5.744	sorption
λ – cyhalothrin	158000	5.199	sorption
λ – cyhalothrin	836000	5.922	sorption
λ – cyhalothrin	69900	4.844	sorption
λ – cyhalothrin	257000	5.410	sorption
λ – cyhalothrin	302000	5.480	sorption

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chem	KOC	logKOC	type
λ – cyhalothrin	294000	5.468	sorption
λ – cyhalothrin	210000	5.322	sorption
λ – cyhalothrin	609000	5.785	sorption
λ – cyhalothrin	398000	5.600	sorption
λ – cyhalothrin	566000	5.753	sorption
λ – cyhalothrin	216000	5.334	sorption
λ – cyhalothrin	95100	4.978	sorption
λ – cyhalothrin	133000	5.124	sorption
λ – cyhalothrin	282000	5.450	sorption
λ – cyhalothrin	425000	5.628	sorption
λ – cyhalothrin	289000	5.461	sorption
permethrin	590000	5.771	desorption
permethrin	120000	5.079	desorption
permethrin	120000	5.079	desorption
permethrin	620000	5.792	desorption
permethrin	230000	5.362	desorption
permethrin	360000	5.556	desorption
permethrin	350000	5.544	desorption
permethrin	240000	5.380	desorption
permethrin	230000	5.362	sorption
permethrin	200000	5.301	sorption
permethrin	260000	5.415	sorption
permethrin	280000	5.447	sorption
permethrin	550000	5.740	sorption
permethrin	520000	5.716	sorption
permethrin	480000	5.681	sorption
permethrin	250000	5.398	sorption
permethrin	130000	5.114	sorption
permethrin	170000	5.230	sorption
permethrin	140000	5.146	sorption
permethrin	200000	5.301	sorption
permethrin	520000	5.716	sorption
permethrin	270000	5.431	sorption
permethrin	110000	5.041	sorption
permethrin	120000	5.079	sorption

APPENDIX II. SUSPENDED SEDIMENT DATA FOR AGRICULTURALLY-DOMINATED TRIBUTARIES. Source: USGS National Water Quality Assessment Studies (available on-line http://ca.water.usgs.gov/sanj_nawqa/)

site	Sample date	SS - Suspended Sediment (mg/L)	POC Particulate Organic Carbon (mg/L)	fOC - fraction organic carbon (=POC/SS)
Colusa Basin Drain	19971112	60	0.7	0.012
Colusa Basin Drain	19961107	60	1.5	0.025
Colusa Basin Drain	19970617	68	1.3	0.019
Colusa Basin Drain	19971030	75	1.1	0.015
Colusa Basin Drain	19961018	75	1.9	0.025
Colusa Basin Drain	19961203	84	0.9	0.011
Colusa Basin Drain	19960723	95	2.7	0.028
Colusa Basin Drain	19960423	101	1.2	0.012
Colusa Basin Drain	19980311	109	1	0.009
Colusa Basin Drain	19960827	109	1.1	0.010
Colusa Basin Drain	19970728	116	0.9	0.008
Colusa Basin Drain	19980415	119	1.4	0.012
Colusa Basin Drain	19970409	121	1.5	0.012
Colusa Basin Drain	19971217	125	1.1	0.009
Colusa Basin Drain	19970710	135	1.3	0.010
Colusa Basin Drain	19960909	136	1	0.007
Colusa Basin Drain	19970114	137	1.4	0.010
Colusa Basin Drain	19970424	142	1.8	0.013
Colusa Basin Drain	19960614	146	0.8	0.005
Colusa Basin Drain	19970918	148	1	0.007
Colusa Basin Drain	19970606	154	1.2	0.008
Colusa Basin Drain	19980121	156	1	0.006
Colusa Basin Drain	19970218	167	2.1	0.013
Colusa Basin Drain	19960522	170	1.3	0.008
Colusa Basin Drain	19980226	199	1.5	0.008
Colusa Basin Drain	19960306	202	1.3	0.006
Colusa Basin Drain	19970826	226	1.8	0.008
Colusa Basin Drain	19960207	373	1.4	0.004
Mud Slough	19931028	23	0.8	0.035
Mud Slough	19931228	25	0.6	0.024
Mud Slough	19931118	25	0.8	0.032
Mud Slough	19940823	40	0.6	0.015

site	Sample date	SS - Suspended Sediment (mg/L)	POC Particulate Organic Carbon (mg/L)	fOC - fraction organic carbon (=POC/SS)
Mud Slough	19940701	40	0.8	0.020
Mud Slough	19940525	40	1	0.025
Mud Slough	19940726	40	1	0.025
Mud Slough	19940428	40	1.6	0.040
Mud Slough	19940301	40	1.9	0.048
Mud Slough	19940324	40	2.1	0.053
Mud Slough	19940203	40	2.5	0.063
Mud Slough	19930330	41	2.2	0.054
Mud Slough	19930429	43	1.6	0.037
Mud Slough	19930727	45	1.3	0.029
Mud Slough	19930526	64	2.7	0.042
Mud Slough	19940928	84	1.4	0.017
Mud Slough	19930622	111	4.5	0.041
Mud Slough	19930930	160	1.8	0.011
Orestimba Creek (Riv rd)	19941229	6	0.3	0.050
Orestimba Creek (Riv rd)	19930129	17	0.8	0.047
Orestimba Creek (Riv rd)	19930322	18	0.9	0.050
Orestimba Creek (Riv rd)	19931229	18	1	0.056
Orestimba Creek (Riv rd)	19930216	20	0.7	0.035
Orestimba Creek (Riv rd)	19930406	24	0.8	0.033
Orestimba Creek (Riv rd)	19921215	26	0.5	0.019
Orestimba Creek (Riv rd)	19930126	31	0.7	0.023
Orestimba Creek (Riv rd)	19920527	33	0.6	0.018
Orestimba Creek (Riv rd)	19930305	35	1	0.029
Orestimba Creek (Riv rd)	19950302	45	5	0.111
Orestimba Creek (Riv rd)	19930309	46	0.7	0.015
Orestimba Creek (Riv rd)	19940301	47	0.7	0.015
Orestimba Creek (Riv rd)	19940202	47	1	0.021
Orestimba Creek (Riv rd)	19940927	47	1.2	0.026
Orestimba Creek (Riv rd)	19940426	47	1.6	0.034
Orestimba Creek (Riv rd)	19940824	47	1.7	0.036
Orestimba Creek (Riv rd)	19940630	47	2.9	0.062
Orestimba Creek (Riv rd)	19940726	47	6.6	0.140
Orestimba Creek (Riv rd)	19941130	47	10	0.213
Orestimba Creek (Riv rd)	19930315	48	1.1	0.023
Orestimba Creek (Riv rd)	19950321	49	0.4	0.008
Orestimba Creek (Riv rd)	19931027	50	1.1	0.022
Orestimba Creek (Riv rd)	19930614	51	1	0.020

site	Sample date	SS – Suspended Sediment (mg/L)	POC Particulate Organic Carbon (mg/L)	fOC – fraction organic carbon (=POC/SS)
Orestimba Creek (Riv rd)	19920522	54	0.8	0.015
Orestimba Creek (Riv rd)	19931117	59	0.6	0.010
Orestimba Creek (Riv rd)	19930414	61	0.4	0.007
Orestimba Creek (Riv rd)	19930312	61	1.5	0.025
Orestimba Creek (Riv rd)	19930211	62	1.1	0.018
Orestimba Creek (Riv rd)	19930122	68	3	0.044
Orestimba Creek (Riv rd)	19970204	71	1.2	0.017
Orestimba Creek (Riv rd)	19920610	72	0.4	0.006
Orestimba Creek (Riv rd)	19970304	74	1.1	0.015
Orestimba Creek (Riv rd)	19920518	78	1	0.013
Orestimba Creek (Riv rd)	19970904	86	0.8	0.009
Orestimba Creek (Riv rd)	19930401	97	0.7	0.007
Orestimba Creek (Riv rd)	19930929	102	1.8	0.018
Orestimba Creek (Riv rd)	19930329	103	1.2	0.012
Orestimba Creek (Riv rd)	19970827	115	0.7	0.006
Orestimba Creek (Riv rd)	19920520	120	1.4	0.012
Orestimba Creek (Riv rd)	19930601	123	1.2	0.010
Orestimba Creek (Riv rd)	19930427	125	1.6	0.013
Orestimba Creek (Riv rd)	19970407	138	0.8	0.006
Orestimba Creek (Riv rd)	19920515	140	1.9	0.014
Orestimba Creek (Riv rd)	19930318	141	1.5	0.011
Orestimba Creek (Riv rd)	19930504	148	1.7	0.011
Orestimba Creek (Riv rd)	19970610	156	1.1	0.007
Orestimba Creek (Riv rd)	19930420	164	1.7	0.010
Orestimba Creek (Riv rd)	19920501	191	1.2	0.006
Orestimba Creek (Riv rd)	19930521	202	2.3	0.011
Orestimba Creek (Riv rd)	19920508	204	2.2	0.011
Orestimba Creek (Riv rd)	19920429	214	1	0.005
Orestimba Creek (Riv rd)	19920504	216	1.6	0.007
Orestimba Creek (Riv rd)	19930907	226	2	0.009
Orestimba Creek (Riv rd)	19920513	229	2.4	0.010
Orestimba Creek (Riv rd)	19920724	235	0.6	0.003
Orestimba Creek (Riv rd)	19920506	236	2.4	0.010
Orestimba Creek (Riv rd)	19920803	255	1.9	0.007
Orestimba Creek (Riv rd)	19920715	264	2.5	0.009
Orestimba Creek (Riv rd)	19920812	265	2.5	0.009
Orestimba Creek (Riv rd)	19920511	272	2.1	0.008
Orestimba Creek (Riv rd)	19920814	310	1	0.003

site	Sample date	SS – Suspended Sediment (mg/L)	POC Particulate Organic Carbon (mg/L)	fOC – fraction organic carbon (=POC/SS)
Orestimba Creek (Riv rd)	19920819	318	2.9	0.009
Orestimba Creek (Riv rd)	19920714	321	3.6	0.011
Orestimba Creek (Riv rd)	19920708	323	3	0.009
Orestimba Creek (Riv rd)	19920427	330	2.8	0.008
Orestimba Creek (Riv rd)	19920424	333	2.7	0.008
Orestimba Creek (Riv rd)	19930715	338	2.6	0.008
Orestimba Creek (Riv rd)	19970630	345	0.3	0.001
Orestimba Creek (Riv rd)	19920731	353	1.7	0.005
Orestimba Creek (Riv rd)	19920617	359	1.2	0.003
Orestimba Creek (Riv rd)	19920729	393	3.9	0.010
Orestimba Creek (Riv rd)	19920801	396	2.9	0.007
Orestimba Creek (Riv rd)	19970730	424	3.5	0.008
Orestimba Creek (Riv rd)	19970708	426	2.9	0.007
Orestimba Creek (Riv rd)	19920624	441	3.3	0.007
Orestimba Creek (Riv rd)	19920721	477	2.9	0.006
Orestimba Creek (Riv rd)	19930825	537	3.4	0.006
Orestimba Creek (Riv rd)	19920807	556	0.3	0.001
Orestimba Creek (Riv rd)	19920702	584	1.6	0.003
Orestimba Creek (Riv rd)	19920717	594	3.7	0.006
Orestimba Creek (Riv rd)	19920826	615	6.5	0.011
Orestimba Creek (Riv rd)	19920706	704	4.5	0.006
Orestimba Creek (Riv rd)	19920810	727	5.4	0.007
Orestimba Creek (Riv rd)	19930803	755	4.4	0.006
Orestimba Creek (Riv rd)	19920722	759	3.9	0.005
Orestimba Creek (Riv rd)	19920727	1050	6	0.006
Orestimba Creek (Riv rd)	19920805	1190	1.4	0.001
Orestimba Creek (Riv rd)	19950124	1300	6.8	0.005
Orestimba Creek (Riv rd)	19930326	1660	13	0.008
Sacramento Slough	19980128	30	0.4	0.013
Sacramento Slough	19971216	37	0.7	0.019
Sacramento Slough	19960311	43	0.5	0.012
Sacramento Slough	19971125	44	0.6	0.014
Sacramento Slough	19960212	47	9.4	0.200
Sacramento Slough	19961205	53	1	0.019
Sacramento Slough	19960523	56	0.3	0.005
Sacramento Slough	19961017	56	0.9	0.016
Sacramento Slough	19970924	65	1.2	0.018
Sacramento Slough	19970813	67	0.9	0.013

site	Sample date	SS – Suspended Sediment (mg/L)	POC Particulate Organic Carbon (mg/L)	fOC – fraction organic carbon (=POC/SS)
Sacramento Slough	19960422	67	0.9	0.013
Sacramento Slough	19961107	68	1	0.015
Sacramento Slough	19960910	69	1.6	0.023
Sacramento Slough	19960826	73	0.6	0.008
Sacramento Slough	19971029	77	0.9	0.012
Sacramento Slough	19960722	79	1.2	0.015
Sacramento Slough	19970619	83	1.1	0.013
Sacramento Slough	19970724	93	1	0.011
Sacramento Slough	19960613	108	2.1	0.019
Sacramento Slough	19980225	134	0.6	0.004
Sacramento Slough	19970306	148	1.5	0.010
Sacramento Slough	19980325	182	0.9	0.005
Salt Slough	19930401	32	0.8	0.025
Salt Slough	19930326	40	1.3	0.033
Salt Slough	19931228	44	1.8	0.041
Salt Slough	19930406	56	1.5	0.027
Salt Slough	19940428	70	0.9	0.013
Salt Slough	19940324	70	1.1	0.016
Salt Slough	19940301	70	1.2	0.017
Salt Slough	19940203	70	1.5	0.021
Salt Slough	19940525	70	1.6	0.023
Salt Slough	19940726	70	2.2	0.031
Salt Slough	19940701	70	2.8	0.040
Salt Slough	19940823	70	2.8	0.040
Salt Slough	19931117	72	0.8	0.011
Salt Slough	19930414	74	1.5	0.020
Salt Slough	19930318	84	1.8	0.021
Salt Slough	19930420	85	2	0.024
Salt Slough	19930305	89	1.6	0.018
Salt Slough	19930129	102	2	0.020
Salt Slough	19930427	103	2.3	0.022
Salt Slough	19930504	106	1.8	0.017
Salt Slough	19940928	119	1.4	0.012
Salt Slough	19931027	131	1.8	0.014
Salt Slough	19930312	146	2.5	0.017
Salt Slough	19930929	172	1.7	0.010
Salt Slough	19930803	174	1.5	0.009
Salt Slough	19930825	186	0.8	0.004

site	Sample date	SS – Suspended Sediment (mg/L)	POC Particulate Organic Carbon (mg/L)	fOC – fraction organic carbon (=POC/SS)
Salt Slough	19930204	204	0.8	0.004
Salt Slough	19930907	206	1.8	0.009
Salt Slough	19930521	207	1.9	0.009
Salt Slough	19930211	208	2.5	0.012
Salt Slough	19930601	208	2.8	0.013
Salt Slough	19930629	217	1.9	0.009
Salt Slough	19930715	222	1.9	0.009
Spanish Grant Drain	19941229	26	0.7	0.027
Spanish Grant Drain	19931229	30	0.2	0.007
Spanish Grant Drain	19940302	60	0.6	0.010
Spanish Grant Drain	19941027	60	0.9	0.015
Spanish Grant Drain	19940202	60	1.4	0.023
Spanish Grant Drain	19940527	60	1.6	0.027
Spanish Grant Drain	19940429	60	1.6	0.027
Spanish Grant Drain	19940929	60	2.7	0.045
Spanish Grant Drain	19940630	60	3.9	0.065
Spanish Grant Drain	19940824	60	5.8	0.097
Spanish Grant Drain	19941130	60	5.8	0.097
Spanish Grant Drain	19940727	60	5.9	0.098
Spanish Grant Drain	19930330	75	0.9	0.012
Spanish Grant Drain	19931028	122	1.4	0.011
Spanish Grant Drain	19930526	197	2	0.010
Spanish Grant Drain	19930727	229	2	0.009
Spanish Grant Drain	19930429	242	2.6	0.011
Spanish Grant Drain	19930622	242	3	0.012
Spanish Grant Drain	19930930	299	1.6	0.005