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Ecological Risks of Diazinon from Agricultural Use in the Sacramento–San Joaquin River Basins, California

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A probabilistic risk assessment was conducted to evaluate the likelihood and ecological significance of potential toxic effects of diazinon in the Sacramento–San Joaquin system. Diazinon, an organophosphorus insecticide, is used in the Sacramento–San Joaquin River Basin as a dormant spray on almonds and other tree crops, as well as for other agricultural and urban applications. Diazinon and other pesticides have been detected in the Sacramento and San Joaquin Rivers and their tributaries. Diazinon exposure was characterized based on monitoring programs conducted in 1991–94. Diazinon effects were characterized using laboratory toxicity data for 63 species, supplemented by results from field mesocosm and microcosm studies. The assessment addressed the possibility that reductions in invertebrate populations could lead to impacts on species of fish that feed on those invertebrates. The risk assessment concluded that fish in these rivers are not at risk from the direct effects of diazinon in the water. Invertebrates are at greater risk, especially in agriculturally dominated streams and drainage channels during January and February. Cladocerans—including *Daphnia magna* and *Ceriodaphnia dubia*, two common bioassay species—are especially sensitive to diazinon and other organophosphates and are likely to be subject to acute toxic effects in some locations at some times. Any ecological damage that may occur, however, is brief and limited to cladocerans. None of the fish species of concern depend on cladocerans as critical components of their diet. Invertebrates that are not affected by observed concentrations of diazinon (copepods, mysids, amphipods, rotifers, and insects) are preferred foods for fish in the Sacramento–San Joaquin system.

KEY WORDS: Diazinon; ecological risk assessment; San Joaquin; fish; aquatic invertebrates

1. INTRODUCTION

1.1. Background

Diazinon is a broad-spectrum contact organophosphorus insecticide widely used on nuts, stone fruits, vegetables, and other crops. Diazinon has been detected in many California surface waters, presumably originating from agricultural and urban stormwater runoff.[(1)] Water samples from some sites have been found toxic to *Ceriodaphnia dubia*, a standard test species for toxicity screening of ambient water and effluents.[(2,3)] These findings, coupled with observed declines in many populations of fish and invertebrates in the region,[(4–7)] have raised concerns about potential impacts of diazinon on aquatic resources in the California central valley.

To address these concerns, Ciba Crop Protection (now Novartis Crop Protection, Inc.) established a multidisciplinary expert panel to conduct a comprehensive aquatic ecological risk assessment of diazi-

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non in the Sacramento and San Joaquin Rivers and their tributaries. This article presents the results of the ecological risk assessment.

This risk assessment was intended only to evaluate the potential effects of diazinon in the Sacramento–San Joaquin River system, not to determine the causes of observed declines in populations of native fish and invertebrates. Water development activities such as dredging, diking, filling of wetlands, and diversion of freshwater flows have altered fish habitat and adversely impacted fish populations.[8] Other chemical contaminants such as chlorpyrifos, carbofuran, ethyl parathion, methidathion, malathion, simazine, copper, lead, and mercury may contribute to environmental impacts in this area.[2,3] Introduction of exotic species has also been suggested as a partial cause of the decline of aquatic resources.[2,8–12] Though other stressors are undoubtedly contributing to ecological impacts in these river systems, this assessment considers only the potential effects of diazinon acting alone.

Because of the many factors potentially affecting the populations in the Sacramento–San Joaquin, it is not possible to determine the impact of diazinon through direct observation and monitoring. The approach taken in this risk assessment, therefore, was to estimate ecologically safe concentrations of diazinon, and then to determine when, where, and how frequently these exposure levels might be exceeded in the Sacramento–San Joaquin River system. From this information, the potential ecological impacts of diazinon in different water bodies can be estimated, and the relevance of the effects to the valued uses of those water bodies can be addressed.

1.2. Conceptual Model

The major use of diazinon in the Sacramento–San Joaquin watershed is for orchard spraying. Spraying of orchards during the dormant season (winter) may lead to transport of diazinon into surface waters through runoff and drift. The highest diazinon concentrations would be expected in small streams dominated by orchard runoff. Concentrations would be lower in the larger tributaries and the mainstem river due to dilution. Because diazinon input would occur mainly during spraying and runoff events and because it dissipates fairly rapidly in surface waters (discussed below), diazinon would be expected to be present in intermittent pulses, rather than continuously. Defining the spatial and temporal distribution of diazinon in the Sacramento and San Joaquin Rivers and their tributaries was a major objective of this risk assessment.

Aquatic organisms vary in their sensitivity to diazinon. Aquatic plants are generally unaffected. Some invertebrate groups are extremely sensitive, while other invertebrates and most fish are relatively tolerant. Diazinon exposure might reduce or eliminate some invertebrate populations, and possibly cause direct toxic effects on fish.

This risk assessment focused on nine fish species of concern in the Sacramento–San Joaquin River system (Table I). The seasonal timing of major diazinon use in agriculture (January and February) and spawning periods of fish species (occurrence of sensitive life stages) are illustrated in Fig. 1. Of the nine fish species listed, there is overlap between the winter period of diazinon use and presence of early life stages for six of the species. Important prey organisms for these fish species include Copepoda (*Eurytemora*, *Cyclops*, and *Sinocalanus*), mysids (*Neomysis*), amphipods (*Corophium*), and Cladocera (*Daphnia*, *Bosmina*, and *Diaphonosoma*). If diazinon exposures reduce prey abundance at times when specific food items are critical to the growth and survival of fish early life stages, fish populations may be affected.

Based on the conceptual model of potential exposure and effects, the following questions were to be addressed in the risk assessment:

1. What is the likelihood that diazinon concentrations in the Sacramento and San Joaquin Rivers and their tributaries are high enough to cause mortality in any of the nine key fish species? (Assessment endpoint: mortality of key fish species. Measure of effect: survival of test organisms in acute toxicity tests with fish.)
2. What is the likelihood that diazinon concentrations are high enough and persist long enough to cause chronic effects on survival, growth, or reproduction of any of the nine key fish species? (Assessment endpoint: sustained populations of key fish species. Measure of effect: survival, growth, and reproduction of test organisms in chronic toxicity tests with fish.)
3. What is the likelihood that diazinon is causing reductions in invertebrate populations? (Assessment endpoint: sustained populations of invertebrate populations, especially those that are critical in the diet of the key fish species. Measure of effect: survival, growth, and reproduction of test organisms in acute and chronic toxicity tests with invertebrates.)

Table I. Food Organisms, Trophic Guild, and Status of Fish Populations in the Sacramento–San Joaquin River Systems

Species	Dominant food organisms (for early life stages)	Trophic guild	Population status
Delta smelt (*Hypomesus transpacificus*)	*Eurytemora affinis*, *Cyclops* sp., harpacticoid copepods, cladocerans, amphipods, insect larvae	Pelagic planktivore	Federal and state threatened protection
Longfin smelt (*Spirinchus thaleichthys*)	*Neomysis mercedis*, cladocerans	Pelagic planktivore	State species of special concern
Sacramento splittail (*Pogonichthys macrolepidotus*)	Benthic invertebrates, aquatic insect larvae, amphipods, *N. mercedis*, oligochaetes, mollusks, copepods, cladocerans	Benthic forager	Federally proposed threatened; state species of special concern
Chinook salmon (*Oncorhynchus tshawytscha*)	Aquatic and terrestrial insects, crustaceans, *N. mercedis*, amphipods, larval fishes	Opportunistic drift predator in river, pelagic predator in delta	Winter-run salmon are afforded federal and state endangered protection
Striped bass (*Morone saxatilis*)	*N. mercedis*, amphipods, copepods, cladocerans, other crustaceans, larval and juvenile fishes	Pelagic planktivore (larvae), pelagic predator (juveniles)	Population in decline, state-regulated sport fishery
White sturgeon (*Acipenser transmontanus*)	Amphipods, *N. mercedis*, other crustaceans, mollusks, *Crangon* sp.	Benthic forager	Population in decline, state-regulated sport fishery
Green sturgeon (*Acipenser medirostris*)	Amphipods, *N. mercedis*, other crustaceans, mollusks, *Crangon* sp.	Benthic forager	Population historically low, state-regulated sport fishery
American shad (*Alosa sapidissima*)	Copepods, cladocerans, *N. mercedis*, amphipods	Pelagic planktivore	Population variable, state-regulated sport fishery
Steelhead (*Oncorhynchus mykiss*)	Aquatic and terrestrial insects, crustaceans, *N. mercedis*, amphipods, larval fishes	Opportunistic drift predator in river, pelagic predator in delta	Population in decline, state-regulated sport fishery

Note: From Novartis Crop Protection.[94]

If acute or chronic toxic effects of diazinon on fish or invertebrates are possible, the following questions would apply:

4. Where and when are the effects likely to be greatest?
5. Which species are at greatest risk?
6. If some invertebrate species are likely to be affected, are these species critical food organisms for fish, such that invertebrate population reductions will affect fish growth and survival?

2. EXPOSURE ANALYSIS

2.1. Diazinon Use in the California Central Valley

In California, diazinon is primarily applied in the winter as dormant spray on almonds and stone fruits to control pests such as peach tree borer and San Jose scale. Dormant sprays are typically applied between rainfall events in December, January, and February. Farmers apply insecticides when the trees are dormant to kill as many of the overwintering populations of insects and scale as possible, preventing earlier and larger pest infestations on the crop. Foliar cover sprays of diazinon begin in mid-April and continue as needed through August, by which time most crops are harvested.

Approximately 300,000 kg (700,000 lb) of diazinon were applied in the California Central Valley each year during 1992–94. Tree and vine use and almond use together constituted 70 to 80% of total diazinon use. Vegetable and row crops and use around structures accounted for most of the rest, with less than 10% of the total application going to grains, landscaping, and alfalfa and forage.

2.2. Chemical/Physical Properties and Environmental Behavior

The key physical and chemical properties of diazinon are summarized in Table II, and their implications are discussed below.

2.2.1. *Solubility and Vapor Pressure*

Diazinon is moderately soluble in water and has a low vapor pressure, implying a relatively low tendency to volatilize from surface water to the atmosphere. The estimated half-life for evaporation

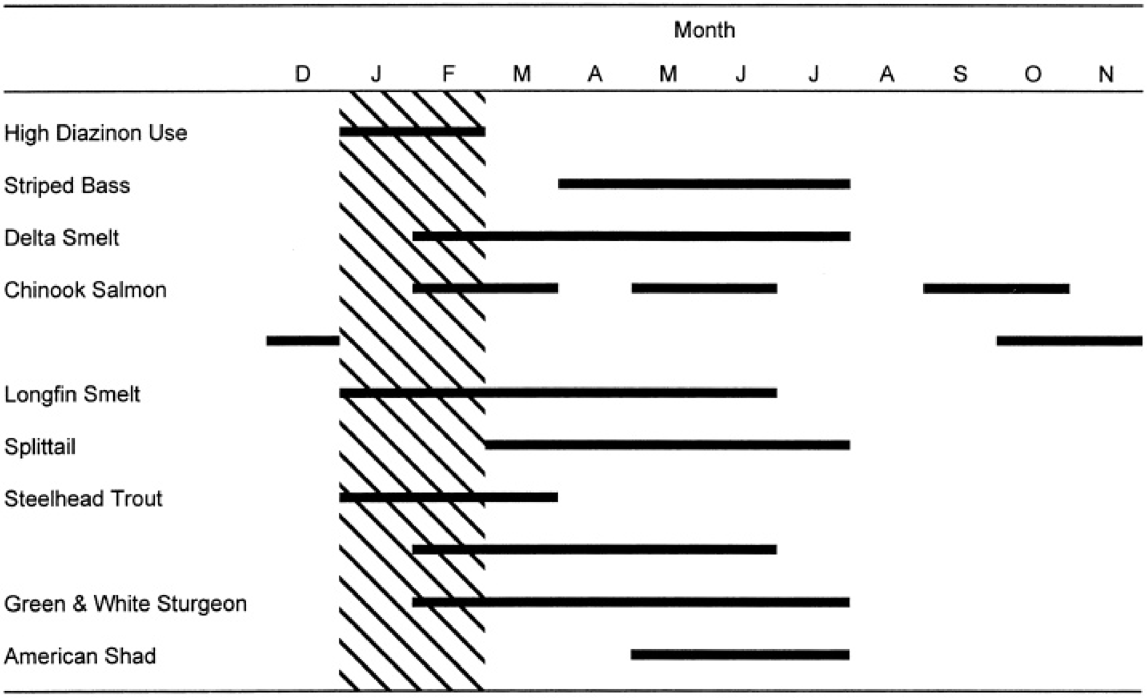


Fig. 1. Temporal distribution of high diazinon use and spawning periods (presence of early life stages) of fish stocks. The four spawning runs (fall, late fall, winter, and spring) of chinook salmon are considered separate species. From Novartis Crop Protection.[94]

from a river 1 m deep flowing at 1 m/s with a wind velocity of 3 m/s is 46 days.[13] Movement of diazinon from treated fields to aquatic systems via volatilization is not an important transport mechanism. Based on flux rates reported by Majewski, Glotfelty, U, and Seiber,[14] only 0.1% of the diazinon applied volatilized from treated soil over 4 days, compared with 0.4% for chlorpyrifos, 11% for lindane, and 14% for nitrapyrin.

Diazinon has been detected in rainfall in the Sacramento–San Joaquin basin (Lisa Ross, California Department of Pesticide Regulation, personal communication, 1997). Rainfall collected in the winter of 1992–93 in the Sacramento–San Joaquin basin contained up to 1,900 ng/L of diazinon. Diazoxon, the activation product of diazinon, was also detected at concentrations up to 220 ng/L. The source of diazinon and diazoxon in rainfall is presumed to be droplets from dormant spray applications. The significance of rainfall as a source of surface water contamination would depend on the volume and surface area of the water body. Depositional inputs would be most important in ephemeral streams: channels containing water only during or shortly after rainstorms.

2.2.2. *Sorption and Partitioning*

With an organic carbon partition coefficient (K_{oc}) of approximately 10^3, diazinon binds only moderately to soil and sediment, because it does not bind strongly to sediment, this risk assessment focused on diazinon in the water column. (Binding to soil reduces the potential for diazinon to wash off treated fields in runoff and to leach through the soil column into groundwater.)

2.2.3. *Photolytic Degradation*

Photolytic decomposition of diazinon to O,O-diethyl-O[2-(2′-propyl)-4-methyl-6-pyrimidinyl]phosphorothioate (hydroxydiazinon) can occur via UV (ultraviolet) irradiation. The photolysis half-life in natural light has been measured as 24.6 days in water[15] and 2.5 days in California sandy loam.[16] Reaction of vapor-phase diazinon with photochemically generated hydroxyl radicals results in an estimated half-life in air of less than 5 hr.[17]

2.2.4. *Hydrolytic Degradation*

In water, diazinon is hydrolyzed following first-order kinetics to form 2-isopropyl-4-methyl-6-

Table II. Chemical and Physical Properties of Diazinon and Degradation Half-lives

Property	Value	Reference
CAS number	333-41-5	
Empirical formula	$C_{12}H_{21}N_2O_3PS$	
Molecular weight	304.4 g/mole	
Solubility	In water: 40 mg/L at room temperature; in petroleum oils: completely soluble; in ethanol, acetone, xylene, ether, and benzene: miscible	18
Log K_{ow} (Log P)	3.296 @ 25°C	
Vapor pressure	1.06×10^{-4} mm Hg at 25°C; 8.47×10^{-5} mm Hg at 20°C	18
Henry's law constant	7.06×10^{-7} (atm)(m^3)/mole	18
Log K_{oc}	Mean 3.16; range 3.0 to 3.26 (four soils)	95
Photolysis half-life (water)	24.6 days in natural light	15
	5.1 days in artificial light	96
	15 days	18
Photolysis half-life (California sandy loam)	2.5 days in natural light	16
	4.6 days in artificial light	97
Hydrolysis half-life	12 days (pH 5); 138 days (pH 7); 77 days (pH 9)	98
	2–3 weeks (neutral pH, room temp.); 14 days (pH 5); 54.6 days (pH 6); 70 days (pH 7); 54 days (pH 8)	18
Half-life in soil	32 days; 43.8 days (pH 4.7, sterile)	18
Aerobic soil metabolism (California sandy loam)	39.5 days (pH 7.8); 31.2 days (pH 5.4)	20
Anaerobic soil metabolism (California sandy loam)	17 days (pH 7.8); 34.3 days (pH 5.4)	20
Anaerobic aquatic metabolism	4.5 days (pH 5.01)	21

hydroxypyrimidine and diethyl thiophosphoric acid or diethyl phosphoric acid under acidic conditions.[18] At pH of 5.0, the half-life ranges from 12 to 14 days. Under neutral or basic conditions, diazinon is more stable, with half-lives reported to range from 54.6 to 138 days (Table II).

2.2.5. *Microbial Degradation*

Microbial species such as *Arthrobacter* and *Streptomyces* have been reported to act synergistically to degrade diazinon.[19] The reported half-life of diazinon in soil ranges from 31.2 to 39.5 days aerobically, and 17 to 34.3 days anaerobically.[20] An anaerobic aquatic metabolism study using natural sediments and natural surface water indicated that diazinon can be degraded with a half-life of 4.5 days.[21] No data were found on aerobic aquatic biodegradation rates during a literature review.

2.2.6. *Overall Disappearance Rates*

Diazinon disappearance rates measured in surface water samples incubated in bottles range from 14 to 99 days depending on the water source, pH, and exposure to light.[22–25] Shorter half-lives, from 5 to 25 days, have been measured in larger, open, outdoor experimental systems.[26,27]

2.2.7 *Bioconcentration*

Diazinon has only a moderate potential to bioconcentrate in aquatic organisms. Based on a log K_{ow} (octanol-water partition coefficient) of 3.3, the estimated bioconcentration factor (BCF) for diazinon is 200. Measured BCF values in fish range from 28 to 500.[28–35] The only BCF available for an arthropod is 2 to 4 for a freshwater penaeid shrimp.[28]

One reason for its low BCF in fish is that diazinon is rapidly metabolized and eliminated. The time to eliminate one half of the body burden was reported to be 1 to 3 days for bluegill sunfish,[35] 9 hours for willow shiner,[30] and 3 hr for perch.[29] Consistent with this rapid depuration, maximum concentrations in fish tissue are reached after only 2 to 4 days of exposure.[28,29,32–34]

2.3. Measured Diazinon Concentrations in the Sacramento and San Joaquin Rivers

Data on the concentrations of diazinon in the San Joaquin and Sacramento Rivers and their tributaries—including agriculturally dominated creeks and irrigation channels—for 1991 to 1994 were obtained from three sources:

1. U.S. Geological Survey (USGS).[36] The USGS data were collected from 1991 to 1994 from the Sacramento River at Sacramento and the San Joaquin River at Vernalis. At Vernalis, samples were collected daily; samples from two or more consecutive days were usually composited for analysis, except during periods of rainfall. At Sacramento, samples were collected daily or three times a week and analyzed separately.
2. Central Valley Regional Water Quality Control Board (CVRWQCB).[2] These data were obtained in 1991 and 1992 as part of a pesticide assessment program for the San Joaquin Basin. Samples were taken from seven agriculturally dominated creeks and constructed drains, four major tributaries (Merced River, Tuolumne River, Stanislaus River, and Salt Slough), and three sites on the San Joaquin mainstem (Vernalis, Laird Park, and Hills Ferry). Samples were collected for *Ceriodaphnia* bioassays, and some were split for pesticide analysis.
3. California Department of Pesticide Regulation (DPR).[37–42] The DPR data were collected from 1991 to 1993 as part of the Environmental Hazards Assessment Program. Samples were collected every two weeks from an index site: the San Joaquin River at Laird Park. When pesticides were detected at the index site, a Lagrangian survey was conducted in which samples were collected at additional sites on the San Joaquin River and some of its tributaries. "The Lagrangian sampling strategy[43] consists of sampling a parcel of water as it moves downstream in a river, also capturing tributary inputs as they are timed to meet the main stem."[37] Thus, the San Joaquin tributaries were sampled at times when pesticides were expected to be detected, whereas the index site, like the USGS sampling stations, was sampled at regular intervals throughout the year.

Sample sites, number of samples collected, and frequency of diazinon detection are presented in Tables III, IV, and V, and Fig. 2. The sampling sites were classified as either *primary sites* (Sacramento River at Sacramento, San Joaquin River at Vernalis, and San Joaquin River at Laird Park) or *secondary sites*, which were the additional sites sampled on the

Table III. Number of Samples and Diazinon Detections, and Diazinon Concentrations at Primary Sampling Sites on the Sacramento and San Joaquin Rivers, 1991–94

	Sacramento River at Sacramento[a]			San Joaquin River at Vernalis[a]			San Joaquin River at Laird Park[b]		
Month	Samples[c]	Max[d]	90th[e]	Samples	Max	90th	Samples	Max	90th
Jan	47 (34)	236	84	74 (69)	395	205	19 (14)	1,290	573
Feb	63 (62)	393	149	84 (75)	714	266	19 (19)	1,220	528
Mar	47 (20)	57	30	71 (63)	110	79	21 (11)	140	133
Apr	39 (1)	15		71 (17)	49	20	24 (5)	50	
May	24 (0)	BDL[f]		42 (24)	41	29	7 (5)	60	
Jun	23 (0)	BDL		40 (3)	18		4 (2)	20	
July	24 (2)	57		43 (5)	39		4 (0)	BDL	
Aug	35 (0)	BDL		44 (22)	250	82	4 (1)	280	
Sep	34 (0)	BDL		43 (7)	27	14	4 (2)	10	
Oct	37 (0)	BDL		41 (5)	23		2 (2)	10	
Nov	33 (0)	BDL		43 (1)	15		1 (1)	10	
Dec	32 (0)	BDL		44 (12)	48	20	6 (0)	BDL	
All	438 (119)	393	45	640 (303)	714	84	115 (62)	1,290	208

[a] Data are from MacCoy, Crepeau, and Kuivila.[36]
[b] Data are from Foe[2]; Ross.[37,39–42]
[c] Number of detections are given in parentheses.
[d] Maximum concentration (ng/L).
[e] 90th centile (ng/L) calculated by lognormal regression for data sets with more than six detections.
[f] BDL = Below detection limits (19 or 38 ng/L at Sacramento and Vernalis, 10 or 50 ng/L at Laird Park). Some values below detection limits were reported by MacCoy *et al.*,[36] and were retained in this analysis.

Table IV. Number of Samples and Diazinon Detections, and Diazinon Concentrations at Secondary Sampling Sites in the San Joaquin River Basin, 1991–93

			Concentration (ng/L)	
Location[a]	Dates	Samples[b]	Maximum	90th centile[c]
Mainstem San Joaquin River				
San Joaquin/Stevenson (2)	4/2/91–2/8/93	9 (3)	260	
San Joaquin/Fremont Ford (3)	4/2/91–2/9/93	9 (4)	320	
San Joaquin/Hills Ferry (4)	4/3/91–2/9/93	19 (14)	1,690	425
San Joaquin/Patterson (5)	4/2/91–2/10/93	9 (4)	1,180	
San Joaquin/Maze Blvd. (7)	4/4/91–2/10/93	9 (4)	370	
San Joaquin/Vernalis[d] (8)	4/2/91–2/10/93	22 (13)	360	242
Tributaries				
Salt Slough (9)	4/2/91–2/8/93	19 (13)	330	229
Los Banos Creek (10)	4/2/91–2/8/93	7 (2)	110	
Mud Slough (11)	4/2/91–2/8/93	9 (9)	170	
Merced/Oakdale (12)	1/14/93–2/7/93	2 (0)	BDL[e]	
Merced River (13)	4/3/91–2/9/93	21 (8)	400	239
Tuolumne River (14)	4/4/91–2/10/93	19 (9)	350	220
Stanislaus River (15)	4/4/91–2/10/93	20 (5)	110	
Agriculturally dominated creeks				
Orestimba Creek (16)	2/25/91–2/9/93	25 (19)	880	608
Del Puerto Creek (17)	3/4/91–2/10/93	29 (20)	2,600	548
Ingram/Hospital creeks (18)	3/4/91–2/10/93	31 (26)	1,800	454
Constructed drainage channels				
Newman wasteway (19)	4/2/91–2/9/93	9 (4)	36,800	
Livingston spillway (20)	1/15/93–2/8/93	2 (4)	1,030	
Highline spillway (21)	2/8/93	1 (1)	2,540	
Stevenson spillway (22)	2/9/93	1 (1)	1,320	
Spanish grant drain (23)	3/4/91–2/9/93	22 (21)	1,200	234
TID[f] #3 (24)	3/4/91–6/22/92	17 (13)	2,600	1,295
TID #5 (25)	3/4/91–2/9/93	28 (18)	1,690	700
TID #6 (26)	5/28/91–6/22/92	17 (7)	910	338

Note: From Foe[2]; Ross.[37,39–42]
[a] Numbers in parentheses indicate site location (see Fig. 2).
[b] Number of detections are given in parentheses.
[c] Calculated by lognormal regression for data sets with more than six detections.
[d] Vernalis was a primary site in the USGS study, but was also included in the California Department of Pesticide Regulation (DPR) and Central Valley Regional Water Quality Control Board (CVRWQCB) studies. Data from the DPR and CVRWQCB samples at Vernalis are not included in Table III.
[e] BDL = Below detection limits (50 ng/L).
[f] TID = Turlock Irrigation District lateral.

San Joaquin River and tributaries during the DPR Lagrangian surveys and the CVRWQCB study.

2.3.1. *Data Analysis*

Diazinon concentrations in surface water were assumed to be log-normally distributed.[44] Other distribution models may have provided a better fit to some data sets, but the log-normal model is generally considered adequate for describing exposure distributions.[45,46] At least six observations above the method detection limit (MDL) were considered necessary to characterize a concentration distribution. For data sets that met this criterion, log-normal distributions of exposure concentrations were determined as follows: The observations in each data set (including nondetects, which, for the purposes of calculating plotting positions, were assigned the dummy value of zero) were ranked by concentration, and for each observation the centile ranking was calculated as $i/(n+1)$, where i was the rank of the observation, and n was the total number of observations, including nondetects.[47] The resulting centile rankings were normalized and a linear regression was performed on values

Table V. Summary of Diazinon Concentrations at Secondary Sampling Sites in the San Joaquin River Basin by Month, 1991–93. Results for All Sites on Mainstem and Tributaries Combined, and All Sites on Creeks and Drainage Channels Combined

	Mainstem and tributaries			Creeks and drains		
Month	Samples[a]	Max[b]	90th[c]	Samples	Max	90th
Jan	28 (14)	150	156	21 (19)	1,030	452
Feb	30 (27)	1,690	615	34 (31)	36,800	3,970
Mar	4 (4)	380		22 (21)	330	323
Apr	44 (8)	170	39	30 (14)	520	67
May	23 (14)	60	62	34 (27)	1,800	457
Jun	21 (10)	20	19	20 (12)	70	39
July	11 (0)	BDL[d]		7 (1)	80	
Aug	11 (4)	320		5 (0)	BDL	
Sep	0			2 (2)	10	
Oct	2 (0)	BDL		1 (1)	190	
Nov	0			1 (0)	BDL	
Dec	0			5 (4)	310	
All	174 (81)	1,690	178	182 (132)	36,800	586

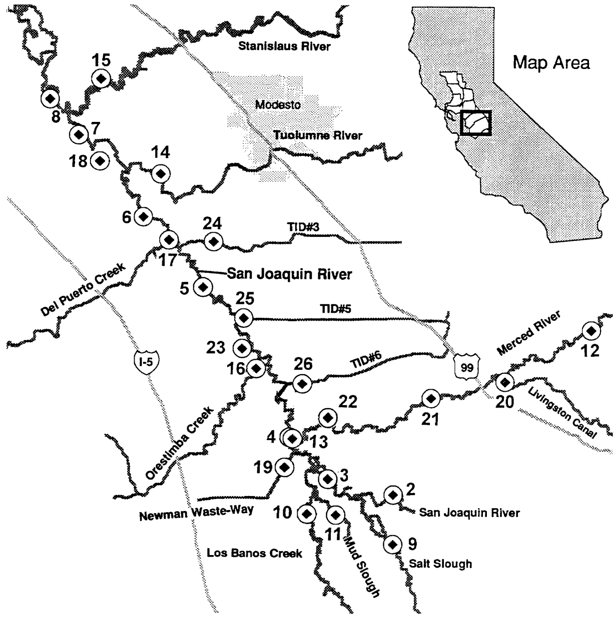
Note: From Foe[(2)]; Ross.[(37,39–42)]
[a] Number of detections are given in parentheses.
[b] Maximum concentration (ng/L).
[c] 90th centile (ng/L) calculated by lognormal regression for data sets with more than six detections.
[d] BDL = Below detection limits (10 or 50 ng/L).

above the MDL, with the logarithm of concentration as the independent variable and normalized rank centile as the dependent variable. Based on the calculated log-normal concentration distributions, the 90th centile concentration was estimated (Fig. 3).

In the MacCoy, Crepeau, and Kuivila[(36)] data sets, some concentrations were reported as actual concentrations even though they were below the MDL. These reported concentrations were retained in the analysis. Where more than one analysis was conducted on the same day at a single site or on aliquots of a single sample, the highest reported concentration was used in the risk assessment.

2.3.2. *Measured Concentrations: Primary Sites*

The results of periodic monitoring of the primary sites (Sacramento River at Sacramento and San Joaquin River at Vernalis and Laird Park) in 1991–94 are presented in Figs. 4, 5, and 6. At each location, values were below MDLs (10 to 50 ng/L) for most of the year. At each site, however, concentrations exceeded detection limits at certain times between January and March, which is when diazinon use as dormant spray coincides with rainfall and runoff events. Brief pulses of diazinon were also measured during



Key to Sampling Sites

Map Site	Description	River	Location
1[a]	Sacramento R. at Sacramento	Sacramento	Tower Bridge
2	SJR/Stevenson	San Joaquin	1 mi S. HWY 140 @ HWY 165 inters.
3	SJR/Fremont Ford	San Joaquin	Fremont Ford Bridge
4	SJR/Hills Ferry	San Joaquin	Hills Ferry Road Bridge, River Mile 118.5
5	SJR/Patterson	San Joaquin	West Main
6	SJR/Laird Park	San Joaquin	Lower Lateral #2, River Mile 90.5
7	SJR/Maze Blvd.	San Joaquin	Highway 132 Bridge
8	SJR/Vernalis	San Joaquin	Airport Way USGS gaging station
9	Salt Slough	San Joaquin	Landers Ave. Bridge, River Mile 129
10	Los Banos Creek	San Joaquin	Highway 140
11	Mud Slough	San Joaquin	USGS gaging station, Kesterson NWA
12	Merced R./Oakdale	Merced	Oakdale Rd. near Winton
13	Merced R.	Merced	Hatfield St. Park, River Mile 118
14	Tuolumne R.	Tuolumne	Shiloh Rd. Bridge, River Mile 83.8
15	Stanislaus R.	Stanislaus	Caswell St. Park, River Mile 75
16	Orestimba Creek	San Joaquin	River Rd. Bridge, River Mile 109
17	Del Puerto Creek	San Joaquin	River Mile 93
18	Ingram/Hospital Creeks	San Joaquin	River Mile 81
19	Newman Wasteway	San Joaquin	Behind Newman WWTP
20	Livingston Spillway	Merced	2 mi. from Liv. via Liv.-Cressey Rd.
21	Highline Spillway	Merced	E. of terminus of Williams Road
22	Stevenson Spillway	Merced	
23	Spanish Grant Combined Drain	San Joaquin	River Mile 105
24	Turlock Irrigation District Lateral #3	San Joaquin	Jennings Road Bridge, River Mile 93.5
25	Turlock Irrigation District Lateral #5	San Joaquin	Carpenter Road Bridge, River Mile 103.5
26	Turlock Irrigation District Lateral #6	San Joaquin	W. of Central Ave., River Mile 115.5

[a] Not shown in Figure 2.

Fig. 2. Sites in the San Joaquin Basin sampled during 1991–93.

August in some years at Vernalis and Laird Park, possibly reflecting urban use.

Overall, concentrations were highest at Laird Park and lowest at Sacramento. The annual peak concentrations at Sacramento ranged from 155 to 393 ng/L;

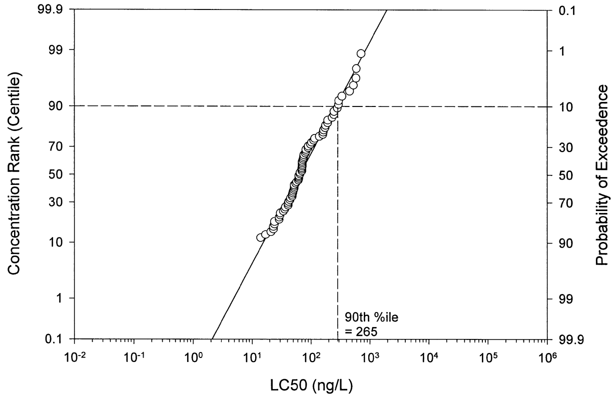


Fig. 3. Distribution of measured diazinon concentrations in the San Joaquin River at Vernalis, 1991–94. From MacCoy, Cepeau, and Kuivila.[36]

at Vernalis, from 288 to 714 ng/L; and at Laird Park, from 350 to 1,290 ng/L. The 90th-centile concentrations for all months combined were 45 ng/L at Sacramento, 84 ng/L at Vernalis, and 208 ng/L at Laird Park (Table III). That is, 90% of the samples collected from each site during the 1991–94 monitoring period contained diazinon concentrations less than or equal to the concentration indicated. If these samples were unbiased representations of all possible sample times, the diazinon concentration in a sample collected at any time would have a 10% probability of exceeding the 90th-centile concentration. When the data were analyzed separately for each month, maximum concentrations and 90th centiles at each primary site were highest in January and February.

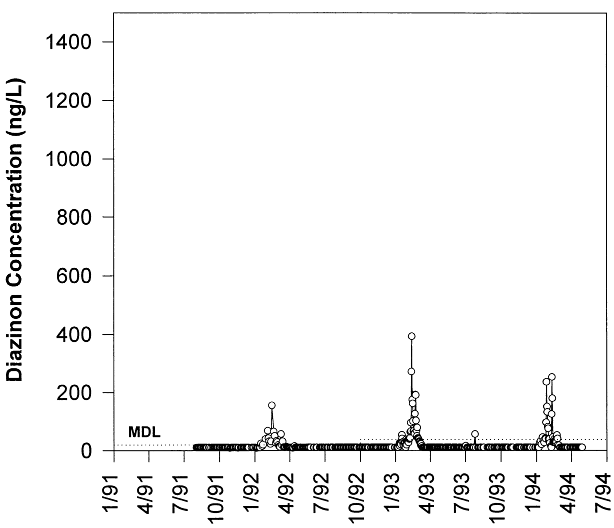


Fig. 4. Diazinon concentrations measured in the Sacramento River at Sacramento, 1991–94. MDL = Method detection limit. From MacCoy, Cepeau, and Kuivila.[36]

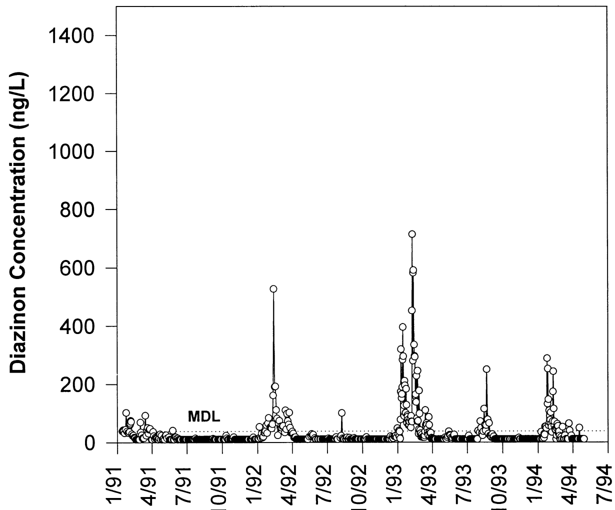


Fig. 5. Diazinon concentrations measured in the San Joaquin River at Vernalis, 1991–1994. MDL = Method detection limit. From MacCoy, Crepeau, and Kuivila.[36]

2.3.3. *Measured Concentrations: Secondary Sites*

Unlike the primary sites, which were sampled on a predetermined, year-round schedule, sampling at the secondary sites focused on times and places where

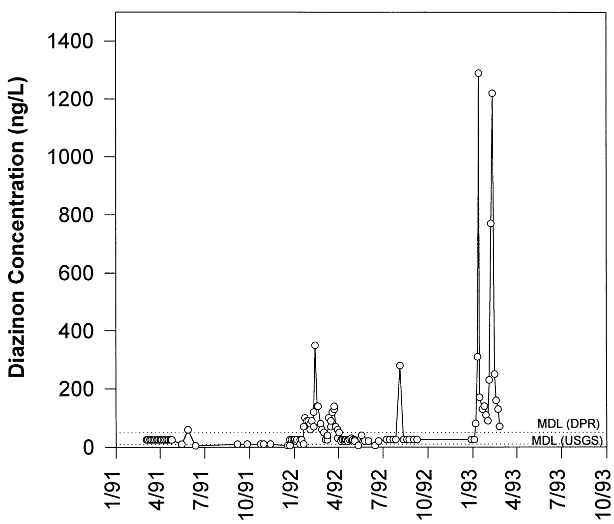


Fig. 6. Diazinon concentrations measured in the San Joaquin River at Laird Park, 1991–93. MDL = Method detection limit. DPR = California Department of Pesticide Regulation. USGS = U.S. Geological Survey. From Foe[2]; Ross.[37,39–42]

high concentrations of pesticides were expected. Samples were collected from agriculturally dominated creeks and constructed drainage channels, as well as larger tributaries and the mainstem of the river. Nearly 90% of the samples analyzed were collected between January and June. The Lagrangian surveys[37–42] were conducted when routine sampling at Laird Park indicated that pesticides were present. Many of the samples analyzed in the CVRWQCB study[2] were selected for analysis because they were toxic in *Ceriodaphnia* bioassays (some nontoxic samples were also selected).

Concentrations at the secondary sites (Tables IV and V) were highest in the creeks and drainage channels, with one extremely high value (36,800 ng/L) recorded in Newman Wasteway in February 1993. The 90th-centile concentrations at the creek and channel sites ranged from 234 ng/L (Spanish Grant Combined Drain) to 1,295 ng/L (Turlock Irrigation District Lateral #3).

Analysis by month (Table V) shows that concentrations in the creeks and drains were highest in February, with a 90th centile of 3,970 ng/L. In several cases, diazinon peaks occurred days after periods of no flow or concentrations near detection limits. For example, Del Puerto Creek was dry on January 30, 1992,[39] and a sample four days later contained 2,600 ng/L, the highest value reported at that site.[2] The same situation occurred at Turlock Irrigation District lateral #3: dry on February 3, 1992, and 2,600 ng/L on February 10.[2] Orestimba Creek was dry for six weeks through January 29, 1992; concentrations of 260 to 600 ng/L occurred from February 10 to 18; and the creek was dry again on March 2.[2,40] These observations suggest that at least some of the high concentrations in the creeks and drains—in 1992, an exceptionally dry year—represent runoff with little or no dilution.

The larger tributaries had lower concentrations, with maxima of 400 ng/L or less and 90th centiles in the low-200-ng/L range (Table IV). Concentrations in the mainstem of the San Joaquin reflected inputs from the tributaries and drains. The lowest mainstem concentrations occurred at Stevenson and Fremont Ford, upstream from the major orchard growing region. The next station, Hills Ferry, below the confluence with Newman Wasteway and the Merced River (receiving water for Livingston, Highline, and Stevenson Spillways), had the highest mainstem concentrations (maximum 1,690 ng/L, 90th centile 425 ng/L). Further downstream, concentrations declined, with maxima of 1,180 ng/L at Patterson, 370 ng/L at Maze Boulevard, and 360 ng/L at Vernalis. The 90th-centile concentration for the DPR and CVRWQCB samples at Vernalis was 242 ng/L, or nearly three times higher than the 90th centile for the USGS samples (84 ng/L, Table III), as expected based on the differences in sampling strategies used in the three studies.

2.3.4. Summary of Exposure Analysis

The monitoring data for 1991–94 indicated that diazinon concentrations in Sacramento River at Sacramento and in the San Joaquin River and its major tributaries were usually below the detection limit of 10 to 50 ng/L from April through December. Pulses of diazinon in the 500 to 1,500 ng/L range occurred, however, in January and February each year. Diazinon concentrations were generally higher in the San Joaquin River than in the Sacramento River at Sacramento. Higher diazinon concentrations (up to 2,600 ng/L, with one extreme value of 36,800 ng/L) were measured in drainage channels and creeks dominated by agricultural runoff. These conclusions were based on measurements made in a period of drought; additional data are needed for years with higher rainfall.

3. EFFECTS ANALYSIS

3.1 Mode of Toxicity

Diazinon exerts its toxicity by inhibiting the neuronal enzyme acetylcholinesterase (AChE).[48] AChE is normally required for the metabolism of the neurotransmitter acetylcholine (ACh). The parent compound, diazinon, is not a potent inhibitor of the AChE enzyme because it must first be converted in vivo or in vitro to its oxygen analogue, diazoxon (diethyl 2-isopropyl-6-methylpyrimidin-4-yl phosphate).[49] Diazoxon is approximately 10^5 times more effective than diazinon in reducing AChE activity.[50] Organophosphorus insecticides like diazoxon bind and phosphorylate AChE, which ultimately inhibits the binding and subsequent metabolism of the endogenous substrate ACh.[51] This results in accumulation of ACh in nerve and tissue effector organs. In vertebrates, the accumulation of ACh causes prolonged stimulation of nicotinic, muscarinic, and central nervous system pathways. Acute poisoning results in asphyxiation due to respiratory paralysis. Inhibition of AChE in insects results in disruption of the nervous system, which eventually leads to death. Due to the mode of action of diazinon, it is more toxic to vertebrates and invertebrates than to plants.

3.2. Acute Toxicity

Diazinon acute toxicity data used in this risk assessment were obtained from the U.S. Environmental Protection Agency (EPA) Pesticide Toxicity Database,[52] the California Department of Fish and Game (DFG),[1] and the AQUIRE (Aquatic Toxicity Information Retrieval) database.[53] The combined database (Table VI) included 132 values for 63 species. Approximately half of the represented species were fish and half were invertebrates. Only one plant (the green alga *Selenastrum capricornutum*) was included in the data.

When more than one toxicity value occurred for a given species, the geometric mean was calculated for that species, consistent with EPA guidelines.[54] The distribution of species sensitivity was then analyzed using the same method as applied to the exposure data. For each data set, the 10th centile of sensitivity, that is, the concentration estimated to protect 90% of the species from acute effects, was calculated from the log-normal linear regression as a convenient indicator of effect concentrations.[44]

Invertebrate species were much more sensitive to diazinon than fish species. For fish, the median lethal concentration (LC_{50}) values ranged from 23,000 ng/L for the goby *Chasmichthys dolichognathus* (geometric mean of three values[55]), to 1,080,000 ng/L for the crucian carp *Carassius carassius* (geometric mean of two values[56]). Invertebrate LC_{50} values ranged from 200 ng/L for the amphipod *Gammarus fasciatus*[57] to 21,500,000 ng/L for the rotifer *Brachionus calyciflorus* (geometric mean of three values[58,59]).

The geometric mean LC_{50} for all 29 fish species was 837,000 ng/L. The 10th centile was 80,000 ng/L (Fig. 7). Acute toxicity data were available for four salmonids: lake trout (*Salvelinus trutta*), brook trout (*Salvelinus fontinalis*), rainbow trout (*Oncorhynchus mykiss*), and cutthroat trout (*Oncorhynchus clarki*). These species, with LC_{50} values ranging from 600,000 ng/L to 2,620,000 ng/L, were intermediate in sensitivity compared with the overall range for fish. Rainbow trout is the same species as steelhead, one of the nine species of concern in the Sacramento–San Joaquin system (Table I). The other salmonid of concern, chinook salmon, is not included in the toxicity database, but it is reasonable to expect that the 10th-centile values—five to seven times lower than the LC_{50} of the most sensitive of the salmonid species tested—are protective of chinook salmon.

Twenty-three species of arthropods were represented in the data set. The 10th centile was 480 ng/L (Fig. 7). The geometric mean for cladocerans (four species) was 887 ng/L; for mysids (two species), 4,320 ng/L; for amphipods (five species), 8,060 ng/L; for aquatic insects (seven species), 30,200 ng/L; and for copepods (two species), 80,300 ng/L. The extreme sensitivity of cladocerans is noteworthy; cladocerans constitute 50% of the arthropod species used to derive a water quality standard for California,[1] and much of the concern about potential effects of diazinon in the Sacramento–San Joaquin stems from results of ambient water toxicity tests with *Ceriodaphnia dubia.*

3.3. Chronic Toxicity

Data on chronic effects of diazinon on fish are summarized in Table VII. The most sensitive endpoints appear to be fecundity, hatching success, and growth of offspring following long-term parental exposure. The lowest concentration reported to cause such effects was 470 ng/L, which reduced the fecundity of sheepshead minnows exposed for 108 days.[34] Shorter exposures (e.g., 30 to 60 days) have little or no effect on fish survival, growth, and reproduction at diazinon concentrations ranging from 10,000 to 1,100,000 ng/L.

The large discrepancy between the results for brook trout[60] and rainbow trout[61] might be related to several factors: (1) differences between species, (2) differences between life stages, or (3) effects of parental exposure on second-generation brook trout. The 200,000 ng/L no-effect level reported by Bresch,[61] however, is even higher than some reported acute LC_{50} values for the same species (Table VI). It is possible that the apparent discrepancies were caused by the impurity (sulfotepp) known to be present in diazinon samples used in earlier studies[62] but no longer present in formulations or technical-grade diazinon (Dennis Tierney, Novartis Crop Protection, Inc., personal communication, 1997). If so, much or all of the toxicity data collected before about 1985 may be unrepresentative of the diazinon in current use.

Diazinon chronic toxicity data for invertebrates are limited to two saltwater species, mysids (*Mysidopsis bahia*) and brine shrimp (*Artemia salina*). Survival of *M. bahia* was reduced at 3,270 ng/L in a 28-day life-cycle test.[63] Hatching of *A. salina* was unaffected at 10,000,000 ng/L.[64]

3.4. Ambient Water Toxicity Tests in the Sacramento–San Joaquin Basin

Numerous studies have demonstrated that surface waters, agricultural and municipal runoff, and municipal effluents in the Sacramento–San Joaquin Basin are at times acutely toxic to selected aquatic

Table VI. Acute Toxicity (EC_{50} and LC_{50} concentrations, ng/L) of Diazinon to Aquatic Organisms. N = Number of LC_{50} or EC_{50} Values Included in Geometric Mean

Species	Common name	EC_{50} or LC_{50} (geometric mean, ng/L)	N	Reference
Gammarus fasciatus	Amphipod	200	1	52
Ceriodaphnia dubia	Daphnid	493	3	69, 99, 100
Daphnia pulex	Daphnid	776	3	69, 101, 102
Daphnia magna	Daphnid	1,020	10	52, 62, 69, 103–106
Simocephalus serrulatus	Daphnid	1,590	2	101
Gammarus pseudolimnaeus	Amphipod	2,000	1	107
Acartia tonsa	Copepod	2,570	1	81
Neomysis mercedis	Mysid	4,150	2	77, 78
Mysidopsis bahia	Mysid	4,500	2	63, 79
Cloeon dipterum	Mayfly	7,800	1	108
Orconectes propinquus	Crayfish	15,000	1	107
Acroneuria ruralis	Stonefly	16,000	1	107
Asellus communis	Amphipod	21,000	1	107
Hyalella azteca	Amphipod	22,000	1	107
Chasmichthys dolichognathus	Goby	23,400	3	109
Baetis intermedius	Mayfly	24,000	1	107
Pteronarcys californica	Stonefly	25,000	1	110
Palaemonetes pugio	Shrimp	28,000	1	52
Penaeus aztecus	Shrimp	28,000	1	52
Seriola quinqueradiata	Yellowtail	40,000	1	55
Paraleptophlebia pallipes	Mayfly	44,000	1	107
Physa gyrina	Snail	48,000	1	107
Lestes congener	Damselfly	50,000		111
Anguilla anguilla	Eel	80,000	1	112
Girella punctata	Green fish	94,700	2	109
Orthetrum albistylum	Dragonfly	140,000	1	108
Leuciscus idus	Golden orf	150,000	1	56
Mugil cephalus	Mullet	150,000	1	113
Gammarus lacustris	Amphipod	184,000	2	107, 114
Lepomis macrochirus	Bluegill sunfish	204,000	13	52, 57, 60, 62, 102, 103, 110, 115–117
Mugil curema	White mullet	250,000	1	113
Notemigonus crysoleucas	Golden shiner	400,000	1	117
Cyprinodon variegatus	Sheepshead minnow	470,000	2	34, 52
Misgurnus anguillicaudatus	Oriental weatherfish	500,000	1	108
Helisoma trivolvis	Snail	528,000	1	107
Salvelinus namaycush	Lake trout	602,000	1	102
Salvelinus fontinalis	Brook trout	624,000	4	60, 117
Oncorhynchus mykiss	Rainbow trout	839,000	7	52, 56, 62, 102, 110, 115
Crassostrea virginica	Oyster	938,000	2	52, 118
Channa punctatus	Snake-head catfish	1,190,000	2	119, 120
Gambusia patruelis	Mosquitofish	1,270,000	1	121
Poecilia species	Molly	1,300,000	1	122
Poecilia sphenops	Molly	1,600,000	1	80
Jordanella floridae	Flagfish	1,630,000	3	52, 60
Hirudo nipponia	Asian leech	1,900,000	2	123
Poecilia reticulata	Guppy	2,010,000	3	32, 56, 105
Heteropneustes fossilis	Indian catfish	2,270,000	1	124
Cyprinus carpio	Common carp	2,490,000	2	125, 126
Cyclops species	Cyclops	2,510,000	1	80
Oncorhynchus clarki	Cutthroat trout	2,620,000	3	52, 57
Tubifex species	Oligochaete	3,160,000	1	80
Brachydania rerio	Zebrafish	4,120,000	2	32
Physa acuta	Snail	4,800,000	1	127
Selenastrum capricornutum	Selenastrum	4,870,000	2	52, 128
Pimephales promelas	Fathead minnow	6,720,000	11	24, 60, 103, 129
Oryzias latipes	Medaka	7,260,000	3	130
Ictalurus melas	Black bullhead	8,000,000	1	56
Carassius auratus	Goldfish	9,000,000	1	115
Semisulcospira libertina	Marsh snail	9,500,000	1	127
Carassius carassius	Crucian carp	10,800,000	2	56
Bufo bufo	Toad	14,000,000	1	108
Indoplanorbis exustus	Snail	20,000,000	1	108
Brachionus calyciflorus	Rotifer	21,500,000	3	58, 59

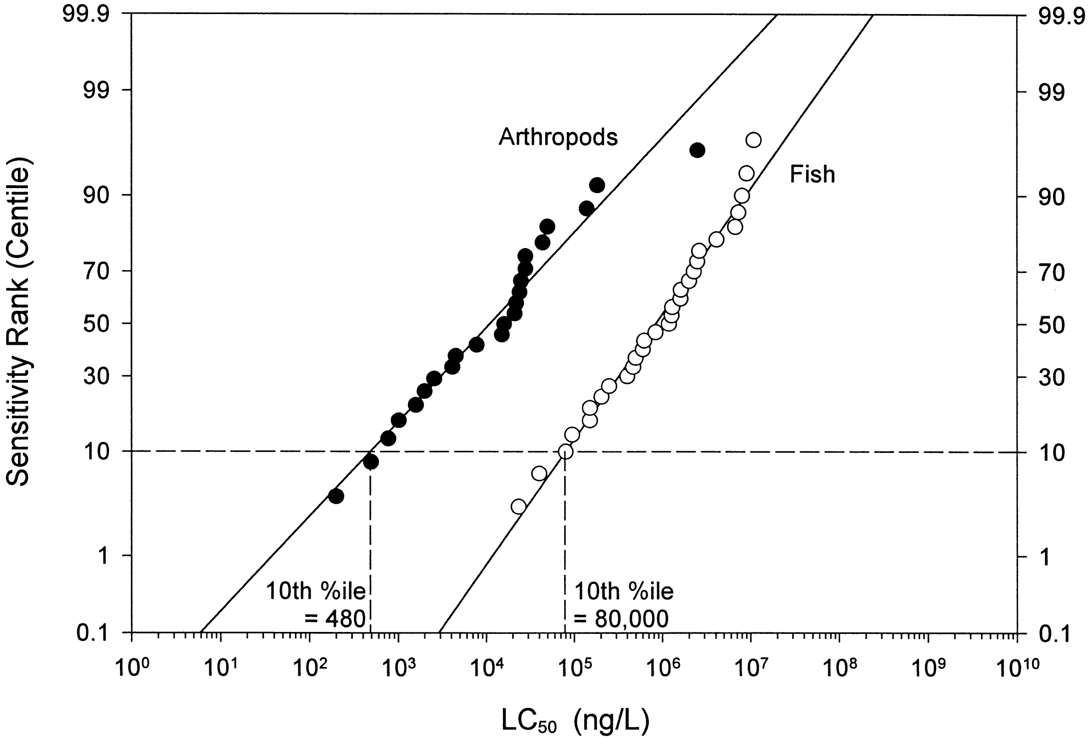


Fig. 7. Distribution of diazinon acute toxicity values for arthropods and fish. Each point represents the geometric mean of all LC_{50} or EC_{50} values for one species.

toxicity test organisms.[2,3,65–68] Foe [2] summarized studies conducted in the San Joaquin Basin by the DPR, the CVRWQCB, and the USGS. Foe stated that a 43-mile reach of the San Joaquin River between the Merced and Stanislaus Rivers tested toxic to *Ceriodaphnia* on about half of the sampling times. Diazinon, carbofuran, parathion, and carbaryl were detected in the river water at concentrations reportedly toxic to *Ceriodaphnia.* Furthermore, "thirty-eight percent of all agricultural return water samples collected in the Basin between April and June of 1991 and 1992 were acutely toxic."[2] Diazinon, chlorpyrifos, fonofos, and carbaryl were detected at toxic concentrations in the return water. Ongoing studies[2] suggest that the same phenomena are occurring in the San Francisco Bay Delta.

Kuivila and Foe[3] published results of more recent studies in the lower San Joaquin and Sacramento Rivers. Pulses of diazinon and methidathion occurred after rainstorms in January and February, following application of the pesticides to dormant orchards. *Ceriodaphnia* bioassays were conducted on water from the Sacramento at Rio Vista and from the San Joaquin at Vernalis. One hundred percent mortality occurred within 24 hr at all diazinon concentrations 553 ng/L or higher; within 48 hr at 330 ng/L or higher; and within 7 days at 186 ng/L or higher (Fig. 8). These results are consistent with reported LC_{50} values for *Ceriodaphnia* (48-hr LC_{50} = 500 ng/L[69]; 96-hr LC_{50} = 470 or 510 ng/L[1]; 7-day LC_{50} = 110 ng/L[70]).

The studies summarized above as well as others are evidence that pesticides and metals are present at some times in some areas of the Sacramento and San Joaquin Basins at concentrations that cause acute toxicity to *Ceriodaphnia dubia* in standard tests. The presence of substances in surface water at levels toxic to *C. dubia* in laboratory tests, however, is not direct evidence that these substances are causing actual ecological damage in the rivers. In general, ambient water toxicity to *Ceriodaphnia* is associated with instream ecological impacts,[71] but the specific case of organophosphorus insecticides may be an exception. Cladocerans, including *C. dubia*, are consistently among the most sensitive groups of aquatic organisms to diazinon and other organophosphates. Four of the five species most sensitive to diazinon—of a total of 63—are cladocerans (Table VI). According to the California DFG's risk assessments, cladocerans rank 2nd and 12th out of 33 species in sensitivity to

Table VII. Chronic Effects of Diazinon on Fish

Species	Concentration (ng/L)	Endpoint	Duration (days)	Reference
Brook trout	800	LOEC, F1 growth	122	60
	4,800	LOEC, F0 growth	91	60
	9,600	LOEC, F0 survival	91	60
	9,600	LOEC, F0 survival	173	60
	9,600	NOEC, F0 growth	173	60
	9,600	NOEC, F1 hatching	F0 lifetime	60
	9,600	NOEC, F0 fecundity	F0 lifetime	60
	11,100	LOEC, F1 growth	30	60
	11,100	NOEC, F1 survival	122	60
Carp	100,000	NOEC, F0 hatching		131
Fathead minnow	3,200	LOEC, F1 hatching	F0 lifetime	60
	6,900	LOEC, F0 fecundity	F0 lifetime	60
	16,500	NOEC, F0 growth	32	132
	60,300	LOEC, F0 survival	274	60
	60,300	NOEC, F0 hatching		60
	60,300	NOEC, F0 growth	97	60
	60,300	NOEC, F0 survival	167	60
	62,600	NOEC, F1 survival	60	60
	62,600	NOEC, F1 growth	60	60
	90,000	LOEC, F0 growth	32	24
	160,000	NOEC, F0 survival	32	132
	229,000	LOEC, F0 growth	61	60
	290,000	LOEC, F0 survival	32	24
	500,000	NOEC, F0 hatching		24
	1,100,000	NOEC, F0 survival	30	60
Rainbow trout	200,000	NOEC, F0 survival	28	61
	200,000	NOEC, F0 growth	28	61
Sheepshead	470	LOEC, F0 fecundity	108	34
Minnow	3,500	LOEC, F0 fecundity[a]	108	34
	6,500	NOEC, F0 survival	108	34
	6,500	NOEC, F1 hatching	108	34
	6,500	NOEC, F1 growth	28	34
	6,500	NOEC, F1 survival	28	34
Zebrafish	200,000	NOEC, F0 hatching		61
	200,000	NOEC, F0 survival	42	61

Note: F0 = Parental generation; F1 = second generation; LOEC = lowest observed effect concentration; NOEC = no observed effect concentration.
[a] Transferred to clean water to spawn.

chlorpyrifos[72]; and 1st, 3rd, and 5th out of 30 species in sensitivity to methyl parathion.[73] Given the extreme sensitivity of *C. dubia* to organophosphorus insecticides relative to other aquatic species, the results of toxicity tests and toxicity identification evaluations in the Sacramento–San Joaquin Basin cannot be interpreted as unequivocal evidence of actual pesticide impact on the aquatic ecology of these river systems.

3.5. Microcosm and Mesocosm Studies with Diazinon

Microcosms and mesocosms (small- and medium-scale experimental ecosystems) are typically used in the later stages of a chemical risk assessment to confirm and extend the results of simpler, more highly controlled laboratory studies such as standard toxicity tests. Because they more closely simulate natural ecosystems, microcosms and mesocosms are generally more variable, and experimental results are less repeatable, than most laboratory tests. These systems can, however, provide valuable information that cannot be obtained easily (or at all) from simpler studies.[47]

Arthur, Zischke, Allen, and Hermanutz[74] treated two outdoor experimental channels (stream microcosms) with diazinon and measured the effects on macroinvertebrates. From mid-May until early Au-

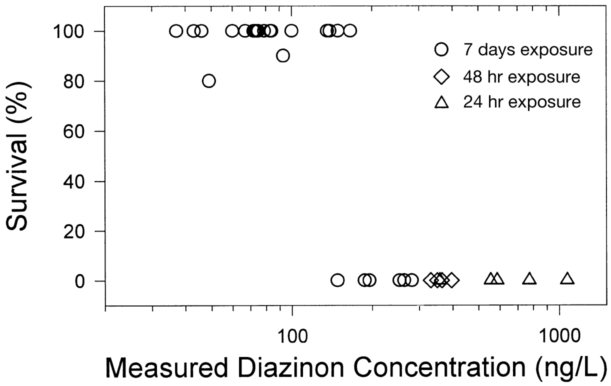


Fig. 8. Survival of *Ceriodaphnia dubia* in water from the San Joaquin and Sacramento Rivers containing measurable concentrations of diazinon. From Kuivila and Foe.[3]

gust, one channel was exposed continuously to 300 ng/L and the other was exposed continuously to 3,000 ng/L. A third channel, not exposed, was used as a control. Because the experimental treatments were not replicated, statistical analysis for treatment-related effects was not valid, and conclusions were based on visual examination of abundance trends over time. The dominant macroinvertebrates in the streams were isopods, amphipods (*Crangonyx*), chironomids, and snails. None appeared to be affected by diazinon treatment. Most of the insects that emerged from the channels were chironomids, and numbers were similar between all channels.

In early August, after 12 weeks of treatment, the diazinon concentration in the 300-ng/L channel was increased to 5,000 ng/L, and that in the 3,000-ng/L channel was increased to 8,000 ng/L. Four weeks later, treatment of the 5,000-ng/L channel was discontinued and treatment of the 8,000-ng/L channel was increased to 22,000 ng/L (mean measured concentrations). During the latter part of the study, snails, isopods, and flatworms were more abundant in the high-diazinon channel than in the other two channels, while the amphipod *Crangonyx* was less abundant in the high-diazinon channel. Mayflies, caddisflies, damselflies, and the amphipod *Hyalella* were absent from the treated channels in the latter part of the study. Chironomids were apparently unaffected by diazinon treatment.

In 1990 and 1991, other ecological studies were conducted with diazinon in large outdoor microcosms[26] and pond mesocosms.[27] The objectives of these studies were to measure the effects of season-long exposures from agricultural runoff and spray drift, and to determine the relationship between diazinon exposure and effects. Effects were measured on major functional groups including phytoplankton, periphyton, macrophytes, zooplankton (cladocerans, copepods, and rotifers), benthic invertebrates (mainly immature insects including chironomids, mayflies, caddisflies, and damselflies), and fish.

The microcosms were established in 11.2-m^3 fiberglass tanks using water and sediment from uncontaminated ponds, and were stocked with juvenile bluegill sunfish (*Lepomis macrochirus*). Eight diazinon loading rates were used, with two microcosms at each level plus two controls. The treatment regimes (applied three times at 7-day intervals) created exposure concentrations ranging from 5,100 to 910,000 ng/L (96-hr maxima). Seventy-day time-weighted averages ranged from 2,400 to 443,000 ng/L.

The mesocosms were 0.1-acre (0.04-hectare) earthen ponds containing sediment and water from the same sources as the microcosms, and were stocked with adult bluegill sunfish. Five treatment levels, plus controls, were used in the mesocosm study, with four control ponds, four ponds at each of the two lowest levels, and three ponds at the three highest levels. The ponds were treated six times with diazinon, alternating between spray (simulating off-target drift) and direct aqueous applications (simulating surface runoff). The mesocosm treatment regimes created 96-hr maximum concentrations ranging from 2,300 to 28,000 ng/L. Time-weighted, 87-day averages ranged from 1,000 to 16,000 ng/L.

Abundances of phytoplankton, periphyton, macrophytes, zooplankton, benthic macroinvertebrates, and emergent insects were monitored in both studies. Fish growth and survival were measured in the microcosm study, and fish reproduction, growth, and survival were measured in the mesocosm study.

The results are summarized in Fig. 9. Cladocerans were severely reduced at all diazinon treatment levels in both microcosms and mesocosms. Copepods and rotifers were less sensitive, with effects first occurring at exposure levels in the 8,000–28,000-ng/L range. Among the insects, caddisflies (trichopterans) and some groups of midges (Ceratopogonidae and Pentaneurini) were affected at the lowest levels (2,000–5,000 ng/L). Mayflies (Ephemeroptera) and several other groups of midges were reduced at 8,000–20,000 ng/L. Damselflies (odonates) were reduced at 14,000 ng/L in the mesocosms, but were unaffected in the microcosms even at the highest treatment level. Bluegill survival was reduced at 110,000 ng/L and above; total fish biomass was reduced at 45,000 ng/L; individual

Parameter		Maximum 96-h Average Concentration (ng/L)								
	Mesocosm	2300	4100	8400	14000	28000				
	Microcosm		5100	9100	20000	45000	1.1×10^5	2.0×10^5	4.4×10^5	9.1×10^5
Total Zooplankton				●	●	●■	●	●	●	●
Copepods				●	●	●■	●	●	●	●
Cladocera		■	●■	●■	●■	●■	●	●	●	●
Rotifers					●■	●■	●	●	●	●
Total Insects				■	●■	●■	●	●	●	●
Diptera				■	●■	■	●		●	●
Chironomidae					●	■	●			●
Chironominae					■	■				
Chironomini				■	■	■	●	●	●	●
Tanytarsini				■	■	■				
Tanypodinae		■	■	●■	●■	●■	●	●	●	●
Pentaneurini		■	●■	●■	●■	●■	●	●	●	●
Procladiini				●	■	●■	●	●	●	●
Orthocladiinae						■	●	●	●	
Ceratopogonidae			●■	●■	●■	●■	●	●	●	●
Ephemeroptera				■	●■	●■	●	●	●	●
Odonata					■	■				
Trichoptera		■	●■	●■	●■	●■	●	●	●	●
Fish Survival							●	●	●	●
Fish Weight and Length										
Fish Biomass						●	●	●	●	●
Fish Reproduction										

■ Effect in Mesocosms
● Effect in Microcosms

Fig. 9. Effects of diazinon on taxa of mesocosms and microcosms. Maximum 96-hr average concentrations are shown in column headings. Squares and circles indicate significant differences ($p < .05$) from control mesocosms and microcosms, respectively, on at least one sampling event (ignoring recovery). From Giddings, Biever, Annunziato, and Hosmer[26]; Giddings.[27]

growth was not affected at any treatment level; and reproduction (measured in mesocosms only) was unaffected by any mesocosm treatment level (up to 28,000 ng/L). Plants and snails were not affected by any of the diazinon exposure levels tested.

The conclusions drawn from the microcosm and mesocosm studies can be summarized as follows.

- Though some effects occurred at the lowest treatment levels, they were confined to cladocerans and certain numerically minor insect taxa and did not alter the overall structure or function of the ecosystem. The lowest adverse ecological effects levels in the mesocosms and microcosms were those at which effects were observed on major invertebrate groups: 8,400 ng/L in the mesocosms and 9,100 ng/L in the microcosms. These concentrations represent 96-hr maxima; concentrations remained within a factor of two of these 96-hr maxima for two months or longer.
- Cladocera were affected by diazinon at 2,300 ng/L, one quarter the lowest adverse effect levels for the ecosystems as a whole.
- Where comparisons could be made for individual taxa, there was reasonably good agreement between the microcosm and mesocosm results and bioassay results.
- Bluegill survival was reduced at diazinon concentrations near the bluegill LC_{50}, but indirect effects on fish (potentially due to reduction in food supply) did not occur. Bluegill sunfish are omnivorous and feed on alternative species if their preferred food sources are reduced.

- The lowest adverse ecological effect levels in the mesocosms (8,400 ng/L) and microcosms (9,100 ng/L) were nearly 20 times higher than the 10th-centile concentration for arthropods (483 ng/L) used as a benchmark for the risk assessment.

3.6. Potential Impacts of Diazinon on the Sacramento–San Joaquin Ecosystem

The toxicity database and mesocosm/microcosm results just described can be used to infer potential direct and indirect effects of diazinon on fish and invertebrates in the Sacramento–San Joaquin system. The fish species of concern and the invertebrates most important in their diet are shown in Table I.

3.6.1. Direct Effects on Fish

The mesocosm and microcosm studies demonstrated that diazinon concentrations less than 110,000 ng/L had no effect on the survival of bluegill sunfish (*Lepomis macrochirus*). The absence of direct toxic effects was expected, based on the laboratory-derived LC_{50} values for this species (204,000 ng/L, geometric mean of 13 values). Of the 29 species in the toxicity database (Table VI), only 6 (goby, yellowtail, eel, green fish, golden orf, and mullet) were more sensitive than bluegill sunfish. The laboratory toxicity data, coupled with the observations on bluegill sunfish in the microcosms and mesocosms, imply that diazinon is unlikely to cause direct acute toxicity to fish in the Sacramento–San Joaquin Basin. Chronic toxicity to fish may occur at lower diazinon concentrations, but only if exposure persists for several weeks or longer (Table VII), which is not the case in the Sacramento and San Joaquin.

3.6.2. Effects on Invertebrates

The critical invertebrates in the Sacramento–San Joaquin, from the point of view of fish production, are the mysid (opossum shrimp) *Neomysis mercedis*, the estuarine copepod *Eurytemora affinis*, the freshwater copepods *Diaptomus* species and *Cyclops* species, the freshwater cladocerans *Daphnia parvula* and *Bosmina longirostris*, and the estuarine amphipods *Corophium spinicorne* and *Corophium stimpsoni.*[4,5,7,75,76] Toxicity data exist only for *N. mercedis* and *Cyclops* species, but inferences can be made about some of the other species.

The California DFG[77,78] determined the LC_{50} of diazinon to *N. mercedis* to be 4,150 ng/L, close to that of another mysid, *Mysidopsis bahia.*[63,79]

The scarcity and variability of the data make it difficult to estimate the sensitivity of *E. affinis* or *Diaptomus* species. AQUIRE[53] includes an LC_{50} value for *Cyclops* species of 2,510,000 ng/L,[80] as well as an LC_{50} of 2,600 ng/L for a marine copepod, *Acartia tonsa.*[81] In mesocosm and microcosm studies, effects on some copepod populations occurred during continuous exposure to 9,100 to 28,000 ng/L (Fig. 9).[26,27]

There are no diazinon toxicity data for *D. parvula* or *B. longirostris*. The toxicity database (Table VI) includes LC_{50} values for four other cladocerans ranging from 493 to 1,590 ng/L. In microcosms and mesocosms, cladocerans were severely affected by exposure to 2,300 ng/L.[26,27] Because of the consistency of these results, it can be concluded that *D. parvula* and *B. longirostris* are probably similar in sensitivity to the other cladocerans tested.

There are no diazinon toxicity data for *Corophium* species. The toxicity database includes data for five other freshwater amphipods: *Gammarus fasciatus* (200 ng/L, $n = 1$); *Gammarus pseudolimnaeus* (2,000 ng/L, $n = 1$); *Asellus communis* (21,000 ng/L, $n = 1$); *Hyalella azteca* (22,000 ng/L, $n = 1$), and *Gammarus lacustris* (184,000 ng/L, $n = 2$). In light of the wide range of sensitivities among amphipods, even among congeneric species, it is impossible to estimate the toxicity of diazinon to *Corophium* species.

Based on these reported acute toxicity values, certain inferences can be made regarding the potential impact of diazinon on key invertebrate species in the Sacramento–San Joaquin river system. *N. mercedis*, perhaps the most important invertebrate food species in the system,[82] would be affected at concentrations above 4,150 ng/L. Effects on *E. affinis* are difficult to predict from the existing toxicity database; based on its euryhaline characteristics,[76] *E. affinis* is likely to be more tolerant than *A. tonsa* (LC_{50} 2,600 ng/L). Freshwater copepods such as *Cyclops* species and others can apparently tolerate concentrations of 10,000 ng/L or more. The amphipod *Corophium* species may be as sensitive as *G. fasciatus* (LC_{50} 200 ng/L), or it may be much less sensitive as are other amphipods in the toxicity database. Cladocerans are uniformly sensitive to diazinon, and those in the Sacramento–San Joaquin could be affected at concentrations as low as 500 ng/L. Clearly, additional toxicity data for native invertebrates would be useful in assessing the risk of diazinon to Sacramento–San Joaquin ecosystems.

3.6.3. Indirect Effects on Fish

To examine possible indirect effects of diazinon on fish, also investigated were the co-occurrence of early life stages of key fish species (Fig. 1), their food organisms, and peak periods of diazinon concentrations (January and February). The following paragraphs discuss the co-occurrences for the nine fish species of concern.

Chinook Salmon and Steelhead Trout. There is overlap of early life stages of these species with peak exposures of diazinon. The risk of diazinon reducing food sources for chinook salmon and steelhead trout, however, is low, because diazinon-tolerant invertebrates, such as aquatic and terrestrial insects, crustaceans, mysids, and amphipods, are the major food organisms of these fish.

Delta Smelt and Longfin Smelt. Early life stages of delta smelt and longfin smelt occur in these basins during the high-diazinon-use period (January and February). Although cladocerans comprise part of the diet of both species of smelt, copepods, mysids, and other small crustaceans are the primary food sources of young life stages.[83] Delta smelt have been shown to shift diets depending on food availability.[7] The effects of dietary shifts on smelt growth, survival, and reproduction is an area of uncertainty that needs additional research.

Green and White Sturgeon. Early life stages of both sturgeon species occur during the high-diazinon-use period. The primary diet of these bottom forage fish species, however, is amphipods and mysids, not the diazinon-sensitive cladocerans. Ecological risk from diazinon indirectly impacting early life stages of green and white sturgeon by impairing their diet is unlikely.

Striped Bass. The principal food of larval striped bass is the copepod *Eurytemora affinis*, but other copepods and cladocerans are also consumed.[4] As the fish grow, their diet shifts to *Neomysis mercedis* as well as *Corophium* species and small threadfin shad.[4,84,85] If cladocerans were reduced but other invertebrates were not, the diet of striped bass would not be greatly affected.

The early life stages of striped bass occur in the Sacramento–San Joaquin Basins after mid-March, several weeks after the peak diazinon exposures have passed. If invertebrates were affected by diazinon exposure in January and February, it is possible that populations would continue to be reduced later in the season, when striped bass larvae depend on these organisms for food. Research on the population dynamics and recovery times of zooplankton in the Sacramento–San Joaquin system would help to resolve this question.

Splittail. Though adult splittail are benthic foragers, early life stages are found in midwater and may feed on zooplankton.[8,86] Early life stages of splittail are not present in the Sacramento–San Joaquin Basins during the peak exposures periods for diazinon (January and February). As discussed for striped bass, however, effects of diazinon on zooplankton populations might persist until later in the year.

American Shad. Early life stages of American shad are not found concurrently in the Sacramento–San Joaquin Basins when peak diazinon exposure occurs. Therefore, ecological risk of diazinon impacting the diet of this fish species is judged to be low.

4. RISK CHARACTERIZATION

The ecological risk of a chemical can be characterized by comparing exposure concentrations with effect concentrations. The simplest form of risk characterization is a simple quotient (or ratio) of single values representing exposure and effects, respectively. Typically, the quotient is calculated using an extreme high value for exposure and an effect concentration representing the most sensitive species for which data are available. This inherently conservative approach can be made even more protective by applying an additional factor to account for the possibility of more sensitive (untested) species and worst-case exposure situations. The quotient method is appropriate in the first stage of a risk assessment[44,87–89] as a screening tool to identify chemicals unlikely ever to exceed toxic concentrations. Chemicals that do not pass this extreme safety criterion are then subjected to more refined analysis to characterize risk more precisely.

One refinement in the risk characterization is to determine the distribution of exposure concentrations under different scenarios, rather than assessing only a single (extreme) exposure situation. A particular point on this distribution (such as the 90th centile) can be selected to represent a reasonable worst-case exposure, and a risk quotient calculated using this value along with the toxicity concentration for the most sensitive species tested. This approach accounts for variability in potential exposure concentrations, but still simplifies the expression of effect concentration.

A further refinement is to determine the distribution of species sensitivities as well as the distribution of exposure concentrations. Points on both distributions (e.g., the 10th centile of the species sensitivity distribution and the 90th centile of the exposure distribution) are used to calculate a risk quotient or "Margin of Safety."[44] Though variation in both exposure and effects is thereby taken into account, risk is still expressed as a simple quotient, and most of the additional information is lost from the risk characterization.

From the same distributions used to calculate the margin of safety, a truly probabilistic risk characterization can be derived. From the exposure distribution, the probability of an exposure exceeding a specified point on the species sensitivity distribution (such as the 10th centile) can be estimated.[90] Such a probabilistic characterization provides much more information than a quotient, but still internalizes a judgment about the level of effect (centile on the species sensitivity distribution) considered acceptable. The Joint Probability Curve (JPC) proposed by The Ecological Committee on FIFRA Risk Assessment Methods (ECOFRAM)[88] avoids this limitation by displaying the full relationship between frequency of exposure and magnitude of effect.[47] JPCs were used to characterize the ecological risk of diazinon in the Sacramento and San Joaquin River systems.

The derivation of a JPC is illustrated (Fig. 10) using the distribution of measured concentrations at Vernalis in February (Fig. 3) and the distribution of toxicity data for arthropods (Fig. 7). Both distributions are characterized by log-normal regression lines (Fig. 10, upper panel). Each concentration on the horizontal axis corresponds to a centile of the arthropod toxicity distribution and to an exceedence probability on the Vernalis concentration regression. The JPC is defined by these pairs of points (Fig. 10, lower panel). The resulting "probability of exceedence" (vertical axis of the JPC) represents the likelihood that a sample selected at random from the set of surface water measurements would contain a higher diazinon concentration than the corresponding centile of the species toxicity values (horizontal axis of the JPC).

JPCs relating exposure concentrations in January, February, and March at the primary sites to arthropod LC_{50}s are presented in Fig. 11. At Sacramento, the probability of exceeding the LC_{50} for 10% of the arthropod species is near zero even in January and February, the months with the highest diazinon concentrations. The JPCs for Vernalis are slightly higher than those for Sacramento, but concentrations exceed the LC_{50} for 10% of the species only 3.5% of the time in February, the worst month. The higher diazinon concentrations at Laird Park are reflected in JPCs shifted up and to the right. The probability of exceeding the LC_{50} for 10% of the species is about 12% in both January and February at Laird Park. A 12% probability of exceedence at Laird Park in January and February means that 12% of the samples collected at Laird Park during January and February—or, on average, three days in January and three days in February each year—would exceed the LC_{50} for 10% of arthropod species.

Analysis of the data from the secondary sites on the San Joaquin River showed that some locations, particularly the agriculturally dominated creeks and drainage channels, had higher frequencies of overlap with the sensitivity distribution than the primary sites. At secondary sites with sufficient data for analysis (i.e., sites where six or more samples contained detectable amounts of diazinon), the frequency of exceeding the 10th centile for arthropods ranged from 3.9% (Spanish Grant Combined Drain) to 19.2% (Turlock Irrigation District Lateral #3). For all creek and drain samples combined, the exceedence frequency was 11.5%. Exceedence probabilities were generally lower at the secondary sites on the San Joaquin mainstem and major tributaries. For all mainstem and tributary samples combined, the frequency of exceeding the 10th centile for arthropods was 4.1%. JPCs (Fig. 12) confirm the greater likelihood of effects in creeks and drains compared with sites on the San Joaquin mainstem and major tributaries.

Though each of the secondary sites was sampled no more than a few times each month, the results were fairly consistent among all the mainstem and tributary sites, and among all the creek and drain sites. Data from these two sets of sites (summarized in Table V), including all of the sites listed in Table IV (some of which were sampled too infrequently for separate distribution analysis), were combined for analysis of concentration distributions by month (Fig. 13). The results indicated that 14.3% of the samples taken during February from secondary sites on the mainstem and tributaries, and 41.9% of the samples from the creeks and drains, exceeded the 10th centile of arthropod sensitivity. Exceedence probabilities were much lower during other months. These results are strongly biased, because the data do not reflect random sampling. Samples for analysis were taken at times and places where high diazinon concentrations were expected.

Even where the risks to arthropods were greatest (creeks and drains in February), risks to fish were very low (Fig. 14). The probability of exceeding the 10th centile for fish (80,000 ng/L) was only 0.3% at

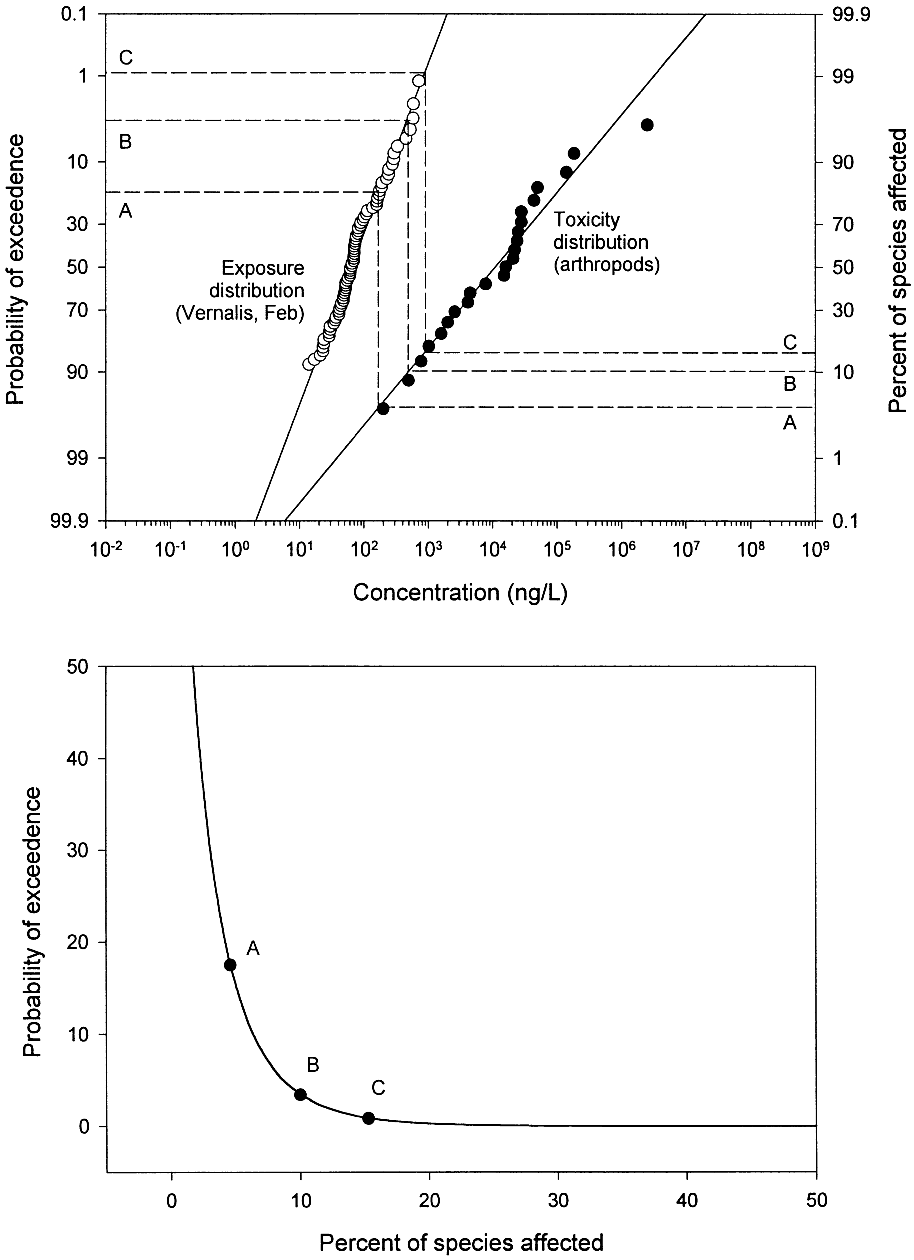


Fig. 10. Derivation of a Joint Probability Curve from distributions of exposure (exceedence curve) and toxicity (species sensitivity curve). Example points A, B, and C on the Joint Probability Curve (lower panel) are derived from the intercepts of concentrations A, B, and C on the exposure and toxicity distributions (upper panel).

this time, and less than 0.1% in other months. Except for a single observation of 36,800 ng/L in the Newman Wasteway, the highest measured concentration in more than 1,500 samples analyzed was 2,600 ng/L. The margin of safety is wide enough that even sublethal effects, or effects on sensitive life stages, are unlikely to result from diazinon exposure in these waters. Though chronic effects have been observed at concentrations less than 1,000 ng/L (Table VII), these occur only after exposure durations of at least several weeks. diazinon concentrations reach these levels in the Sacramento–San Joaquin for shorter periods of time, if at all; in general, the higher the concentration, the more compressed the exposure period.[3] These

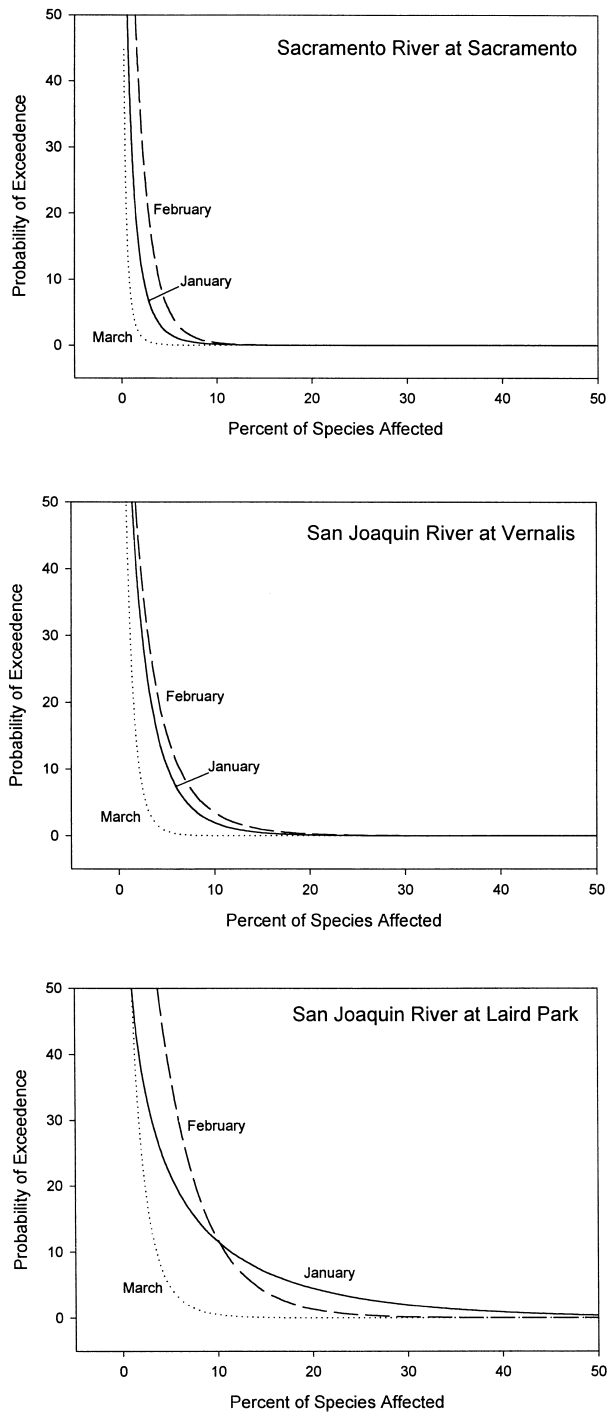


Fig. 11. Joint Probability Curves relating probability of exceedence at primary sites to percent of arthropod species affected.

data suggest that direct toxic effects of acute or chronic diazinon exposure are unlikely for fish in the Sacramento and San Joaquin River systems.

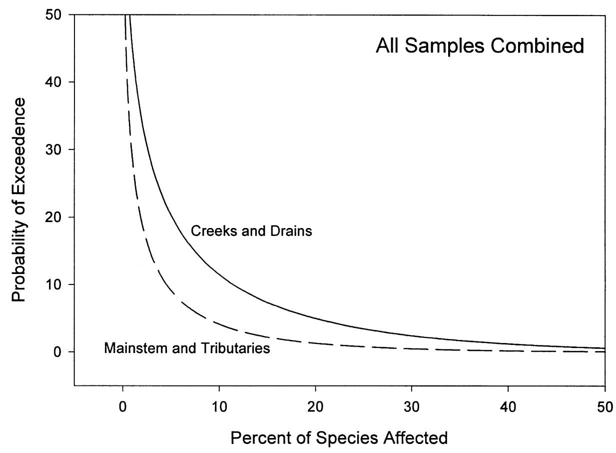


Fig. 12. Joint Probability Curves relating probability of exceedence at secondary sites (all months combined) to percent of arthropod species affected.

5. SOURCES OF UNCERTAINTY

5.1. Uncertainty Associated with Exposure Characterization

The primary sources of diazinon exposure data used in this risk assessment had limited temporal (1991–94) and spatial (26 stations) coverage for an ecosystem that covers more than 350 river miles. In particular, diazinon exposure data were lacking in the low-order streams and upper reaches of both of these basins during the high-diazinon-use period when diazinon-sensitive arthropod species (important for early life stages of fish populations) are present. Other specific sources of uncertainty associated with exposure characterization are presented below.

5.1.1. Sampling Frequency

The monitoring programs upon which this assessment was based did not incorporate uniform or random sampling designs compatible with unbiased statistical analysis of frequency distributions. The USGS study and the DPR sampling at Laird Park came closest to this objective, with samples taken at regular, predetermined intervals. The DPR Lagrangian surveys and the CVRWQCB sampling program were purposefully directed toward times and places when high diazinon concentrations were expected, and were not designed for use in probabilistic risk assessment. Thus, the exposure database was severely biased toward extreme high values and excluded a much greater number of low concentrations.

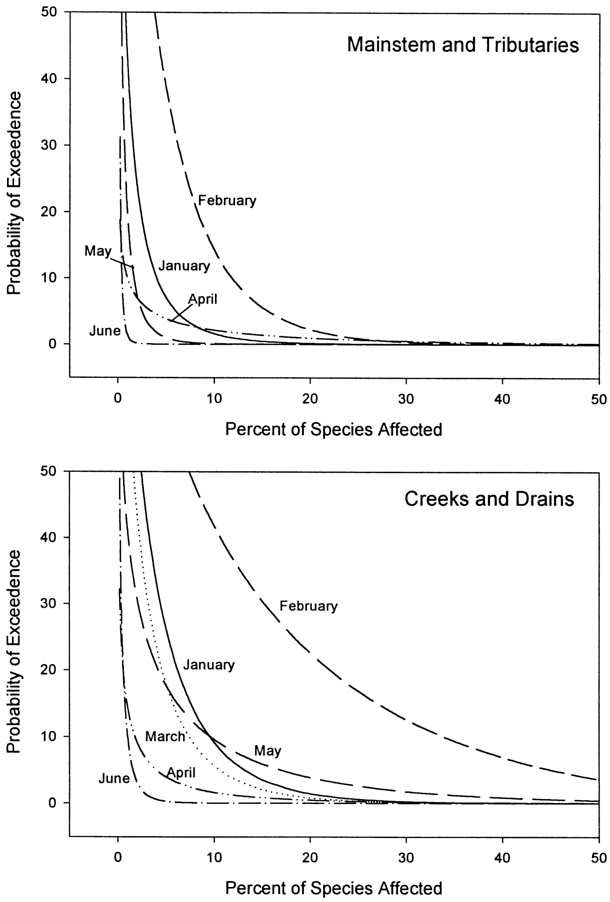


Fig. 13. Joint Probability Curves relating probability of exceedence at secondary sites to percent of arthropod species affected.

5.1.2. *Geographic Variability*

The exposure database was limited to 26 sites, many of which were sampled fewer than a dozen times. No data were available for tributaries of the Sacramento River, and only one location on the Sacramento mainstem was sampled. There were also no measurements from the delta region except those reported by Kuivila and Foe,[3] which were too incomplete to be incorporated into the probabilistic risk assessment. Within the San Joaquin system, some consistency was noted among various sites on the mainstem and major tributaries, and among sites on agriculturally dominated creeks and drainage channels. Diazinon concentrations, however, sometimes differed greatly from site to site, presumably reflecting differences in land use and watershed hydrology. Future monitoring programs should expand the geographical range of the sampling sites with an emphasis on ecologically important habitats.

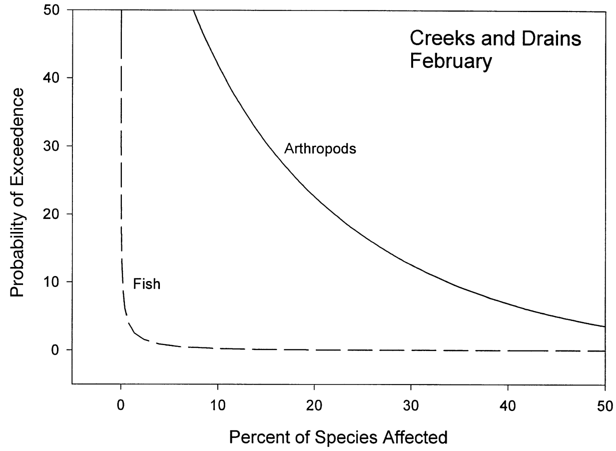


Fig. 14. Joint Probability Curves relating probability of exceedence at secondary sites in February to percent of fish species and arthropod species affected.

5.1.3. *Climatic Variability*

Concentrations of diazinon in surface waters fluctuate greatly from year to year depending on weather patterns, particularly the amount and timing of rainfall. The measurements spanned three years (1991 to 1994), some of which were unusually dry. The effects of drought on diazinon concentrations in surface waters are not known. Reduced precipitation would be expected to reduce pesticide runoff (potentially leading to lower diazinon concentrations than normal years), but also to reduce the volume of water available for pesticide dilution (potentially leading to higher diazinon concentrations than normal years). Data spanning wet and dry years would be more representative.

5.2. Uncertainty Associated with Ecological Effects Data

Due to the relatively small number of species that can be routinely cultured and tested in laboratory toxicity studies, there is uncertainty when extrapolating these toxicity data to responses of natural taxa found in the environment of interest. For example, only 6% of the 769 freshwater fish species in North America have been tested with any of the priority pollutants.[91] In the case of diazinon in the Sacramento–San Joaquin Basins, this is particularly relevant since diazinon toxicity data for resident fish and invertebrates species were limited. Therefore, the possibility exists of incorrectly assessing risk to a keystone species critical to the structure and function of the Sacramento–San Joaquin ecosystem. Additional acute and chronic diazinon toxicity data for resident invertebrates and early life stages of fish would greatly reduce uncertainty in this risk assessment.

Even when data are available for resident species, there is uncertainty when extrapolating from single-species measurement endpoints (e.g., toxicity to arthropods) to assessment endpoints (e.g., sustainability of fish populations). One goal of this risk assessment was to determine the risk of indirect effects on fish species if diazinon adversely impacts their food source during a key life stage when food is essential. Many fish can change diets (e.g., switch from diazinon-sensitive cladocerans to more diazinon-tolerant organisms such as copepods) without experiencing nutrition problems, but this assumption is a source of uncertainty in the risk assessment.

The use of acute data for predicting ecosystem effects is sometimes assumed to be a source of uncertainty. Slooff, van Oers, and de Zwart,[92] however, in their review of single species and ecosystem toxicity for various chemical compounds (diazinon not included) concluded that acute tests are reliable predictors of ecosystem effects. The use of acute toxicity distributions for a wide range of species, as well as mesocosm/microcosm data, reduces the uncertainty associated with using acute data.

Ecological uncertainty includes the effects of confounding stressors (such as other pesticides) and the ecological redundancy of the functions of affected species. Investigators have reported potential impacts of other pesticides (including chlorpyrifos, azinphos methyl, ethyl parathion, malathion, and fonofos) on the resident biota of the Sacramento–San Joaquin Basins.[2,3,65–68] Because several of these pesticides may be present in the surface waters at the same time as diazinon, joint toxicity might be expected.[2] Bailey *et al.*[93] reported that pesticides with the same mode of action, such as organophosphorus insecticides, may cause additive toxicity. The presence of these pesticides at the same time as diazinon, particularly the more toxic organophosphorus insecticides such as chlorpyrifos, makes it difficult to assess the risk of diazinon alone.

6. CONCLUSIONS

Based on the available exposure and toxicity data, diazinon does not present a direct ecological risk to fish populations in the Sacramento–San Joaquin Basins. Furthermore, diazinon does not present a risk to most of the important invertebrates in the system. Diazinon concentrations exceed the toxic level for the most sensitive 10% of arthropod species (primarily cladocerans) during January and February at some locations, especially in the agricultural drainage waters flowing to the San Joaquin River between the Merced and Stanislaus Rivers. Indirect effects on some fish populations cannot be dismissed if sensitive native arthropods are reduced at critical periods when they are needed as food by early life stages of fish. The present analysis, however, indicates that indirect effects of diazinon exposure are unlikely in the Sacramento–San Joaquin Basins, because the most sensitive invertebrates are not a major food source for the fish species of concern.

The six risk assessment questions proposed in the Introduction are addressed below.

1. *What is the likelihood that diazinon concentrations in the Sacramento and San Joaquin Rivers and their tributaries are high enough to cause mortality in any of the nine key fish species?* The probability of diazinon concentrations exceeding the 10th centile for fish toxicity (80,000 ng/L) was less than 0.4% at all primary and secondary sites. When results were analyzed by month, the probability of exceeding the 10th centile for fish sensitivity was always less than 0.1% on mainstem and tributaries, and less than 0.3% on creeks and drains. These probabilities reflect all measured concentrations for the sites in question during the 1991–94 monitoring period. That is, fewer than 0.1% of the measurements made on samples from the Sacramento and San Joaquin mainstem and tributaries in 1991–94 exceeded the 10th centile of fish toxicity.

Only one fish species of concern in the Sacramento–San Joaquin—steelhead (same species as rainbow trout, *Oncorhynchus mykiss*)—was included in the toxicity database. The database is sufficiently extensive, however (29 fish species), to be considered representative. *Fish in the Sacramento and San Joaquin Rivers are unlikely to be at risk of acute effects from diazinon residues in the water.*

2. *What is the likelihood that diazinon concentrations are high enough and last long enough to cause chronic effects on survival, growth, or reproduction of any of the nine key fish species?* For diazinon, the most sensitive chronic toxicity endpoints for fish are fecundity, hatching success, and growth of offspring following long-term continuous parental exposure. The lowest concentration reported to cause such effects was 470 ng/L. Chronic toxicity occurs, however, only if exposure persists for several weeks or longer, which is not the case in the Sacramento and San

Joaquin Rivers. Shorter exposures (e.g., 30 to 60 days) have little or no effect on fish survival, growth, and reproduction at diazinon concentrations ranging from 10,000 to 1,100,000 ng/L. *Fish in the Sacramento and San Joaquin Rivers are unlikely to be at risk of direct chronic effects from diazinon residues in the water.*

3. *What is the likelihood that diazinon is causing reductions in invertebrate populations?* The probability of diazinon concentrations exceeding the 10th centile for arthropod toxicity (480 ng/L) was 0.3% on the Sacramento River at Sacramento, 0.9% on the San Joaquin River at Vernalis, and 4.6% on the San Joaquin River at Laird Park. At secondary sites on the San Joaquin mainstem and tributaries, the overall probability of exceeding the 10th centile for arthropods was 4.1%; at secondary sites on creeks and drains, 11.5%. *Subject to the qualifications expressed below, it can be concluded that sensitive arthropods in the Sacramento and San Joaquin River Rivers and their major tributaries are occasionally exposed to toxic concentrations of diazinon in the water. The most sensitive arthropods (mainly cladocerans) are more frequently exposed to toxic diazinon concentrations in small creeks and drains.*

4. *Where and when are the effects likely to be greatest?* The probability of diazinon concentrations exceeding the 10th centile for arthropod sensitivity is highest in small, agriculturally dominated creeks and drains such as the Turlock Irrigation District Laterals and Orestimba, Del Puerto, and Ingram/Hospital Creeks. These are typically intermittent streams, and some of the highest diazinon concentrations measured during the study period occurred shortly after intervals of no flow. Diazinon concentrations toxic to sensitive arthropods occur most frequently in January and February. *Based on the data for 1991–94, the highest probability of toxic effects of diazinon on arthropods occurs in agricultural drainage channels during two winter months.*

5. *Which species are at greatest risk?* Except for *Gammarus fasciatus* (LC_{50} = 200 ng/L), the four daphnids are the most sensitive of the 63 species in the toxicity database. The geometric mean of the LC_{50} values for the four species of cladocerans is 887 ng/L. Mysids (geometric mean LC_{50} = 4,320 ng/L, 2 species) and amphipods (geometric mean LC_{50} = 8,060 ng/L, 5 species) are moderately sensitive to diazinon. Aquatic insects (30,200 ng/L, 7 species), copepods (80,300 ng/L, 2 species), and rotifers (21,500,000 ng/L, 1 species) are relatively insensitive. *Cladocerans are by far the most sensitive group of invertebrates to diazinon, and are therefore at greatest risk of direct toxic effects.*

6. *If some invertebrate species are likely to be affected, are these species critical food organisms for fish, such that invertebrate population reductions will affect fish growth and survival?* Of the nine fish species of concern in the Sacramento–San Joaquin Rivers, only five (delta and longfin smelt, Sacramento splittail, striped bass, and American shad) feed on the most sensitive invertebrates: cladocerans. Cladocerans, however, are not the primary food source for any of these species. Less sensitive invertebrates, especially mysids, copepods, and amphipods, are more important in the diets of the fish early life stages. *Fish in the Sacramento–San Joaquin are unlikely to be affected by reductions in the populations of sensitive invertebrates.*

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