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Diazinon in San Francisco Bay

Impairment Assessment/Conceptual Model

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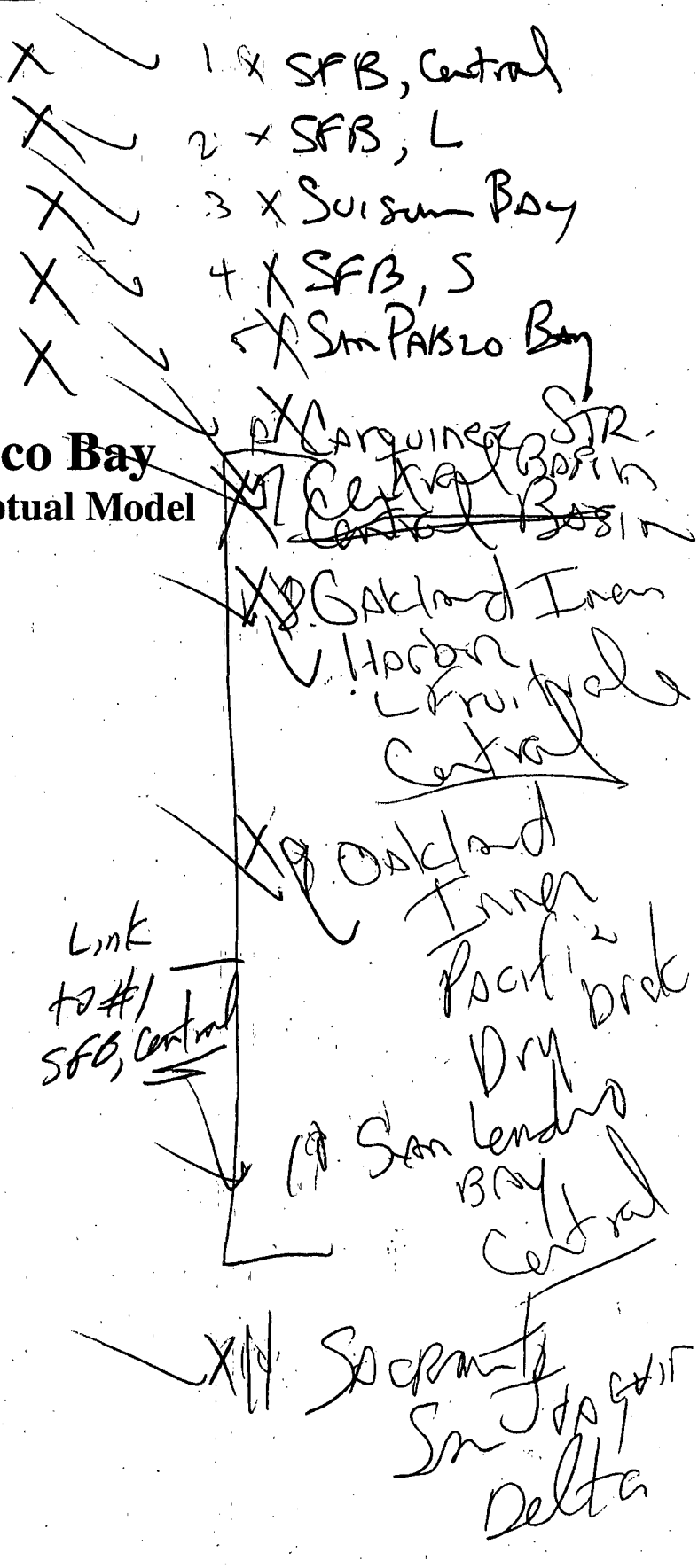

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1. Introduction

Section 303(d) of the federal Clean Water Act (CWA) requires states to identify those water bodies not attaining water quality standards (i.e., waters whose beneficial uses have been impaired), to identify the pollutant causing the impairment, and to develop remediation plans (known as "total maximum daily loads" or TMDLs) for each pollutant in each water body that will reduce and eventually eliminate the impairment and restore the beneficial use(s). In response to observations of ambient water toxicity in northern San Francisco Bay that were believed to result from runoff-related pesticides, the San Francisco Bay Regional Water Quality Control Board identified San Francisco Bay as an impaired water body due to pesticide toxicity in 1998; the US EPA subsequently narrowed the 303(d)-listing to be specific for diazinon, a widely-used organophosphate pesticide that had been shown to cause ambient water toxicity in many studies of upstream ambient waters in the Bay's watersheds.

This report includes a current impairment assessment and a conceptual model for diazinon in San Francisco Bay. The impairment assessment presents the rationale for the initial 303(d) listing and summarizes existing data on diazinon and ambient water toxicity in San Francisco Bay. The conceptual model describes the sources of pesticides to the Bay and the processes that determine the occurrence and concentrations of diazinon in the system. Because there have been significant changes in the use of diazinon over the past 10 years, an important part of this document is the assessment of recent developments that affect the potential impairment of San Francisco Bay by diazinon, as well as consideration of other "emerging use" pesticides, which are seeing increased use as replacements for diazinon.

1.1 Regulatory Background

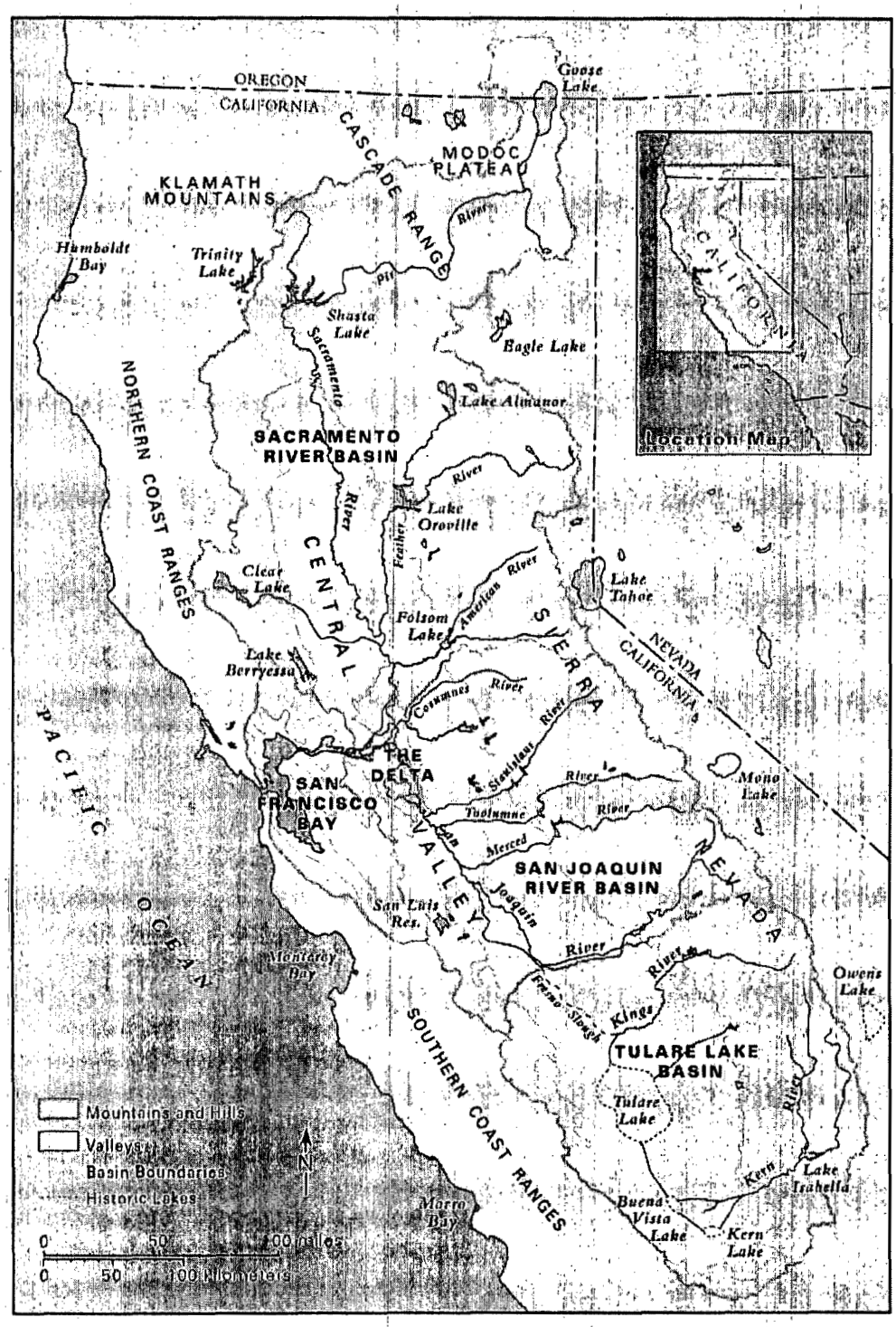
Section 303(c)(2)(a) of the federal Clean Water Act requires that states develop water quality standards to protect human health and the environment, and Section 303(d) requires that states develop lists of waterbodies that do not meet those standards.

In California, the Porter-Cologne Water Quality Control Act, which is contained in the California Water Code, identifies the State Water Resources Control Board (SWRCB) and Regional Water Quality Control Boards (RWQCBs) as the principal agencies responsible for controlling water quality. These boards are responsible for compiling the 303(d) lists of impaired waterbodies, which are determined using state policy and EPA guidelines, and which are subject to approval by EPA. In complying, these agencies have developed successive lists of "impaired" water bodies since 1976. The SWRCB has subsequently issued a draft **Functional Equivalent Document** to formalize this process, establishing the *Water Quality Control Policy for Developing California's Clean Water Act Section 303(d) List* (SWRCB 2003) to provide the guidelines to be used for listing waters and developing TMDLs, as well as for removing waterbodies from the 303(d) list if the listing was based on faulty data, if objectives or standards have been revised and the waterbody meets the new standards, or if the standards have been fully attained.

1.2 San Francisco Bay: The Impaired Waterbody

San Francisco Bay is the largest estuary on the West Coast of the United States, draining an overall watershed area of 60,000 square miles (Figure 1), and the Bay's deepwater channels, tidal mudflats and wetlands, and freshwater streams and rivers provide a wide variety of important ecological habitats. The Sacramento and San Joaquin Rivers enter the northern reach of the Bay via the Delta, at the eastern end of Suisun Bay, and contribute almost all of the freshwater flow into the Bay (with 90% of the annual runoff occurring during the winter rainy season), although there are many smaller tributary rivers and streams within the Bay's immediate watershed. Suisun Bay, which is the largest brackish-water marsh in the United States, flows through the Carquinez Straits into San Pablo Bay. The South Bay, at the other end of the Bay system, receives much less freshwater inflow than does the northern reach, and acts more like a tidal lagoon. The northern and southern Bay segments meet in the Central Bay, which is the Bay's connection to the Pacific Ocean, and which is heavily influenced by oceanic conditions.

Diazinon is on the 303(d) list for all 8 "segments" of San Francisco Bay (i.e., parts of the bay recognized on the list): Sacramento/San Joaquin River Delta, Suisun Bay, Carquinez Strait, San Pablo Bay, Richardson Bay, Central San Francisco Bay, Lower San Francisco Bay, and South San Francisco Bay (Figure 2). Diazinon is also on the 303(d) list for waters upstream of the San Francisco Bay system; however, these bodies of water are under the regulatory jurisdiction of the Central Valley Regional Water Quality Control Board (CVRWQCB).



Map by Ben Pease (www.peasepress.com); data courtesy of the Bay Institute of San Francisco and the San Francisco Estuary Institute, 1998

Figure 1. The San Francisco Estuary watershed, including the Sacramento River Watershed and the San Joaquin River watershed in the Central Valley, and the San Francisco Bay watershed.

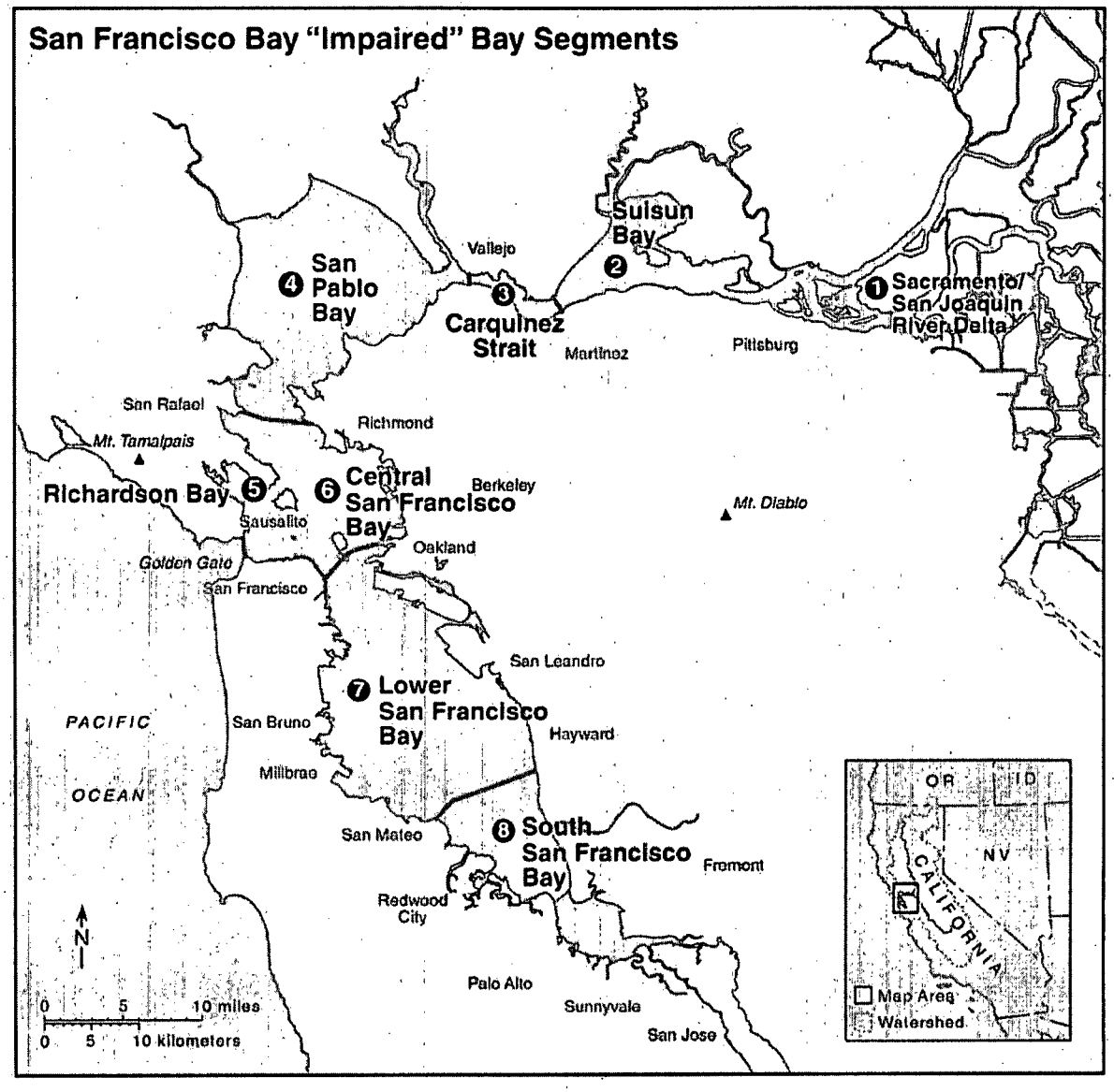


Figure 2. The San Francisco Bay system, including the 8 segments of the Bay that have been placed on the 303(d) list for impairment by diazinon.

1.3 Diazinon: Background Information

Diazinon (Figure 3) is the trade name for *O,O*-diethyl *O*-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] ester, a broad-spectrum organophosphate (OP) insecticide and nematicide. OP pesticides are used in a wide variety of agricultural applications, as well as numerous urban applications (landscape maintenance/gardening, structural maintenance of buildings [e.g., termite control]). Until very recently, diazinon was one of the most widely-used and heavily-applied pesticides in both agricultural and urban settings.

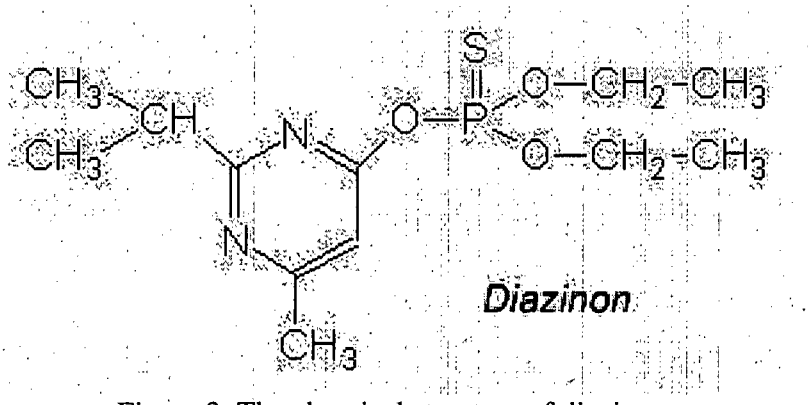


Figure 3. The chemical structure of diazinon.

Like all of the OP pesticides, diazinon is a synthetic compound that does not occur naturally in the environment. Diazinon is sold under a wide variety of trade names for both commercial usage and over-the-counter consumer use products. Diazinon is relatively water-soluble, and when released into the environment via its intended application and/or improper disposal, it readily finds it way into surface waters where it can come into contact with aquatic organisms. Once inside the cells of these organisms, diazinon is metabolized to form diazoxon, which is the toxic form of diazinon. Diazoxon, in turn, inactivates the enzyme acetylcholinesterase (AChE). The normal function of AChE is to metabolize acetylcholine (ACh), a neurotransmitter that allows the transfer of nerve impulses from nerve cells to receptor cells (e.g., muscle cells). When exposure to diazinon causes the inactivation of AChE, the metabolism of ACh is inhibited, and the nerve impulses continue indefinitely, causing paralysis and eventually death.

2. Impairment Assessment: the 303(d) Listing

2.1 Basis for the 303(d) Impairment Listing

2.1.1 Observations of Episodic Ambient Water Toxicity in San Francisco Bay

The San Francisco Estuary Regional Monitoring Program for Trace Substances (the RMP) is a multi-component monitoring and research program that has been assessing the degree and nature of contamination in San Francisco Bay since 1993. Toxicity testing of the Bay's ambient surface waters has been an integral component of the RMP since its conception. The fundamental approach of toxicity testing is to expose selected aquatic organisms to samples of the Bay's ambient waters under laboratory conditions, and to assess potential adverse effects, such as reduced survival and/or impairment of important sub-lethal responses (e.g., growth, reproduction, development) that may result.

As part of the RMP monitoring, ambient water samples were collected at selected stations located throughout San Francisco Bay. Toxicity testing performed on these water samples during the first several years of monitoring these waters indicated that there was no significant toxicity in the Bay.

However, Year 4 (1996) of the RMP ambient water toxicity testing saw dramatic and significant developments. In February, there was region-wide toxicity to the test organisms (the mysid shrimp, *Americamysis bahia*) with dramatic and significant reductions in survival at the 4 northern-most stations: Napa River, Grizzly Bay, the Sacramento River, and the San Joaquin River (Figure 4). No mysid toxicity was observed for any of the other February water samples. Again in July, there was region-wide toxicity to the mysid with slight, but statistically significant reductions in survival at the Grizzly Bay, the Sacramento River, and the San Joaquin River stations (Figure 4).

Year 5 (1997) of the RMP also saw dramatic toxicity in the baseline ambient water toxicity testing. In January, there was once again region-wide toxicity to the mysid with significant reductions in survival at the four northern-most stations: Napa River, Grizzly Bay, the Sacramento River, and the San Joaquin River (Figure 4).

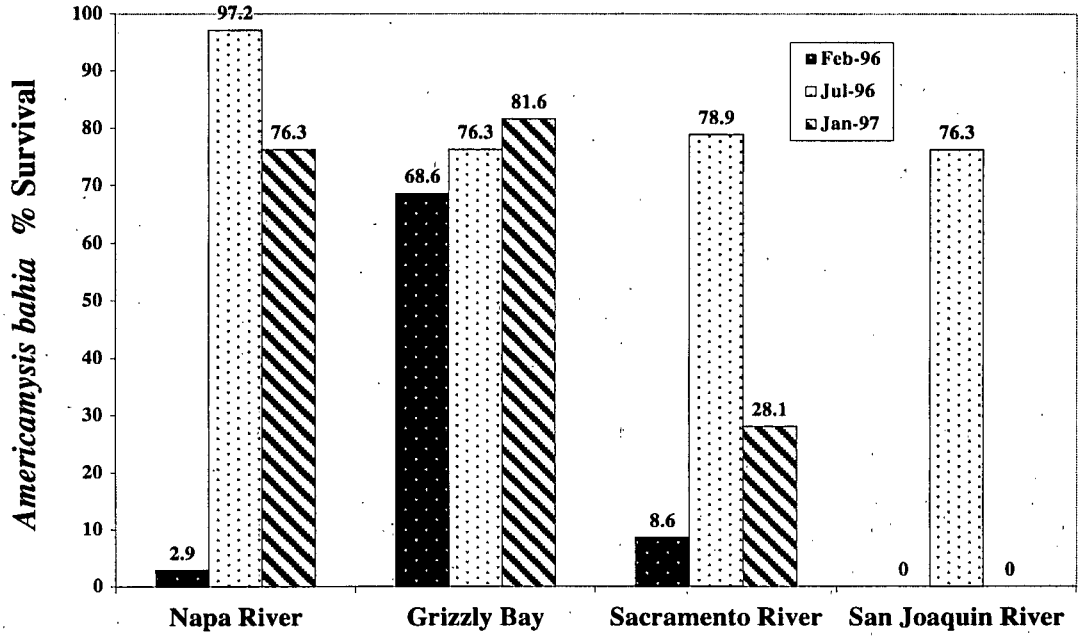


Figure 4. Toxicity of RMP ambient water samples to *Americamysis* (formerly *Mysidopsis*) *bahia*. Percent survival data have been normalized to the Control treatment responses. With the exception of the July 1996 Napa River sample, each sample resulted in a statistically significant reduction in mysid survival relative to the Control treatment response.

2.1.2 Hypothesis: Ambient Water Toxicity in San Francisco Bay is Due to Event-Based, Episodic "Pulses" of Pesticides

Interestingly, the February 1996 sampling was the first time that the RMP baseline sampling had occurred following significant rainfall in the Estuary's watersheds. Earlier studies had already reported that agricultural runoff in the San Joaquin and Sacramento River watersheds was frequently toxic to aquatic organisms, particularly following significant rainfall events (Foe and Connor 1991; Foe 1995). In 1988, the CVRWQCB began conducting monitoring studies of ambient water toxicity in the San Joaquin River basin. They found that much of the San Joaquin River was toxic "about half the time" to *Ceriodaphnia dubia*, a freshwater planktonic invertebrate (Foe and Connor 1991). It was hypothesized that pesticides in agricultural runoff were causing the observed toxicity; concurrent monitoring of agriculturally-dominated tributaries of the river revealed similar toxicity problems (Foe and Connor 1991). Follow-up monitoring in 1991-92 observed that 22% of the water samples collected from the San Joaquin Basin were toxic to *Ceriodaphnia* (Foe 1995). Most of the observed toxicity could be attributed to the concentrations of four pesticides: diazinon, chlorpyrifos, fonofos, and carbaryl, although other pesticides were also detected in the water samples. When the pesticide concentrations were normalized to their toxicity to *Ceriodaphnia* (in a Toxic Units approach), it was found that diazinon, chlorpyrifos, and parathion accounted for over 90% of all toxicity. More recent ambient water toxicity monitoring the Sacramento River watershed and in the Delta revealed significant toxicity to *Ceriodaphnia*, and concurrent Toxicity Identification Evaluations (TIEs)

demonstrated that diazinon, chlorpyrifos, and carbofuran were the main causes of this toxicity (Werner et al. 2000).

2.1.3 The 303(d) Impairment Listing

In response to the RMP observations of ambient water toxicity, and given the linkage established between similar toxicity and pesticides in upstream ambient water, the SFBRWQCB identified all San Francisco Bay segments as being impaired due to "Pesticides" in 1998:

> "***Pesticides*** have been added as a cause of impairment to all Bay segments. The pesticide diazinon has been measured at levels that cause water column toxicity. The pesticide chlorpyrifos may also be a problem. This listing is consistent with listing of the Delta for these pesticides by the Central Valley Regional Water Quality Control Board." (SFBRWQCB 1998).

This impairment listing was subsequently made specific for the OP pesticide diazinon by the US EPA (T. Mumley, personal communication).

2.1.4 Uncertainties Associated with the 303(d) Listing

At the time of the observations of significant ambient water toxicity by the RMP (Figure 4), funding for follow-up Toxicity Identification Evaluations (TIEs) to definitively identify the cause(s) of the toxicity was not available. In the absence of definitive information, the assumptions that the observed ambient water toxicity in the northern reach of Bay was similar to the ambient water toxicity being observed in upstream waters and that pesticides being transported into the Bay by stormwater runoff were the likely causes of the toxicity (as they were in the upstream waters) seem reasonable.

However, the diazinon and chlorpyrifos concentrations reported for water samples that were collected at the same time and same place as the toxicity testing water samples (Table 1) are well below toxicity threshold levels reported for the *Americamysis bahia* test organisms (Table 2). This does not mean, however, that the observed toxicity was not due to pesticides. For one thing, the toxicity of the OP pesticides have been shown to be additive, that is, the partial toxicity caused by one OP pesticide must be added to whatever partial toxicity is being contributed by other OP pesticides (or even other pesticides which have the same mechanism of toxicity [i.e., other acetylcholinesterase inhibitors]) as well (Bailey et al. 1997; Norberg-King et al. 1991). More importantly, studies have indicated that the toxicity of the OP pesticides is synergistic (i.e., increased dramatically, more so than just additively) with triazine pesticides (e.g., atrazine, cyanazine) or pyrethroid pesticides (Beldon and Lydy 2000; Jin-Clark et al. 2002; Denton et al. 2003). Unfortunately, the RMP has not monitored triazine or pyrethroid pesticide concentrations in San Francisco Bay's ambient waters, so we are unable to assess the likelihood of such synergistic interactions causing 'combined' pesticide toxicity. Clearly, there remains significant uncertainty regarding the actual causes of the ambient water toxicity observed by the RMP.

Table 1. Reported concentrations (ng/L) of OP pesticides in the toxic RMP water samples.						
Date	Pesticide	Phase	Napa River	Grizzly Bay	Sacramento River	San Joaquin River
February 1996	diazinon	dissolved	39	58	25	26
	chlorpyrifos	dissolved	0.68	0.36	0.44	0.30
July 1996	diazinon	dissolved	5.6	6.4	3.2	4.5
	chlorpyrifos	dissolved	0.10	<0.01	<0.01	<0.01
January 1997	diazinon	dissolved	17	not reported	31	37
	chlorpyriifos	dissolved	0.26	0.46	0.59	0.33

Table 2. Comparative toxicity of diazinon and chlorpyrifos to selected test organisms.		
Species	Diazinon 96-hr LC_{50} (ng/L)	Chlorpyrifos 96-hr LC_{50} (ng/L)
Ceriodaphnia dubia	320, 350[a]; 410, 470[b]; 470[c]; 510[d]	53-55[a]; 60[b]; 80, 130[h]
Americamysis bahia	4,200[e]; 4,820[f]; 8,500[g]	35[i,j]; 40[i*]; 56[k]

a. Bailey et al. 1997 (static exposures of neonates to measured concentrations);
b. Bailey et al. 1996 (static-renewal exposures of neonates to measured concentrations);;
c. CDFG 1992a (static exposures of neonates to measured concentrations);
d. CDFG 1992b (static exposures of neonates to measured concentrations);
e. Surprenant 1988 (flow-through exposures of <24-hr neonates to measured concentrations);
f. Nimmo et al. 1981 (static exposures of <48-hr neonates to nominal concentrations);
g. Cripe 1994 (static exposure of juveniles to measured concentrations);
h. CDFG 1992c (static exposures of neonates to measured concentrations);
i. Mayer 1987 (flow-through exposure of adults to nominal concentrations);
j. Schimmel et al. 1983 (flow-through exposure of 1-d olds to nominal concentrations);
k. Borthwick and Walsh 1981 (static exposures of juveniles to nominal concentrations).

3. Conceptual Model

The conceptual model of the fate and effects of diazinon in the San Francisco Estuary watershed synthesizes information on the sources of diazinon to the bay, and the linkages. It describes the chemical characteristics of the pesticide and the dominant processes that determine its fate within the Bay, both narratively and pictorially (Figure 5).

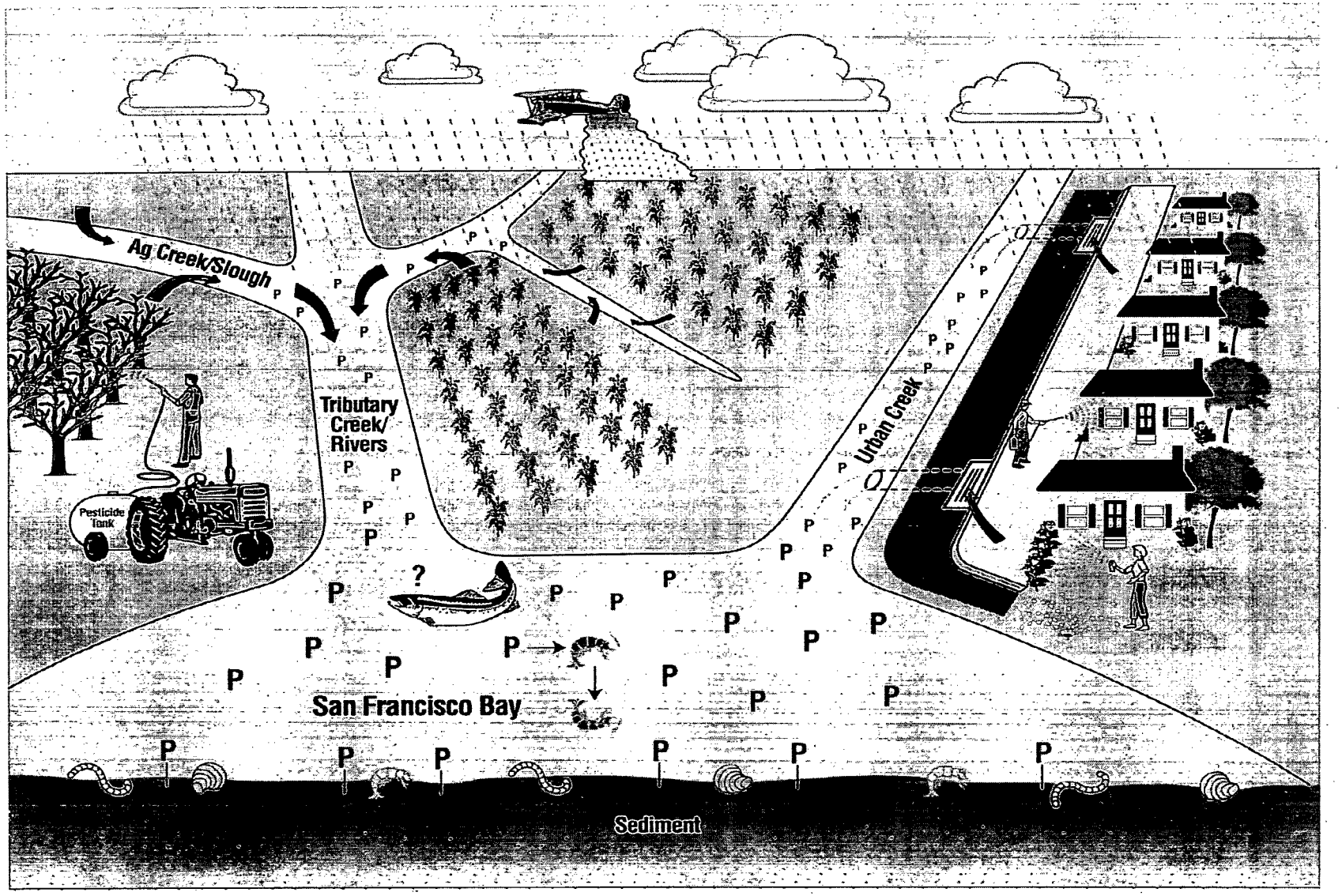


Figure 5. A conceptual model of the fate and effects of diazinon in the San Francisco Bay watersheds.

3.1 Sources and Related Fate Processes

Diazinon is a synthetic compound, and does not occur naturally in the environment. Furthermore, once released to the environment, it is subject to relatively rapid degradation. As a result, its occurrence in San Francisco Bay ambient waters results almost entirely from ***recent*** pest-control applications. The primary source for influx of diazinon into San Francisco Bay is non-point source runoff via the tributary creeks and rivers draining the agricultural and urban areas within the Sacramento River, San Joaquin River, and San Francisco Bay watersheds. Lesser, and potentially negligible, sources include: (1) point sources, including wastewater effluent and runoff from specific areas where the pesticides were used or handled, and (2) atmospheric deposition.

3.1.1 Non-Point Source Runoff from the Bay's Watersheds

Relative to many pesticides (particularly the "legacy" organochlorine pesticides [SFEI 2004]), diazinon is readily soluble in water (solubility = 40 mg/L @ 20°C [Kamrin 1997]). As a result, surface residues of diazinon remaining from applications to plants, soils, and/or anthropogenic materials will readily partition, or dissolve, into water with which they come into contact (e.g., rainfall, irrigation water, sprinklers, etc). If the volume of contact water is sufficient, then surface water runoff results, transporting the diazinon away from the application/release site, down through the watershed, and eventually into San Francisco Bay. This process can basically be characterized into 2 primary source types: agriculture applications and urban applications, which are discussed below.

3.1.1.1 Agricultural Runoff of Diazinon - Because of the extent of agricultural land use that involves the application of pesticides in the Central Valley, surface water runoff from the Sacramento River and San Joaquin River watersheds is arguably the major source of diazinon (and other current-use pesticides) to the Bay. Examination of the reported diazinon applications in the Sacramento River, San Joaquin River, and San Francisco Bay watersheds during 1990-2002 reveals that the diazinon applications in the Central Valley watersheds are much greater than in the San Francisco Bay watershed, and that agricultural applications in the Central Valley watersheds are much greater than the non-agricultural applications (Figure 6 [CDPR 2004]); at its peak in 1993, there were over 227,000 and 697,000 pounds of diazinon applied in agricultural uses in the Sacramento and San Joaquin River watersheds, respectively (CDPR 2004), although it is important to note that the applications of diazinon have been reduced significantly since then (Figure 6).

The primary agricultural applications of diazinon are during the winter orchard dormant season, typically between mid-December and early March of each year (CVRWQCB 2003). Unfortunately, this is the same period of time in which the greatest rainfall occurs: about 90% of the annual precipitation in the Central Valley falls during November-April (CVRWQCB 2002). As a result, while the degradation of the applied diazinon is relatively rapid (see discussions of degradation processes later in this report), enough is applied such that rainstorm events can mobilize a significant amount of diazinon residues (Kuivila and Foe 1995; Domagalski 1996; Domagalski et al. 1997; Holmes and DeVlaming 2003). The result of this is episodic "pulses" of pesticides that flow down through the watersheds and on into San Francisco Bay (Figure 7 [Kuivila and Foe 1995]).

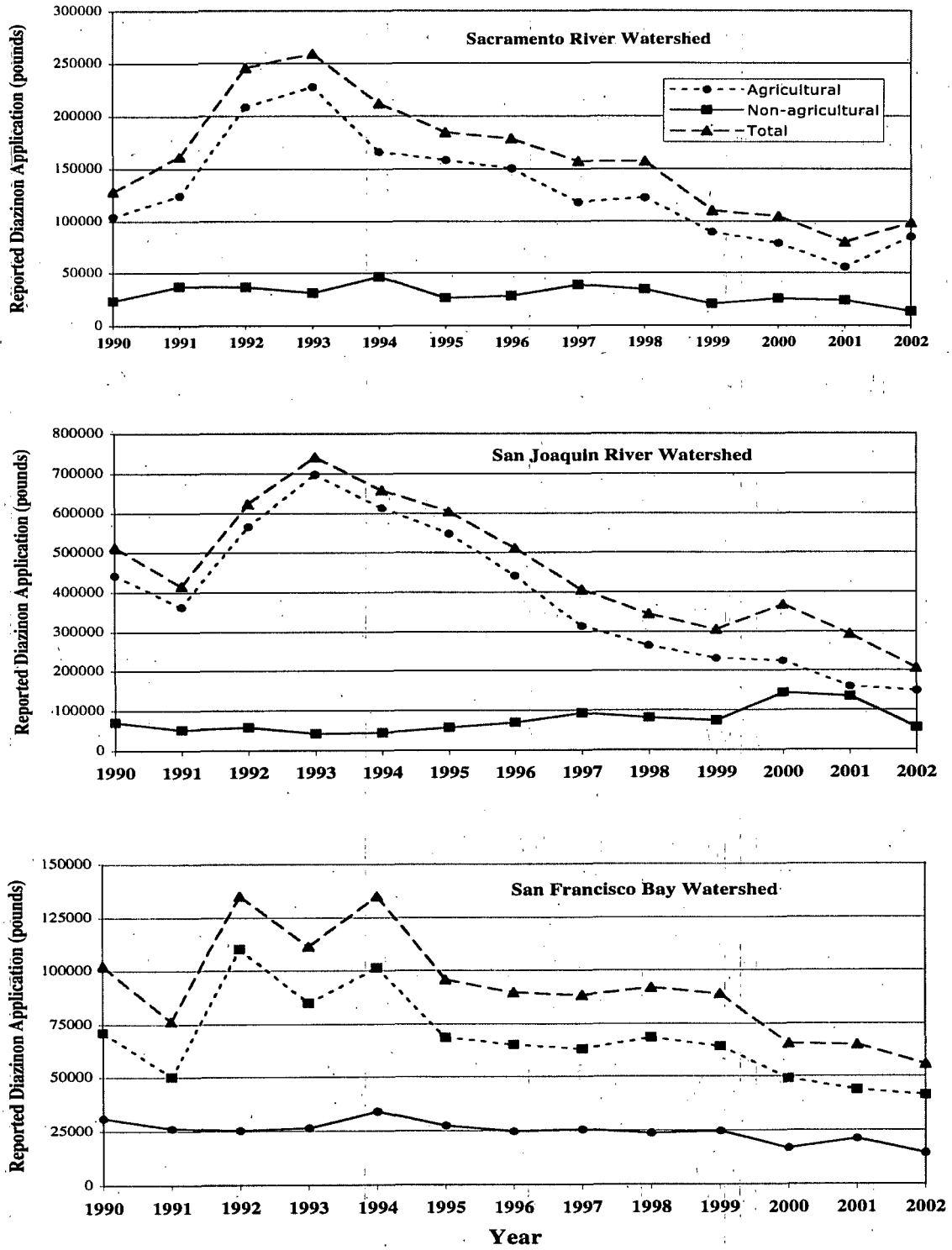


Figure 6. Trends in the application of diazinon in the Sacramento River, San Joaquin River and San Francisco Bay watersheds, 1990-2002 (CDPR 2004).

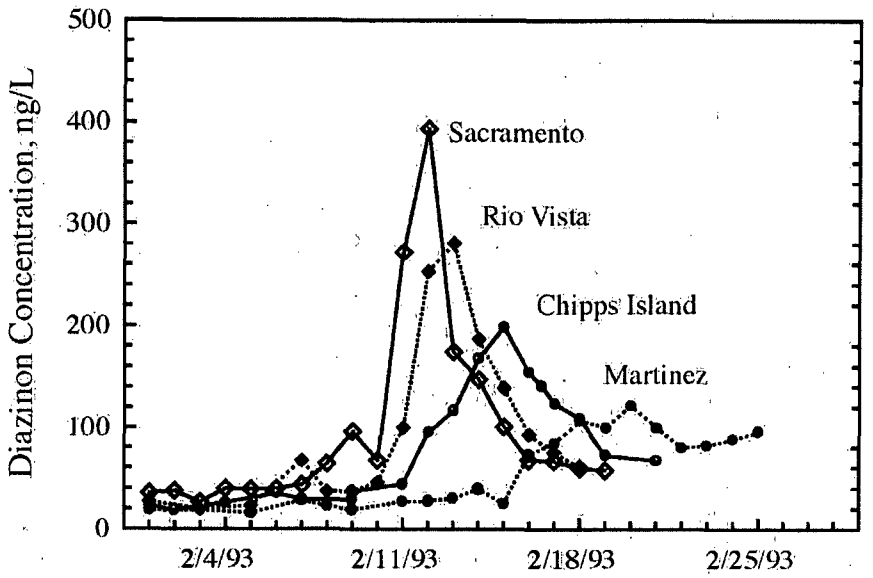


Figure 7. Concentrations of diazinon measured in the Sacramento River and northern reach of San Francisco Bay following a rainstorm in February 1993 (from Kuivila and Foe 2000; used with permission)

3.1.1.2 Urban Runoff of Diazinon - The principal urban uses of diazinon are structural pest control and landscaping and gardening, but include other more esoteric uses such as flea collars for pets. While markedly less of the total diazinon applied in the Central Valley, non-agricultural uses (much of which is urban usage) still constitute a significant amount of pesticide (Figure 6). And in the San Francisco Bay watershed, non-agricultural applications are actually greater than agricultural applications (Figure 6). Moreover, while agricultural and commercial pest control applications are legally required to be reported (and comprise part of the database represented in Figure 6), pesticide applications resulting from over-the-counter consumer uses are not reported. Alameda County and the city of Palo Alto have estimated that these unreported uses account for up 50-60% of all urban diazinon applications (cited in SBRWQCB 2002), effectively doubling the applications shown in Figure 6). Clearly, urban uses can result in significant amounts of pesticides being released within the immediate urban watershed.

Reported use of diazinon for structural pest control is relatively constant throughout the year, while the reported use of diazinon for landscaping and gardening is highest in summer and lowest in winter (CVRWQCB 2002). Because diazinon does degrade relatively quickly (see discussion of degradation processes later in this report), much of the diazinon residues remaining from these applications will have been degraded into non-toxic compounds before any significant surface water runoff. However, because much of the urban surface landscape is relatively impermeable (e.g., buildings, parking lots, streets, sidewalks, etc), there is markedly less percolation, storage, and degradation in the surface soils layers. As a result, any pesticide residues that do persist will arguably be more likely to become washed off by surface water runoff, again, ultimately flowing into San Francisco Bay.

This process has been confirmed by a wide variety of urban stormwater monitoring programs in the Central Valley and San Francisco Bay watersheds (BASMAA 1996; Bailey et al. 2000; Russick 2001), and in fact, 35 San Francisco Bay watershed urban creeks have been placed upon the CWA 303(d) list for diazinon and pesticide-related toxicity (SFBRWQB 2002). However, it is important to note that the dilution that results when these urban creeks flow into the Sacramento and San Joaquin Rivers and/or San Francisco Bay will greatly lower the resultant diazinon concentrations in the Bay's ambient waters.

3.1.1.3 Particulate-Bound Advective Transport - Diazinon has a low-to-moderate tendency to adsorb to soils (organic carbon adsorption coefficient [K_{OC}] = ~1000-1800 [USDA 1995]). Therefore, although diazinon is relatively soluble in water, some of the diazinon residues will partition, or adsorb, to soil or sediment particles, and USGS studies have indicated that particulate-associated pesticides, including OP pesticides, are, in fact, transported into San Francisco Bay following stormwater runoff events (Bergamaschi *et al.*, 2001). However, this is not thought to be a significant source of diazinon, as ~98% of the diazinon in San Francisco Bay is in the dissolved phase (Domagalski and Kuivila 1993).

3.1.2 Point Sources

Publicly owned treatment works (POTWs) receive inputs of diazinon and other pesticides primarily from stormwater runoff within their service area, although runoff from landscaping/gardening overwatering and from improper disposal of the commercial pesticide products also contribute to POTW inputs. US EPA studies have indicated that diazinon was detected in over half of the POTW effluents investigated in 1988 by the National Effluent Toxicity Assessment Center (Norberg-King et al. 1989). This and other studies (Amato et al. 1992; Burkhard and Jenson 1993; Bailey et al. 1997) have indicated that the diazinon in POTW effluents can cause toxicity, and potentially cause an adverse impact on the receiving water communities. Unfortunately, because diazinon and most other current-use pesticides are not among the required compliance monitoring analytes for most NPDES dischargers, there is very little data available with which to assess the magnitude of these dischargers as sources of diazinon to San Francisco Bay ambient waters. However, as with urban runoff, it is important to note that the dilution that results when POTWs discharge into San Francisco Bay will greatly lower the resultant diazinon concentrations in the Bay's ambient waters.

3.1.3 Atmospheric Deposition

Diazinon's vapor pressure is relatively low (0.0001 torr) and is readily soluble in water, so it tends to stay in water rather than evaporate into the atmosphere. However, although not a significant fate process, some diazinon does move into the atmospheric phase during spraying applications, and some will also evaporate from surfaces (Glotfelty et al. 1990). Atmospheric diazinon can exist in particulate and vapor forms, as well as a solute dissolved in fog (Seiber et al. 1993).

Once in the atmosphere, diazinon can re-enter surface waters though both wet and dry deposition processes (e.g., rainfall). Analysis of rainwater samples collected in the immediate vicinity of recent applications revealed that the diazinon concentrations typically ranged from 100-1000 ng/L, with some samples containing as much as 15,000 ng/L diazinon (Alameda County 2001). However, given the relatively much, much larger volume of water within the Bay system, the dilution of diazinon from atmospheric deposition almost certainly results in this being negligible as a source of diazinon to the Bay's waters. Furthermore, given the prevailing winds in the San Francisco Bay basin, it is almost certain that most of any atmospheric diazinon is rapidly transported east towards the Central Valley (Seiber et al. 1993; Zabik and Seiber 1993).

3.2 Degradation Processes

3.2.1 Degradation in Water

There is very little information regarding the fate of diazinon in estuarine/marine waters, most fate studies having taken place in freshwater ecosystems. These studies have indicated that degradation of diazinon in water occurs primarily via two processes: chemical hydrolysis and microbial degradation, with lesser losses due to photolysis. All of these processes are strongly influenced by temperature, pH, and salinity.

While stable in water as long as 6 months at pH 7.0, diazinon is subject to hydrolysis at both acidic and alkaline pH's, and hydrolysis may be a significant fate process with reported half-lifes that range from 31 to 185 days (Gomaa et al. 1969). Biodegradation is also expected to be a major fate process (Howard 1991). Photolysis is also a possible fate process in water, with as much as 37% of waterborne diazinon reported to have been photolyzed within 24 hrs (Burkhard and Guth 1979).

3.2.2 Degradation in Soils and Sediment

Diazinon is not expected to bind tightly to soils, and is therefore readily degraded by hydrolysis reactions: the half-life for hydrolysis of diazinon in soils ranges from 34-45 days. However, the major degradation process in soils is via microbial biodegradation, with reported half-lives of 1-5 weeks in non-sterile soils vs. 6-12 weeks in sterile soils. Diazinon residues at the soil surface are also subject to photolysis. The overall half-life of diazinon in soils is reported to be 2-4 weeks (Kamrin 1997).

3.2.3 Atmospheric Degradation

Vapor phase diazinon is rapidly degraded, with a half-life of about 4 hours (Howard 1991). Atmospheric diazinon is also subject to direct photolysis (Howard 1991).

3.3 Other Processes

Other fate processes that are typically of concern in the assessment of contaminant risks are discussed below.

3.3.1 Bioaccumulation

Studies with freshwater fish indicated that tissue diazinon concentrations reached a peak within 3 days, with bioconcentration factors that ranged from 62 to 188; the half-life for diazinon in the fish tissues was <7 days (Seguchi and Asaka 1981; Keizer et al. 1993). In a long-term saltwater study with sheepshead minnows, the tissue concentrations again quickly reached a plateau, within 4 days, with bioconcentration factors ranging from 147 to 213 (Goodman et al. 1979). Given the relatively low reported bioaccumulation factors coupled with the very low concentrations at which diazinon occurs, the bioaccumulation of diazinon is not expected to problematic (Howard 1991).

4. Impairment Assessment: Current Conditions

4.1 Recent and Current Water Quality Conditions

The RMP has monitored water chemistry in San Francisco Bay since 1993. The results of the analyses of diazinon in San Francisco Bay ambient waters are summarized in Table 3. Numerical water quality objectives for diazinon (and chlorpyrifos) to protect aquatic life have been established by the CA Dept. of Fish & Game and by the U.S. EPA (Table 4).

Comparison of the concentrations of diazinon reported by the RMP with the EPA saltwater criteria reveals that there have been no exceedances of the criteria; similarly, the reported concentrations of chlorpyrifos have never exceeded either the CDFG or US EPA salt water quality criteria.

However, it is difficult to interpret the RMP data for these pesticides and achieve meaningful comparisons with the established water quality criteria with any degree of certainty. Unlike many contaminants whose concentrations in the Bay's water are relatively consistent, the

Table 3. Results of RMP analyses of San Francisco Bay ambient waters for OP pesticides.

RMP Station	Diazinon (ng/L)				Chlorpyrifos (ng/L)			
	1993-2001		July 2000	Aug 2001	1993-2001		July 2000	Aug 2001
	mean	max			mean	max		
Sacramento River	8.5	46.6[a]	1.3	0.5	0.31	1.42[a]	NA	0.30
San Joaquin River	8.4	35.2[a]	1.2	0.7	0.25	0.61[a]	0.35	0.08
Grizzly Bay	7.7	58.0[b]	1.2	0.8	0.16	0.46[c]	0.11	0.05
Napa River	6.0	39.0[b]	1.0	0.5	0.18	0.68[b]	0.08	0.04
Davis Point	6.6	44.0[b]	0.8	0.5	0.20	1.20[b]	0.04	0.02
Pinole Point	9.3	44.0[a]	0.7	0.3	0.14	0.57[a]	0.04	0.02
San Pablo Bay	5.3	31.0[b]	0.6	0.4	0.13	0.71[a]	0.03	0.02
Petaluma River	4.1	13.8[a]	0.6	0.2	0.14	0.71[e]	0.02	0.02
Red Rock	3.4	32.0[b]	0.3	0.2	0.07	0.31[f]	0.03	0.01
Yerba Buena Island	2.9	13.0[b]	0.4	0.2	0.24	1.76[a]	0.02	0.04
Alameda	2.7	9.5[b]	0.6	0.6	0.10	0.31[a]	0.05	0.05
Redwood Creek	3.1	7.1[b]	1.3	0.5	0.12	0.54[a]	0.02	0.03
Dunbarton Bridge	6.2	18.4[a]	1.4	0.6	0.17	0.97[d]	0.02	0.03

a – sample collected February 1994.
b – sample collected February 1996.
c – sample collected January 1997.
d – sample collected March 1993.
e – sample collected February 1999.
f – sample collected February 1998.

Table 4. Water quality criteria for diazinon and chlorpyrifos

Regulating Agency	OP Pesticide	Freshwater Criteria		Salt Water Criteria	
		Acute	Chronic	Acute	Chronic
CA Dept. Fish & Game[c]	Diazinon	80 ng/L[a]	50 ng/L[b]	n.c.	n.c.
	Chlorpyrifos	25 ng/L[a]	14 ng/L[b]	20 ng/L[a]	9 ng/L[b]
U.S. EPA	Diazinon[d]	100 ng/L[a]	100 ng/L[b]	820 ng/L[a]	400 ng/L[b]
	Chlorpyrifos[e]	83 ng/L[a]	41 ng/L[b]	11 ng/L[a]	5.6 ng/L[b]

a - 1-hr average, not to be exceeded more than once every 3 years.
b - 4-day average, not to be exceeded more than once every 3 years.
c - Siepmann and Finlayson 2000
d - U.S. EPA 2000
e - U.S. EPA 1986
n.c. - not calculated.

concentrations of current-use pesticides like diazinon are tightly linked to the combined effects of time-of-application and the timing and amount of rainfall, with the highest concentrations of pesticides occurring as episodic pulses, typically following rainstorm events (Kuivila and Foe 1999). This was the rationale for the RMP's implementation of an "episodic" ambient water toxicity study in 1996-97: in order to characterize the highest pesticide concentrations and

concomitant potential for toxicity, the sampling must 'capture' these episodic pulses of the pesticides. Given the low frequency of the RMP baseline sampling, it seems unlikely that their sampling efforts 'happened' to coincide with the peak concentrations in the Bay, suggesting that higher concentrations have, in fact, occurred in the Bay's ambient waters. This suggests that there have been instances in which the true peak concentrations of diazinon (and other pesticides) in the Bay's ambient waters may have exceeded the water quality criteria.

However, it is important to note that the maximum concentrations of diazinon observed by the RMP occurred during the mid-1990's. This is important because there have been several recent regulatory and/or legal actions that will have effectively reduced the concentrations expected to occur in the Bay's ambient waters (discussed later in this report). Review of the most recent RMP data for 2000 and 2001 indicate ambient water concentrations in the Bay that are at least an order of magnitude below the water quality criteria, and data reported from studies of upstream tributary waters also indicate a marked decline in the ambient water concentration of diazinon and chlorpyrifos (Spurlock 2002; Kuivila and Orlando 2002; Hall 2003a,b) review of the trends in diazinon applications in the Bay's watershed's (Figure 6) suggest that these concentrations will continue to decline over the next several years.

4.2 Sediment Conditions

There are currently no state or federal regulatory criteria for sediment diazinon concentrations in the State of California. Nor are there any sediment quality guidelines, such as the National Oceanic and Atmospheric Administration (NOAA) "Effects Range-Low" (ERL) and "Effects Range-Medium" (ERM) screening values.

Sediment concentrations of OP pesticides are not monitored by the RMP, or any other monitoring effort. However, sediment toxicity testing and follow-up TIEs have not observed any results that suggest potential sediment toxicity by these pesticides (Thompson et al. 1999; RMP Contribution 43).

4.3 Recent and Current Ambient Water Toxicity Conditions

4.3.1 The Basin Plan Narrative Objective for Toxicity

There are 2 types of water quality objectives in the San Francisco Bay Water Quality Control Plan (Basin Plan): narrative and numerical (SFBRWQCB 1995). Narrative objectives provide general descriptions of water quality conditions that must be met. The San Francisco Basin Plan narrative objective for ambient water toxicity states:

> "All waters shall be maintained free of toxic substances in concentrations that are lethal to or that produce other detrimental responses in aquatic organisms. Detrimental responses include, but are not limited to, decreased growth rate and decreased reproductive success of resident or indicator species. There shall be no acute toxicity in ambient waters. ... There shall be no chronic toxicity in ambient waters."

The narrative objective is most appropriate for the regulation of toxicity as it takes into account the toxicity that might result from the interactions of co-occurring toxicants for which numerical objectives do not exist.

4.3.2 Ambient Water Toxicity in San Francisco Bay

Monitoring for aquatic toxicity of San Francisco Bay's ambient waters by the RMP has demonstrated that ambient water toxicity has occurred in the Bay (Figure 4). These toxic events, which have been hypothesized to be caused by agricultural and urban runoff following rainstorms, or from other surface water releases following application of pesticides in agricultural areas, were the basis for the 303(d) listing of pesticides, and later, diazinon.

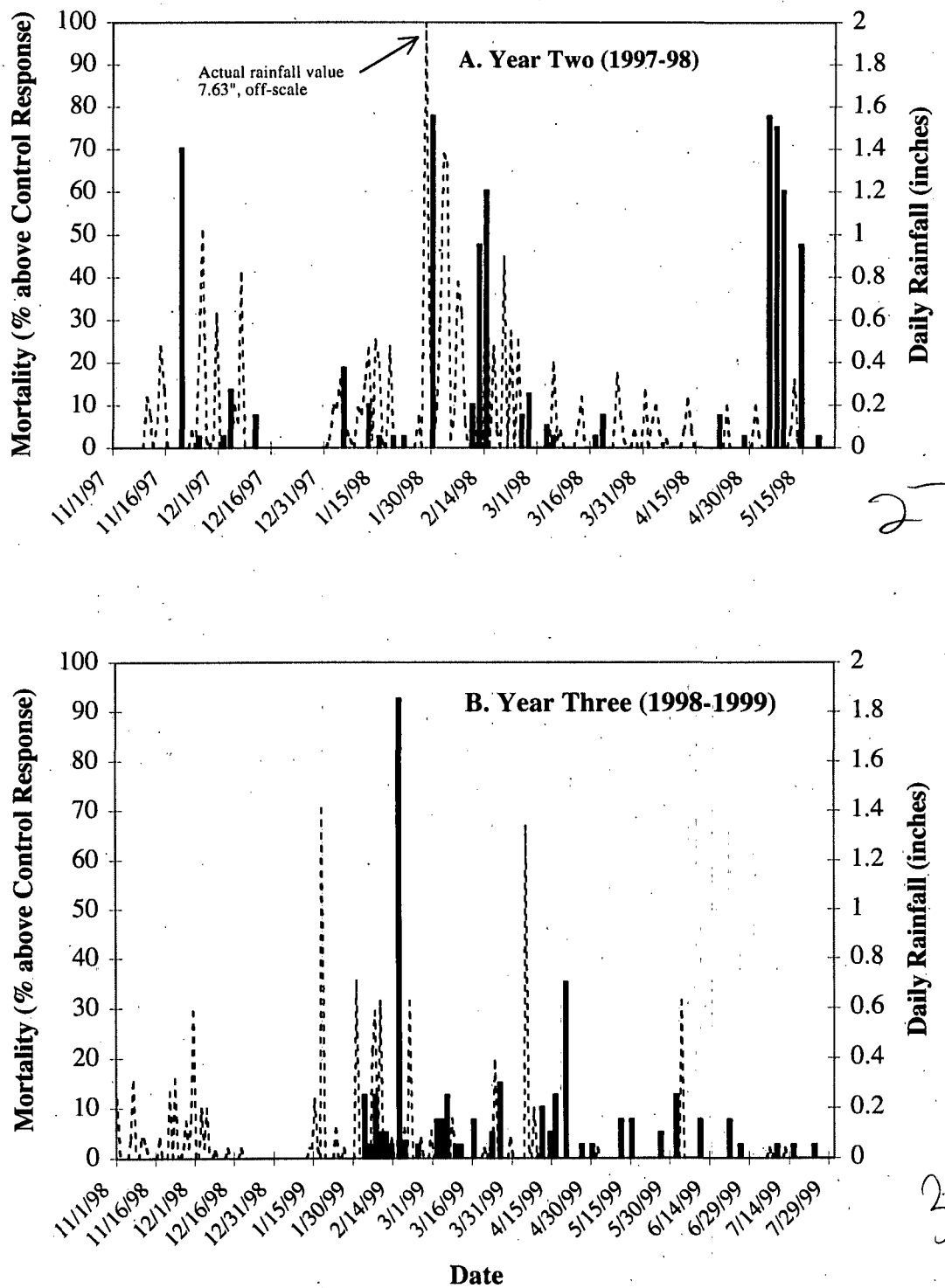
However, ambient water toxicity in San Francisco Bay appears to have disappeared. The results of ambient water toxicity monitoring at Mallard Island indicate a significant reduction in the frequency, duration, and magnitude of toxicity: only 4-5% of the ambient water samples were toxic in 1998-99 and 1999-2000 (Figure 8b,c), relative to 14% toxicity frequency observed in 1997-98 (Figure 8a); none of the samples collected during the 2000-2001 season (Figure 8d) were significantly toxic. In addition, the 1998-2000 and 2000-2001 monitoring at Mallard Island did not document any sets of consecutively toxic samples indicative of an extended period of ambient water toxicity, such as were observed in February and May of 1998 (Figure 8a). Moreover, the magnitude of toxicity (as reflected by the degree [or percentage] of test organism mortality) is also markedly reduced in the later years (Figure 8b, 8c, 8d), again suggesting a reduction in the degree of ambient water toxicity.

Subsequent RMP monitoring of ambient water toxicity in water samples collected from October, 2001 through April 2003, also indicated an absence of toxicity to the test organisms (Ogle and Gunther 2002, 2003). This trend for reduced ambient water toxicity has also been observed by similar monitoring projects taking place upstream in the watershed (Spurlock 2002; Kuivila and Orlando 2002) that have indicated significant reductions in the concentrations of OP pesticides in the watershed's ambient waters, and a corresponding reduction in the observation of toxicity.

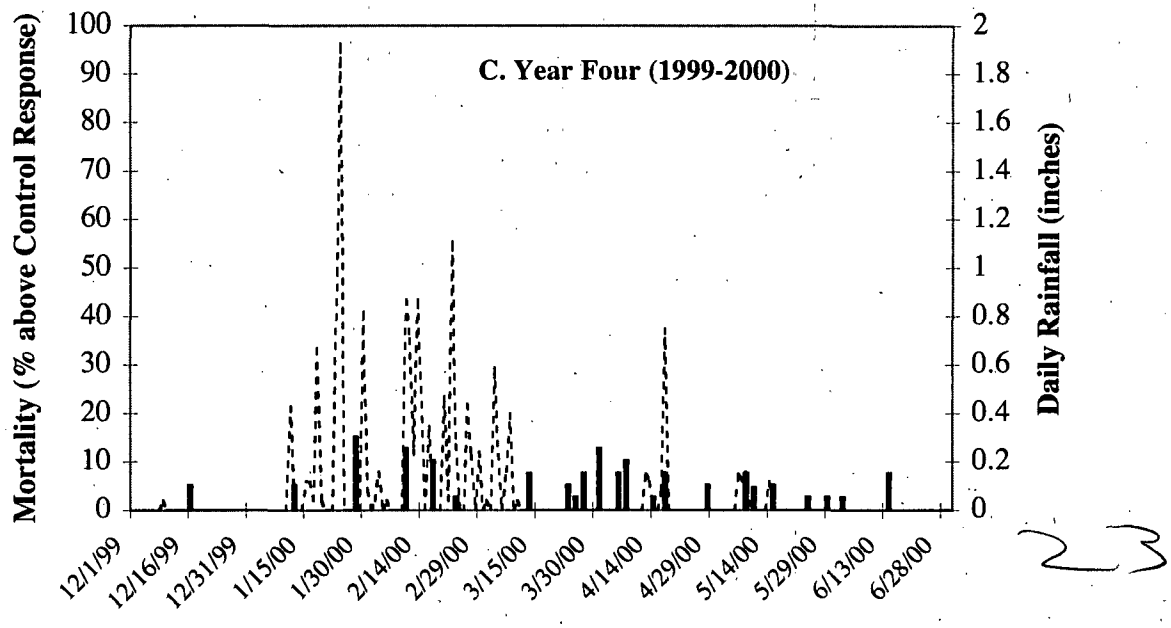
Based upon the observations of decreased applications of diazinon in the Bay's watersheds, decreased concentrations and toxicity in the upstream tributary waters of the Bay, and apparent disappearance of ambient water toxicity in the Bay, it may well be that the environmental risk associated with diazinon has declined to the point of being non-problematic, and that the water quality objective of maintaining the Bay's waters free of toxic substances in toxic concentrations are being met (Table 5).

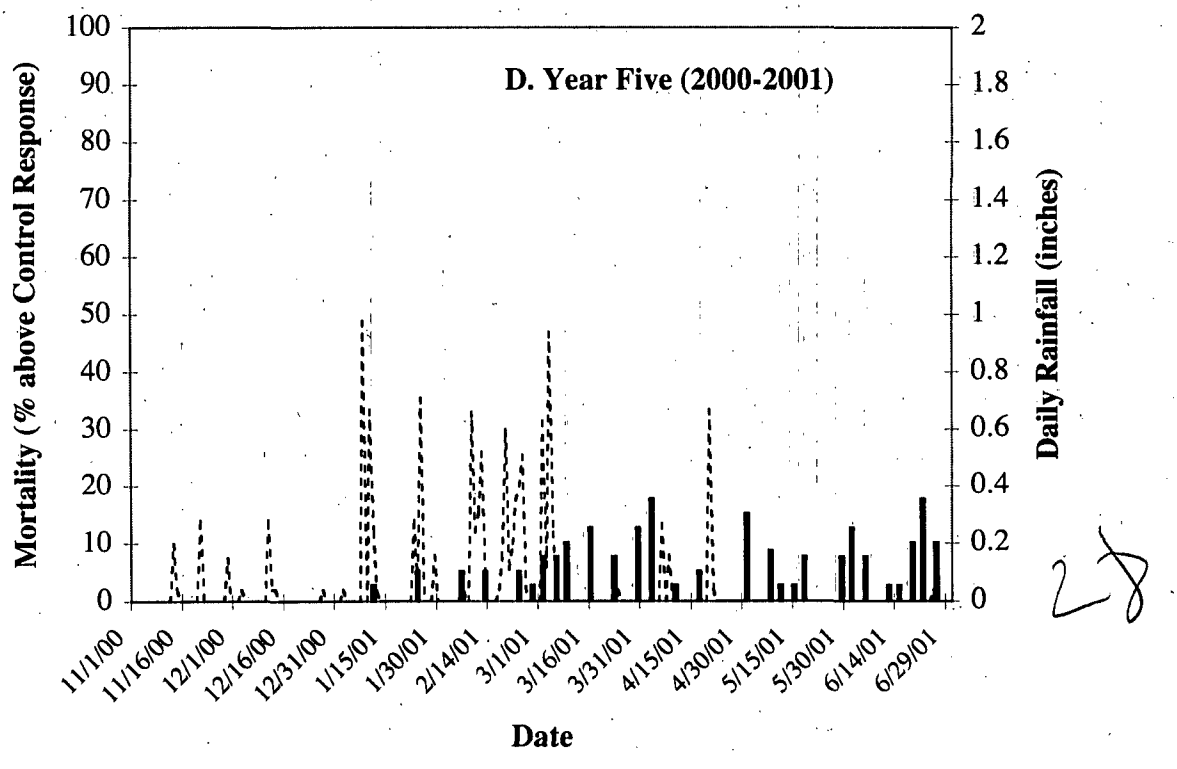
Table 5. Current status of compliance with water quality objectives for ambient water toxicity.

San Francisco Basin Plan Narrative Objective	Current Status
There shall be no acute toxicity in ambient waters	Water quality objective is being met
There shall be no chronic toxicity in ambient waters	Water quality objective is being met



Figures 8a-8d. Trends in ambient water toxicity at Mallard Island, based upon RMP studies.





Figures 8a-8d (continued). Trends in ambient water toxicity at Mallard Island, based upon RMP studies.

4.4 Recent Actions Affecting Diazinon Applications

4.4.1 Agency Outreach: Best Management Practices

In response to reports and observations of toxicity from agricultural and urban applications of diazinon, the first tier of action for State and local agencies (e.g., RWQCBs, CDPR) was to encourage voluntary use of 'best management practices' (BMPs) to reduce movement of OP pesticides into surface waters. In the urban arena, this has taken the form of regional boards, stormwater agencies, and watershed groups reaching out to educate the public through a wide variety of mechanisms, including TV and radio ads, billboard ads, presentations to interested citizen groups, and even painting warnings on sidewalks and streets near stormdrains. Outreach to agriculture has included education programs regarding the best management practices for applying pesticides and preventing runoff, including adoption of alternative integrated pest management (IPM) practices, and funding of studies to develop new BMPs (e.g., use of different types of riparian buffer zones) with stakeholder participation. The net result of these actions is reduced runoff of diazinon into surface waters, a trend that seems to be reflected in the reported diazinon application rates (Figure 6).

4.4.2 U.S. EPA Phases Out Most Uses of Diazinon (and Chlorpyrifos)

The Food Quality Protection Act (FQPA) of 1996 requires the U.S. EPA to reassess the risk associated with many pesticides, including diazinon. The FQPA increases the safety standards for these pesticides, with special attention to children's health. In compliance with the FQPA, the U.S. EPA performed a new risk assessment for diazinon, with special emphasis on human health. Their assessment concluded that all residential applications result in unacceptable health risks, particularly for children (U.S. EPA 2000).

Regarding risks to aquatic life, the U.S. EPA's revised risk assessment concluded:

> "Because of diazinon's widespread use in the U.S. and documented widespread presence in water bodies at concentrations of concern to aquatic life, there is a high level of certainty that aquatic organisms will be exposed to potentially toxic levels of diazinon in surface water. Additionally, since diazinon and its major degradate oxypyrmidine are mobile and persistent in the environment, and found at significant levels in both ground and surface waters, it is quite probable that they will be available in quantity and for times that will exceed acute and chronic toxicity endpoints."

4.4.2.1 Phase-Out of Urban Use Products – In response to the revised risk assessment, on December 5, 2000, the U.S. EPA established a Memorandum of Agreement (MOA) with the diazinon technical registrants to phase out urban sales of products containing diazinon. Indoor uses were to be phased out first, and all retail sales of diazinon-containing products intended for indoor use ended on December 3, 2002. Non-agricultural outdoor uses were phased out more slowly, with sales of related diazinon-containing products to retailers ending August 2003. Any and all retail sales of any diazinon products are scheduled to end December 31, 2004, at which time all unsold retail products will be returned to the manufacturer.

The U.S. EPA will allow diazinon over-the-counter products sold before January 1, 2005, to be used indefinitely by the consumer. And some agricultural uses within urban areas, such as greenhouse applications may continue as well. Nevertheless, the phase-out of most urban uses should effectively reduce the amount of diazinon that is released to urban creeks and ultimately, to San Francisco Bay. A similar phase-out plan for chlorpyrifos should effectively reduce the amount of that OP pesticide being released to urban creeks and San Francisco Bay, as well.

4.4.2.2 Phase-Out of Agricultural Uses – In addition to the banning of urban uses, consideration of the revised risk assessment resulted in the prohibition of diazinon application to ~30% of the agricultural crops for which it had been previously approved by February 2001; diazinon application to over 40 other agricultural crops will continue. Use of chlorpyrifos was similarly banned for some agricultural crops.

Again, the net result of these actions is reduced diazinon applications and reduced runoff of diazinon into surface waters, a trend that seems to be reflected in the reported diazinon application rates (Figure 6).

As a follow-up to the December 5, 2000 MOA between the EPA and the diazinon registrants, in a letter dated April 8, 2003, Syngenta Crop Protection, Inc. requested a voluntary cancellation of all its remaining registrations for products containing diazinon, including agricultural products, effective June 30, 2003. Syngenta's request to terminate registrations for all of Syngenta's diazinon products is consistent with the December 5, 2000, MOA, and has been approved by the EPA.

Later that year, a petitioner requested that CDPR put all diazinon products (to include products other than dormant sprays) and all chlorpyrifos products into re-evaluation. DPR reviewed the petition, and announced that they would not perform such re-evaluations at this time. However, the DeltaKeeper has subsequently sued the CDPR to force these re-evaluations, so the ultimate status of diazinon and chlorpyrifos agricultural uses in California are still uncertain.

4.4.3 U.S. District Court Decision

On January 22, 2004, the U.S. District Court for the Western District of Washington ruled in the case of Washington Toxics Coalition (WTC) v. EPA, establishing buffer zones around certain water bodies in California where any of 55 pesticides (Table 6) cannot be used. The court order established a 20-yard buffer zone for ground pesticide applications, and a 100-yard buffer zone for aerial pesticide applications, adjacent to waters providing habitat for the following salmonid populations:

Sacramento River winter-run Chinook salmon
California Central Valley spring-run Chinook salmon
California Central Valley steelhead
California coastal chinook salmon
Central California coast steelhead
Central California coast coho salmon
South-Central California coast steelhead
Southern California steelhead

Table 6. List of pesticides subject to US District Court ban on use near salmonid habitats.		
1,3-dichloropropene	dimethoate	norflurazon
1,2-D	disulfoton	oryzalin
acephate	diuron	oxyfluorfen
alachlor	ethoprop	paraquat dichloride
atrazine	fenamiphos	pebulate
azinphos-methyl	fenbutatin-oxide	pendimethalin
bensulide	iprodione	phorate
bentazon	lindane	phosmet
bromoxynil	linuron	prometryn
captan	malathion	propargite
carbaryl	methamidophos	simazine
carbofuran	methidathion	tobuthiuron
chlorothalonil	methomyl	terbacil
chlorpyrifos	methyl parathion	thiobencarb
coumaphos	metolachlor	thiodicarb
diazinon	metribuzin	triclopyr
dicamba	methidathion	trifluralin
dichlobenil	molinate	
diflubenzuron	naled	

This order is in effect until the EPA (and, when appropriate, the National Marine Fisheries Service [NMFS]) completes an evaluation of whether endangered Pacific salmon and steelhead are sensitive to exposure from any of the 55 pesticides. Under the Endangered Species Act, EPA must ensure that these pesticides do not jeopardize the species listed as endangered and threatened, or adversely affect their habitat.

The Federal Government is currently reviewing the order and considering whether to appeal the decision. EPA's risk assessment process for pesticides is supposed to provide protection to all non-target plants and animals, including endangered species. The Agency has reviewed over half of the 55 pesticides subject to this litigation. More than a dozen of those reviewed have been determined to have no effect on salmon and steelhead, others are now undergoing the consultation process, and some pesticide uses are still under evaluation at EPA. The Agency is on schedule to complete review of the remaining pesticides by December 1, 2004.

At this early date, it is uncertain what effect the U.S. District Court decision will have on diazinon (and/or other pesticide) runoff into surface waters. At a minimum, if the court decision stands, then it seems probable that there will be additional reductions in the amount of diazinon being applied, and in the amount of diazinon entering surface waters in these watersheds.

5. Emerging Concerns: Alternative Pesticides

5.1 Changes in Pesticide Use

For many years, diazinon has been one of the most widely-applied pesticides for both agricultural and urban uses. However, recent regulatory and legal actions are effectively eliminating most uses of diazinon (and chlorpyrifos), which in turn is resulting in increased usage of other pesticides as alternatives to diazinon (and chlorpyrifos). The pesticides alternatives to diazinon (and chlorpyrifos) may actually pose new water quality risks, if these emerging-use pesticides are more toxic or have other qualities that may create new types of toxicity problems.

This transition from diazinon to alternative pesticides has already been seen in changing agricultural practices: many farmers have reduced or eliminated use of diazinon for dormant spraying, and have begun using pyrethroid pesticides as alternatives (Epstein et al. 2000). Similar changes are taking place in urban usages of pesticides. Bay Area retail sales data indicated that from 2002 to 2003 diazinon sales dropped 92% (Marin County 2003), and a recent retail shelf survey of pesticide sales in Bay Area stores indicated that pyrethroids are taking over the over-the-counter marketplace (TDC 2003). The most common over-the-counter pyrethroid is permethrin, followed by cyfluthrin, bifenthrin, and esfenvalerate. Malathion, carbaryl, and other potential alternatives appear to be less common (TDC 2003).

5.2 Pyrethroid Pesticides vs. OP Pesticides

The potential toxicity implications of the transition from OP pesticides to pyrethroid pesticides were evidenced in a recent investigation performed in the Central Valley comparing the toxicity of diazinon to the pyrethroid pesticide esvenvalerate in orchard runoff (Werner et al. 2002). In this study, the pesticides were applied to adjacent areas of an orchard, and samples of surface water runoff were collected from within the orchard following a rainstorm that occurred 2 days after application. The diazinon-contaminated samples were much more toxic to *Ceriodaphnia* than were the esvenvalerate-contaminated samples (400-800 Toxic Units for diazinon relative to 10-20 Toxic Units for esvenvalerate). However, the reverse was true for toxicity to fathead minnows: for diazinon-contaminated water, there was <5-26% mortality within 96 hrs, whereas 96-hr mortality for fathead minnows ranged from 93-100% for the esvenvalerate-contaminated waters.

Interestingly, the comparative toxicity of diazinon and esfenvalerate runoff to *Ceriodaphnia* reported by Werner et al. (2000) seems contrary to the comparative toxicities of diazinon and pyrethroids as reported in the scientific literature, which indicates that the pyrethroid pesticides tend to be much more toxic than diazinon (Table 7).

Table 7. Comparative toxicity of diazinon and pyrethroid pesticides.				
Pesticide	Taxa	10^{th} percentile of LC/EC50 values (ng/L)	r^2	N
Diazinon[a]	arthropods	483	0.96	23
Cypermethrin[b]	arthropods	6.4	0.98	42
Permethrin[b]	arthropods	76	0.96	36
Fenvalerate[b]	arthropods	8	0.90	16

a. Novartis (1997)
b. Solomon et al. (2001)

The apparently anomalous results observed by Werner et al. (2000) may be due to the chemical characteristics of the pyrethroids that reduce their bioavailability to water column organisms like *Ceriodaphnia*. Relative to the OP pesticides, pyrethroid pesticides tend to strongly sorb to sediment particulates with a relatively long half-life in sediments (Schimmel et al. 1983; Muir et al. 1985). In Werner et al.'s study, it seems likely that much of the applied esfenvalerate was "stuck" to the soils and sediment particulates such that it could not come into contact with the *Ceriodaphnia*. This key fate characteristic will have significant implications in how we assess the toxicity risk of the emerging use pesticides, i.e., it may well be that the type of "ambient" toxicity that might result from the pyrethroids differs from that due to the OPs.

5.3 Implications of Pyrethroid Sorption to Particulates

It should be noted that the Werner et al. (2000) study represents a "worst-case" scenario for water column toxicity in which the water samples were collected directly from within the orchards. Before such water reaches the San Francisco Bay system, it will have come into contact with and sorbed to surface soils, waterborne suspended particulates, and bedded sediments, and as a result, the likelihood of pyrethroid toxicity to water column organisms may be minimal; however, while this may reduce or even eliminate the potential for toxicity to water column organisms, increases in the frequency and magnitude of particulate-associated (e.g., sediments) toxicity might be an expected consequence of increased use of pyrethroid pesticides.

There have, in fact, been reports that agricultural runoff from pyrethroid-treated fields can result in toxicity of the sediments in the receiving water ecosystems (D. Weston, personal communication). However, considerable uncertainty remains whether or not such particulate associated toxicity will be transported down the watershed and into San Francisco Bay. There remains similar uncertainty whether pyrethroids applied in urban areas will be transported into San Francisco Bay.

5.4. Monitoring for Pesticide Toxicity in San Francisco Bay: New Approaches

Toxicity monitoring programs must be aware of changes in activities (e.g., pesticide use) in the watersheds being studied, and must adapt the monitoring tools (e.g., sampling design, toxicity tests, and chemical analyses) to reflect those changes. For example, knowing that diazinon and chlorpyrifos had been linked to ambient water toxicity in upstream waters, and that OP pesticides

can remain dissolved in the water, are very toxic to crustaceans, and are relatively non-toxic to fish, the approach of ambient water sampling and toxicity testing with *Ceriodaphnia dubia* or *Americammysis bahia* was an appropriate monitoring approach. However, the fate and effects of the pyrethroid pesticides are different than the OP pesticides. This suggests that transitions in pesticide use in the Bay's watershed may need to be reflected in changes in the way we assess potential toxicity. The current water column approach may not be the optimal approach for assessment of the effects of "emerging-use" pesticides on the San Francisco Bay aquatic ecosystems.

In order to address this issue, the Clean Estuary Partnership is preparing a new study plan for the monitoring of San Francisco Bay urban creeks as part of the Diazinon/Pesticide-Related Toxicity in Urban Creeks TMDL process. The purpose of this monitoring program will be to address the key management questions for the Diazinon/Pesticide-Related Toxicity in Urban Creeks TMDL Implementation Plan:

Is the phase-out of diazinon resulting in reduced concentrations in urban creeks?
If diazinon concentrations have declined, is there still a toxicity problem?

While the exact scope of work for this monitoring plan remains to be worked out, it seems likely that assessment of potential pyrethroid toxicity in urban creek sediments may comprise a key monitoring element of the study plan.

This question is also being addressed by the RMP and the San Francisco Estuary Institute, in a planned multi-project investigation of the sources and effects of pyrethroid pesticides in watersheds of the San Francisco Estuary. This investigation is focused directly on the monitoring of potential sediment toxicity resulting from pyrethroid applications in the Bay's watersheds via the collection of sediments from selected tributaries of local watersheds that reflect specific agricultural and/or urban land uses, and the performance of sediment toxicity tests (S. Lowe, personal communication).

Clearly, the decline of diazinon use and apparent elimination of potential diazinon toxicity in San Francisco Bay is to be celebrated. However, maintained vigilence to keep abreast of changing pesticide uses within the Bay's watersheds, and adapting the monitoring tools to reflect those changes, has been and continues to be the responsibility of those tasked with the protection of this great resource.

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