Final Report

Diazinon in San Francisco Bay

Conceptual Model/ Impairment Assessment

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Executive Summary

Section 303(d) of the Clean Water Act requires states to identify 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 total maximum daily loads (TMDLs) to reduce and eventually eliminate the impairment and restore the beneficial uses. 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 being impaired due to pesticide toxicity in 1998; the US EPA subsequently narrowed the 303(d)-listing to be specific for diazinon, a widely-used organophosphate (OP) pesticide that had been shown to cause ambient water toxicity in the Bay's upstream watersheds.

The general objectives of this Conceptual Model/Impairment Assessment (CM/IA) report are:

- Develop a conceptual model that describes the current state of knowledge for diazinon, including sources of diazinon to the Bay and the processes that determine the occurrence and concentrations of diazinon in the system;
- Evaluate the current level of impairment of beneficial uses;
- Recommend studies or other actions needed to reduce uncertainties in the conceptual model and impairment.

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 pesticides that are seeing increased use as replacements for diazinon.

Background Information

Basis for the 303(d) Impairment Listing for Diazinon: Observations of Ambient Water Toxicity in San Francisco Bay

In February 1996, toxicity testing of the Bay's ambient surface waters by the Regional Monitoring Program for Trace Substances (RMP) revealed region-wide toxicity with dramatic and significant reductions in mysid shrimp survival at the 4 northern-most stations: Napa River, Grizzly Bay, the Sacramento River, and the San Joaquin River. Similar toxicity was observed again in July 1996 and in January 1997. Earlier studies had already reported that agricultural runoff in the San Joaquin and Sacramento River watersheds and urban runoff in the San Francisco Bay watershed were causing similar ambient water toxicity within those watersheds, particularly following significant rainfall events, and testing had indicated that organophosphate (OP) pesticides, including diazinon, were a primary cause of the observed toxicity.

In response to the RMP observations of ambient water toxicity in 1996 and 1997, and given the linkage established between similar toxicity and OP pesticides in upstream ambient waters, the San Francisco Bay Regional Board identified San Francisco Bay as being impaired due to "pesticides" in 1998. The US EPA subsequently made this 303(d) listing specific for the OP pesticide diazinon.

Uncertainties Associated with the 303(d) Listing - At that time, the assumption that pesticide transport into the Bay via stormwater runoff was the likely cause of toxicity in the northern reach of Bay (as it was in upstream waters) seemed reasonable. However, the diazinon concentrations reported for water samples that were collected at the same time and same place as the toxicity testing water samples were well below toxicity threshold levels. As a result, there currently remains significant uncertainty regarding the actual causes of the ambient water toxicity observed by the RMP.

Conceptual Model

Diazinon: Background Information

Diazinon is an organophosphate (OP) pesticide, which until recently was one of the most widely-used pesticides in both agricultural and urban settings. Diazinon is relatively water-soluble, and is readily transported into surface waters where it can cause toxicity to aquatic animals.

Sources of Diazinon to San Francisco Bay

Like all of the OP pesticides, diazinon 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 surface water 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, and can basically be characterized into 2 primary source types: agriculture applications and urban applications.

Agricultural Runoff of Diazinon - Surface water runoff from agricultural pesticide use in the Sacramento River and San Joaquin River watersheds is the major source of diazinon (and most other current-use pesticides) to the Bay. The primary agricultural applications of diazinon are during the winter orchard dormant season (December through early March). Unfortunately, this is also when the greatest rainfall and runoff occur. The result is episodic “pulses” of pesticides that flow down through the watersheds and into San Francisco Bay.

Urban Runoff of Diazinon - The principal urban uses of diazinon have been structural pest control and landscaping and gardening. While markedly less than the agricultural applications, urban usage nevertheless constitutes a significant source of pesticide loading to the Bay.

Transport and Fate

- **Water vs. Suspended Particulates/Sediments -** Particulate-associated diazinon is not a significant source of diazinon, as ~98% of the diazinon in San Francisco Bay is in the dissolved phase.
- **Degradation in Water and Sediments -** Studies have indicated that degradation of diazinon is relatively rapid.
- **Bioaccumulation -** The bioaccumulation of diazinon is not expected to problematic.

Impairment Assessment: Current Conditions

Ambient Water Toxicity Conditions
Monitoring of San Francisco Bay's ambient waters has demonstrated that ambient water toxicity has historically occurred in the Bay. These toxic events were the basis for the 303(d) listing of pesticides, and later, diazinon. However, ambient water toxicity in the Bay appears to have disappeared: recent monitoring of ambient water toxicity by the RMP has indicated an absence of toxicity to the test organisms. Similar monitoring projects taking place upstream in the watershed have also 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 appears that the water quality objectives of maintaining the Bay's waters free of toxic substances in toxic concentrations are being met.

Water Quality Conditions
Evaluation of the RMP-measured concentrations of diazinon indicates that there have been no exceedances of the EPA saltwater criterion for the protection of aquatic life. Furthermore, there have been several recent regulatory and/or legal actions such that the diazinon concentrations should continue to decline over the next several years.

303(d) Listings and TMDLs in Upstream Waters - Selected water bodies in observed in the Central Valley and in the urban creeks of the San Francisco Bay watersheds have previously been placed on the 303(d) list for impairment due to diazinon:

- Sacramento and Feather Rivers – TMDL completed and Basin Plan amendment underway;
- Lower San Joaquin River – TMDL underway;
- Sacramento San Joaquin Delta – TMDL underway;
- Sacramento "Urban Creeks" – TMDL completed, awaiting EPA approval;
- San Francisco Bay Area Urban Creeks – TMDL underway.

These upstream TMDLs can be expected to further reduce and limit the amount of diazinon that enters the Bay.

Most Uses of Diazinon are Being Phased Out - The US EPA has phased out urban sales of products containing diazinon. In addition to the phase-out of urban uses, the EPA has also prohibited diazinon application to many of the agricultural crops for which it had been previously approved. Again, this is resulting in reductions in the amount of diazinon being applied, and in the loading of diazinon to surface waters in the Bay's upstream watersheds.

Impairment Summary: Is San Francisco Bay Being Impaired by Diazinon?
Any assessment of impairment of the Bay's waters will by necessity be based upon a "weight of evidence" approach, with review and evaluation of all available relevant information. Based upon this current review of available information, it is this study's conclusion that:

<u>Impairment of San Francisco Bay by diazinon is unlikely.</u>

Emerging Concerns: Alternative Pesticides

Recent regulatory actions are effectively eliminating most uses of diazinon (and chlorpyrifos), which in turn is resulting in increased usage of other pesticides. These alternative pesticides may actually pose new water quality risks if they are more toxic or have other qualities that may create new types of toxicity problems. Many farmers have reduced or eliminated use of diazinon, and have begun using pyrethroid pesticides as alternatives. Similar changes are taking place in urban pesticide usages. Relative to the OP pesticides, pyrethroid pesticides tend to strongly sorb to sediment particulates. 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 OPs.

Uncertainties and Data Gaps Associated with this Impairment Assessment

Potential Sub-Lethal Toxicity of Diazinon to Fish Reproduction

A recent study reported that exposure of salmonid sperm and eggs to diazinon resulted in reductions in egg hatchability. While salmonids do not spawn in the Bay's waters, there are several species of fish (e.g., Pacific herring, Delta smelt, longfin smelt) that do spawn in the Bay's waters at times that coincide with the maximum applications and runoff of diazinon. The potential for such an impact in San Francisco Bay is currently unknown.

Pesticide Interactions May Increase the Toxicity of Diazinon

The measured diazinon concentrations in the Bay's waters have always been well below reported toxicity levels. However, studies have indicated that the toxicity of OP pesticides is synergistic (i.e., increased dramatically) with triazine pesticides and pyrethroid pesticides. The potential for such interactions in the Bay's waters is currently unknown.

Changing Pesticide Usage May Cause "New" Impairments

Pyrethroid pesticides in surface water runoff will likely have sorbed to waterborne suspended particulates and bedded sediments before reaching San Francisco Bay. As a result, increases in the frequency and magnitude of particulate-associated (e.g., sediments) toxicity might be an expected consequence of increased use of pyrethroid pesticides. However, considerable uncertainty remains whether or not such particulate associated toxicity will be transported down the watershed and into San Francisco Bay.

Clearly, the decline of diazinon use and apparent elimination of potential diazinon toxicity in San Francisco Bay is to be celebrated. However, it is important to note that the continued monitoring of the Bay's waters and sediments to ensure the absence of diazinon (and other pesticide)-related toxicity will continue to be the responsibility of those tasked with the protection of this great resource. An integral element of this continued monitoring effort will be an ongoing vigilance in keeping abreast of changing pesticide uses within the Bay's watersheds, and adaptation of the monitoring tools to reflect those changes.

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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 pesticides in surface water runoff, 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 (OP) 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.

This report has been produced for the Clean Estuary Partnership (CEP). The CEP is a collaboration of the Bay Area Clean Water Agencies, Bay Area Stormwater Management Agencies Association, and the San Francisco Bay Regional Water Quality Control Board. Other important participants include the San Francisco Estuary Institute, Clean Water Fund, San Francisco Bay Keeper, Port of Oakland, and the Western States Petroleum Association. This cooperative partnership facilitates efforts to improve water quality in San Francisco Bay by providing financial and staff support for technical studies, discussion of management questions and strategies, and stakeholder outreach activities.

Several Conceptual Model/Impairment Assessment (CM/IA) reports have been commissioned by the CEP for pollutants that have been identified in the past as possible causes of impairment to beneficial uses in San Francisco Bay. The general objectives of these CM/IA reports are:

- Develop a conceptual model that describes the current state of knowledge for the pollutant of concern, including sources, loads, and pathways into and out of the Bay and its water, sediment and biota;
- Evaluate the current level of impairment of beneficial uses, including description of standards or screening indicators and relevant data;
- Recommend options for the next steps needed to reduce uncertainties in the conceptual model and impairment, to assist the CEP partners in balancing priorities for data gathering along with other pollution prevention activities.

This CM/IA report should be viewed as a tool for planning and an important step in resolution of diazinon-related issues, and not as a conclusive statement on the conceptual model, beneficial use impairment, or next steps needed to resolve diazinon-related issues.

2. Background Information: the 303(d) Listing

2.1 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 (Figure 2), 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.

2.2 Regulatory Background for the 303(d) Impairment Listing

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 (State Board) and Regional Water Quality Control Boards (Regional Boards) as the principal agencies responsible for controlling water quality in California. This joint agency responsibility couples state-level coordination with regional familiarity with local conditions. Accordingly, the San Francisco Bay Regional Board has the responsibility for regulating and protecting water quality within the San Francisco Bay region, which it addresses within its basin-specific Water Quality Control Plan (Basin Plan). The key elements of the San Francisco Bay Basin Plan consist of:

- A statement of the beneficial uses of San Francisco Bay that are to be protected;
- Identification of the water quality objectives needed to protect these beneficial uses;
- An implementation plan to protect these beneficial uses, primarily via regulation of discharges to the Bay (SFBRWQCB 1995).

In meeting the requirements of the Clean Water Act, and consistent with the Basin Plan, when water quality objectives are not being met such that any one or more of the Bay's beneficial uses are impaired, the San Francisco Bay Regional Board is responsible for placing the impaired body

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.

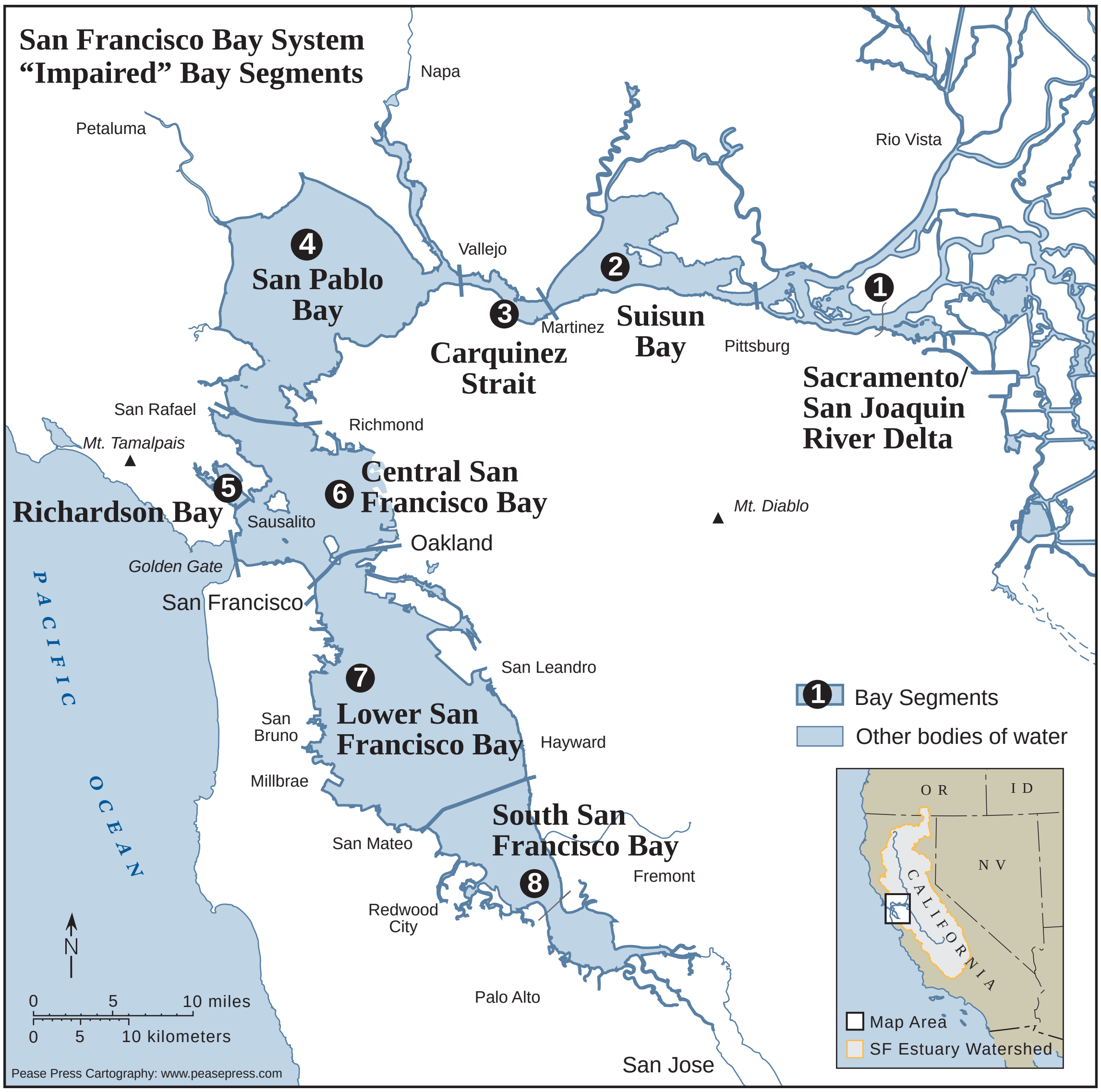


Figure 2. The San Francisco Bay system, including the 8 segments of the Bay that have been placed on the 303(d) list for impairment by diazinon.

of water on the 303(d) list, with the listing being subject to approval by EPA. In complying, the San Francisco Bay Regional Board has developed successive lists of “impaired” water bodies since 1976. The State Board has subsequently issued the *Water Quality Control Policy for Developing California’s Clean Water Act Section 303(d) List* (SWRCB 2004) to formalize this process and provide the guidelines to be used for listing waters and developing TMDLs, as well as for “de-listing” waters (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).

2.3 Basis for the 303(d) Impairment Listing for Diazinon

2.3.1 Observations of Episodic Ambient Water Toxicity in San Francisco Bay

The San Francisco Estuary Regional Monitoring Program for Trace Substances (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, that may result.

As part of the RMP monitoring, ambient water samples were collected at stations located throughout San Francisco Bay. The first several years of testing these water samples 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*, which is an EPA standard toxicity test organism, and which is among the most sensitive estuarine/marine organisms to diazinon and many other pesticides) 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 3). 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 3).

Dramatic toxicity in the baseline ambient water toxicity testing was also observed in Year 5 (1997) of the RMP. In January, there was once again region-wide toxicity to the mysid, with significant reductions in survival at the 4 northern-most stations: Napa River, Grizzly Bay, the Sacramento River, and the San Joaquin River (Figure 3).

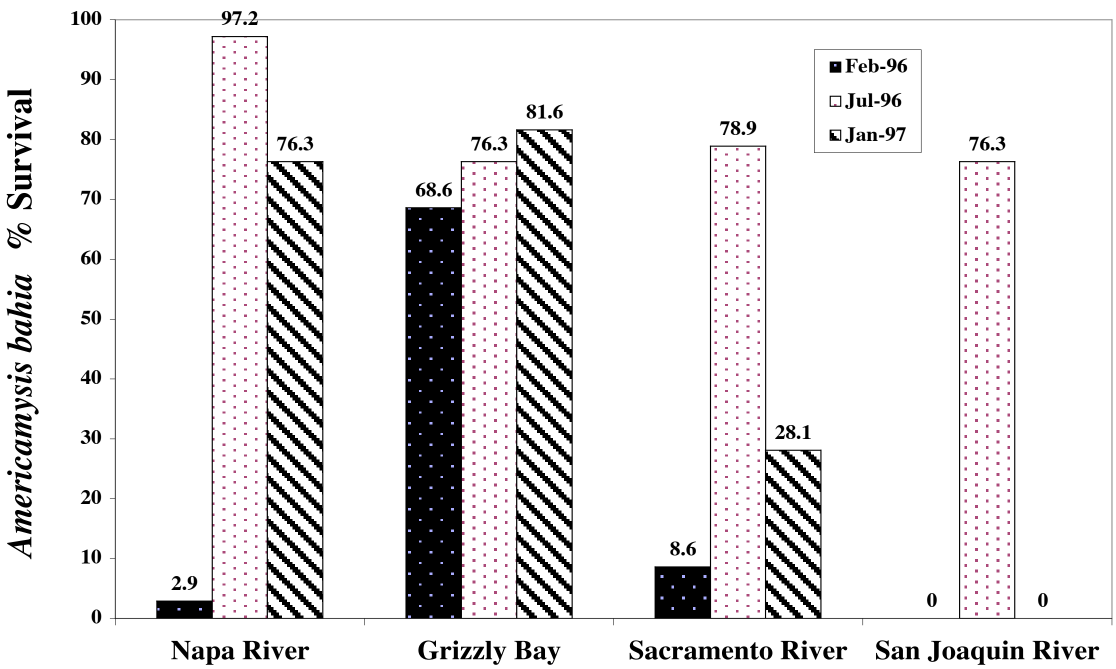


Figure 3. Toxicity of RMP ambient water samples to *Americamysis* (formerly *Mysidopsis*) *bahia*. Percent survival data have been normalized to the Control treatment responses. With the exception of the July 1996 Napa River sample, each sample resulted in a statistically significant reduction in mysid survival relative to the Control treatment response.

2.3.2 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 Central Valley Regional Board began monitoring of ambient water toxicity in the San Joaquin River basin, and 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); a Toxics Unit accounting of toxicity indicated that the OP pesticides diazinon, chlorpyrifos, and parathion accounted for over 90% of the observed toxicity, although other pesticides were also detected in the water samples. More recent ambient water toxicity monitoring in the Sacramento River watershed and in the Delta revealed significant toxicity to *Ceriodaphnia*, and Toxicity Identification Evaluations (TIEs) demonstrated that diazinon was one of the main causes of this toxicity (Werner et al. 2000).

2.3.3 The 303(d) Impairment Listing

In response to the RMP observations of ambient water toxicity in 1996 and 1997, and given the linkage established between similar toxicity and pesticides in upstream ambient waters, the San Francisco Bay Regional Board identified all 8 San Francisco Bay segments (Figure 2) 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).

2.3.4 Potential Impairment of the Bay's Beneficial Uses

The toxicity of the Bay's ambient waters to the mysid shrimp test organisms suggests the potential for both direct *and* indirect toxicity to other organisms in San Francisco Bay:

- <u>direct toxicity</u> in that sensitive invertebrates may suffer significant mortalities as a result of exposure to such waters; as a result, beneficial uses that include invertebrate resources (e.g., estuarine habitat, marine habitat, and shellfish harvesting) may be impaired by such toxicity.
- <u>indirect toxicity</u> in that the direct toxicity to invertebrates could result in a concomitant reduction in available invertebrate prey organisms that would have otherwise been used by fish and waterfowl, resulting in reduced productivity, particularly if such toxicity occurred during critical life stage periods. This indirect toxicity to fish and waterfowl could potentially impair related beneficial uses (e.g., ocean, commercial, and sport fishing, fish migration, preservation of rare and endangered species, fish spawning, and wildlife habitat)

As a result, several of the Bay's beneficial uses are potentially subject to impairment by diazinon toxicity (Table 1).

2.3.5 Consistency of the 1998 303(d) Listing with Current State Policy

Although this listing occurred prior to the issuance of the State Board's formal 303(d) listing policy, it is consistent with current state policy that water segments shall be placed on the section 303(d) list if any of the following conditions are met (SWRCB 2003):

1. exceedance of numeric water quality objectives for toxic pollutants (e.g., California/National Toxics Rule water quality criteria);
2. exceedance of numeric water quality objectives for conventional pollutants;
3. exceedance of bacteria water quality standards;
4. issuance of a health advisory against consumption of edible resident organisms, or issuance of a shellfish harvesting ban;
5. tissue contaminant concentrations in resident organisms that exceed a pollutant-specific evaluation guideline;
6. <u>**exhibition of statistically significant water or sediment toxicity**</u>;
7. exceedance of a nutrient-related evaluation guideline that is associated with "nuisance" excessive algal growth, unnatural foam, odor or taste;

8. exceedance of any other acceptable (non-nutrient) evaluation guideline for "nuisance" taste, color, oil sheen, turbidity, litter, trash, and odor;
9. exhibition of adverse biological responses in resident organisms relative to reference conditions;
10. exhibition of any significant degradation of biological populations or communities relative to reference conditions;
11. exhibition of any *trend* of declining water quality.

Table 1. Beneficial uses of San Francisco Bay that could potentially be impaired from ambient water toxicity due to diazinon.

Use	Abbreviation	Definition
Ocean, commercial, and sport fishing	COMM	Uses of waters for commercial or recreational collection of fish, shellfish, or other organisms in oceans, bays, and estuaries, including but not limited to, uses involving organisms intended for human consumption.
Estuarine habitat	EST	Uses of waters that support estuarine ecosystems, including, but not limited to, preservation or enhancement of estuarine habitats, vegetation, fish, shellfish, or wildlife (*e.g.*, estuarine mammals, waterfowl, shorebirds), and the propagation, sustenance, and migration of estuarine organisms.
Marine habitat	MAR	Uses of waters that support marine ecosystems, including preservation or enhancement of marine habitats, plants, fish, shellfish, or wildlife.
Fish migration	MIGR	Uses of waters that support habitats necessary for migration, acclimatization between fresh water and salt water, and protection of aquatic organisms that are temporary inhabitants of waters within the region.
Preservation of rare and endangered species	RARE	Uses of waters that support habitats necessary for the survival and successful maintenance of plant of animal species established under state and/or federal law as rare, threatened, or endangered.
Shellfish harvesting	SHELL	Uses of waters that support habitats suitable for the collection of crustaceans and filter-feeding shellfish (*e.g.*, clams, oysters, and mussels) for human consumption, commercial, or sport purposes.
Fish spawning	SPWN	Uses of waters that support high quality aquatic habitats suitable for reproduction and early development of fish.
Wildlife habitat	WILD	Uses of waters that support wildlife habitats, including, but not limited to, the preservation and enhancement of vegetation and prey species used by wildlife, such as waterfowl.

2.3.6 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, it seems reasonable to have assumed that the observed ambient water toxicity in the northern reach of the Bay was similar to the ambient water toxicity being observed in tributary waters and that pesticides transported into the Bay by upstream waters were the likely causes of toxicity.

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 2) are well below toxicity threshold levels reported for *Americamysis bahia* (Table 3). 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; George et al. 2003). 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 2. 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
	chlorpyrifos	dissolved	0.26	0.46	0.59	0.33

Table 3. Comparative toxicity of diazinon to selected test organisms.		
Test Species	Diazinon Acute LC_{50} (ng/L)	Reference
Freshwater		
Ceriodaphnia dubia	320, 350; 410, 470; 470; 510	Bailey et al. 1997; Bailey et al. 1996; CDFG 1992a; CDFG 1992b
Estuarine/Marine		
Acartia tonsa (copepod)	2570	Khattat and Farley 1976
Palaemonetes pugio (grass shrimp)	2800	Thursby and Berry 198
Americamysis bahia	4200; 4820; 8500	Surprenant 1988; Nimmo et al. 1981; Cripe 1994
Ampelisca abdita (benthic amphipod)	6600	Thursby and Berry 1988
Penaeus duorarum (pink shrimp)	21,000	Cripe 1994
Neanthes arenacoedentata (polychaete)	>2,880,000	Thursby and Berry 1998
Arbacia punctulata (sea urchin)	>9,600,000	Thursby and Berry 1998
Cyprinodon variegatus (sheepshead minnow)	1,400,000	Goodman et al. 1979; Mayer 1987
Menidia beryllina (inland silversides)	1,170,000	Thursby and Berry 1998

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 4).

3.1 Diazinon: Background Information

Diazinon (Figure 5) 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 that has been sold under a wide variety of trade names for both commercial usage and over-the-counter consumer use products. OP pesticides are used in a wide variety of agricultural applications, as well as numerous urban applications (landscape maintenance/gardening and controlling pests in and around buildings, 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.

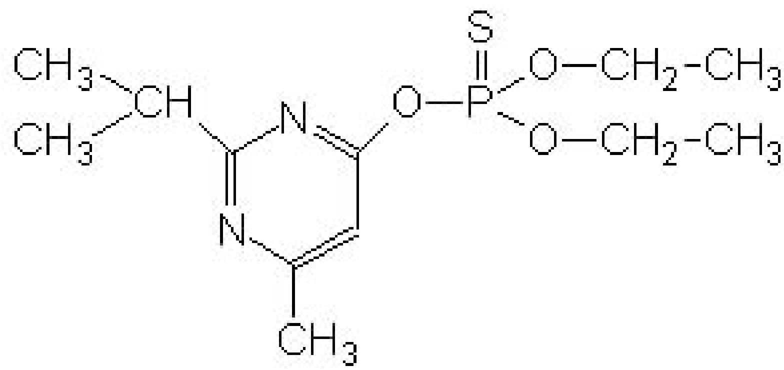


Figure 5. The chemical structure of diazinon.

Like all of the OP pesticides, diazinon is a synthetic compound that does not occur naturally in the environment. Diazinon is relatively water-soluble, and when released into the environment via its intended application and/or improper disposal, it is readily transported 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.

Diazinon is generally much more toxic to arthropod invertebrates (particularly crustaceans) than to fish, and is generally more toxic to freshwater organisms than estuarine/marine organisms (Table 3). *Americamysis bahia*, the organism that triggered the 303(d) listing, is one of the most sensitive estuarine/marine organisms to diazinon (and many other pesticides).

3.2 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 surface water 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 sources include: (1) point sources, including wastewater effluent and runoff from specific areas where the pesticides were used or handled, and (2) atmospheric deposition.

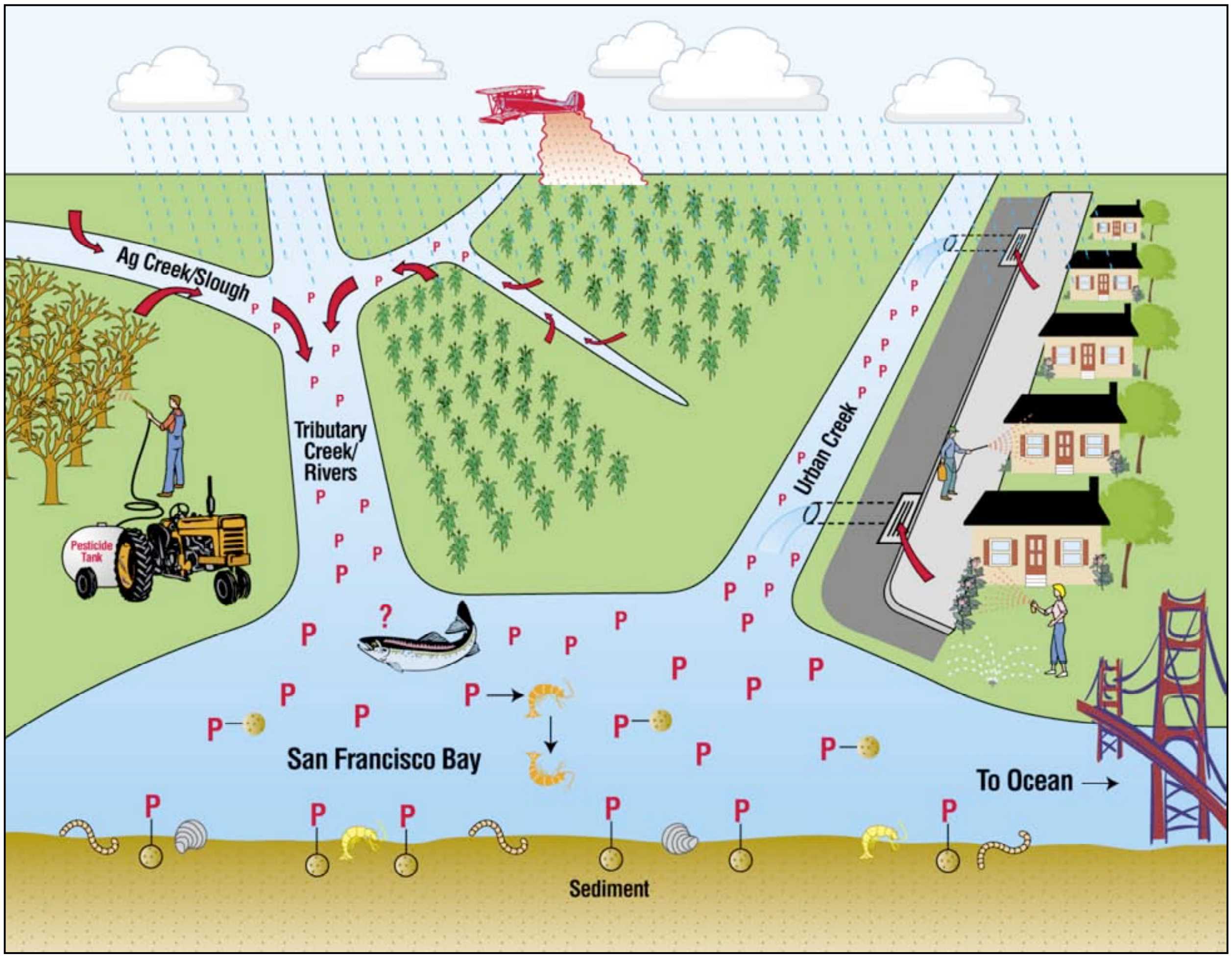


Figure 4. A conceptual model of the fate and effects of diazinon in the San Francisco Bay watersheds:

P = waterborne pesticide, dissolved; **P**- ● = pesticide associated with suspended particulates/sediments.

Sources: The major source of diazinon to San Francisco Bay is surface water runoff from agricultural applications in the Central Valley, primarily in stormwater runoff after dormant spray applications; however, runoff from urban applications, primarily from structural pest control applications (e.g., ant control) and gardening/landscape maintenance, can also be significant.

Diazinon is expected to occur primarily in the dissolved phase, with negligible sorption to suspended particulates or sediments; however, other pesticides that are replacing diazinon (e.g., pyrethroids) may rapidly become effectively bound to particulates and sediments.

Degradation: degradation of diazinon in water occurs primarily via hydrolysis and microbial degradation, with reported half-lifes that range from several to 185 days. Diazinon is very short-lived in sediments, with half-lives ranging from 14-21 days in aerobic sediments. However, other pesticides (e.g., pyrethroids) may persist much longer.

Effects: Diazinon is generally much more toxic to arthropod invertebrates (e.g., crustaceans) than to fish, and is generally more toxic to freshwater organisms than estuarine/marine organisms. *Americamysis bahia*, the organism that triggered the 303(d) listing, is one of the most sensitive estuarine/marine organisms to diazinon (and many other pesticides). Recent data suggest the potential for *sublethal* toxicity to fish reproduction.

3.2.1 Surface Water Runoff from the Bay's Watersheds

Relative to many pesticides (e.g., "legacy" organochlorine pesticides [SFEI 2004] and pyrethroid pesticides), diazinon is readily soluble in water (solubility = 40 mg/L [Kamrin 1997]). As a result, residues remaining from applications of diazinon to plants, soils, or anthropogenic materials will readily partition, or dissolve, into water (e.g., rainfall, irrigation water, sprinklers, etc). If the volume of water is sufficient, then surface water runoff transports 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.

3.2.1.1 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 almost certainly 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; Guo et al. 2004). 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; Guo et al. 2004). 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; Guo et al. 2004). 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]).

3.2.1.2 Urban Runoff of Diazinon - The principal urban uses of diazinon are structural pest control and landscaping/gardening. 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 source (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 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.

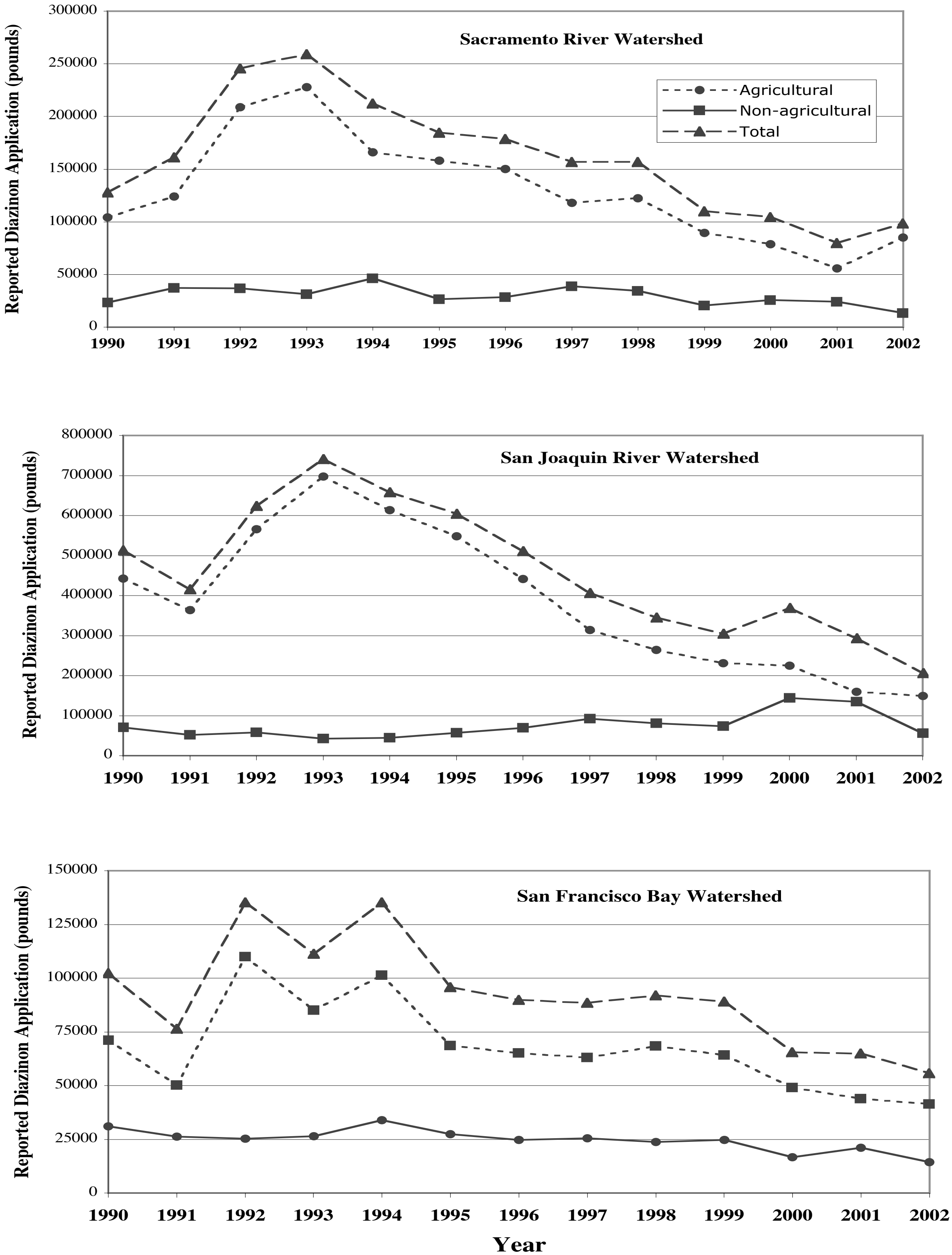


Figure 6. Trends in the application of diazinon in the Sacramento River, San Joaquin River, and San Francisco Bay watersheds, 1990-2002 (CDPR 2004). Data are for pesticides applied county-wide for counties partially or completely within the watershed boundaries.

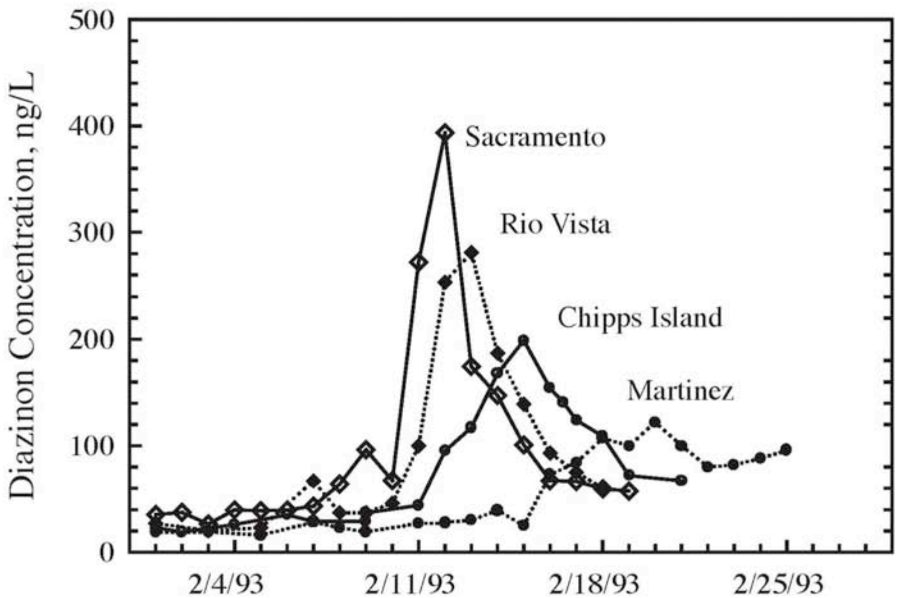


Figure 7. Concentrations of diazinon measured in the Sacramento River and northern reach of San Francisco Bay following a rainstorm in February 1993 (from Kuivila and Foe 1995; used with permission)

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). Although diazinon does degrade relatively quickly in soils (due primarily to microbial degradation - see discussion of degradation processes later in this report), the diazinon and other structural pesticides applied in urbanized areas are most often applied to relatively impermeable surfaces (e.g., buildings, parking lots, streets, sidewalks, etc), and there is markedly less percolation and degradation. 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, 37 San Francisco Bay watershed urban creeks have been placed on the CWA 303(d) list for diazinon and pesticide-related toxicity (Johnson 2004). However, it is important to note that the dilution that results when urban creek runoff waters are mixed into the Bay's waters will greatly lower the resultant diazinon concentrations.

3.2.2 Point Sources

Sources of diazinon to wastewater treatment plants include:

- use of diazinon-containing products that are discharged to sewers (i.e., treatment of interior drains),
- discharge of water used to clean diazinon-treated surfaces (i.e., carpets),
- cleanup of pesticide application equipment,
- spills and dumping (TDC Environmental 2001).

And while studies of Bay Area publicly-owned treatment works (POTWs) indicated that, on average, 85% of the diazinon in POTW influent is removed during treatment, there still remained occurrences of elevated diazinon concentrations in POTW effluents (Chew et al. 1998). 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. Given the recent EPA-mandated prohibition of urban retail sales of diazinon-containing products (see Section 4.3.3.1), it is difficult to assess the current magnitude of diazinon loading in POTW effluents, although it seems safe to conclude that the POTW effluent concentrations and loading rates are less than they were at the time of the studies performed in the 1980s and 1990s. However, for POTWs with shallow water discharges, the effluents may receive little dilution for considerable distances from their outfalls. As a result, while POTW discharges are a minor source of diazinon to the Bay overall, there may still remain localized potential for toxicity.

3.2.3 Atmospheric Deposition

Diazinon's vapor pressure is relatively low (0.0001 torr) and it is readily soluble in water, so it tends to stay in water rather than evaporate into the atmosphere. However, some diazinon can 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). However, vapor-phase diazinon is subject to very rapid degradation (see Section 3.3.2).

Nevertheless, once in the atmosphere, diazinon can re-enter surface waters though both dry and wet 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, direct deposition (i.e., rainfall falling directly onto the Bay's waters) is unlikely to cause toxicity given the relatively much larger volume of water within the Bay system and the resultant dilution of the diazinon. 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).

3.2.4 Transport and Fate

3.2.4.1 Water vs. Suspended Particulates/Sediments - Diazinon has a low-to-moderate tendency to adsorb to soils or sediments (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 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).

The RMP has not measured sediment diazinon concentrations in San Francisco Bay, and we are unaware of any other studies that have done so. Analysis of San Francisco Bay watershed urban creek sediments have indicated diazinon concentrations ranging from 2.8 to 55.5 mg/kg (cited in Johnson 2004). However, these data may be anomalous. Based upon its low K_{oc}, diazinon did not meet the selection criteria for expected sediment accumulation (USGS 2002; Nowell et al. 1999). This is consistent with USGS NAWQA observations that despite measurement of concentrations as high as 720 ng/L in the overlying surface waters, measurable concentrations of diazinon were not detected in suspended or bedded sediments at sites in the San Joaquin River and selected tributaries (Pereira et al. 1996). Diazinon is not bound to suspended sediments entering the Bay (Domagalski and Kuivila 1993), so advective transport into the Bay's sediments is likely negligible.

3.2.4.2 Bioaccumulation - Based upon its low partitioning coefficient (e.g., Kow, the octanol-water partitioning coefficient), diazinon did not meet the selection criteria for potential bioaccumulation in a screening of pesticides by the USGS (USGS 2002; Nowell et al. 1999). This is consistent with USGS NAWQA observations that despite measurement of concentrations as high as 720 ng/L in the overlying surface waters, measurable concentrations of diazinon were not detected in clams at sites in the San Joaquin River and selected tributaries (Pereira et al. 1996). Other studies with freshwater fish indicated that tissue diazinon concentrations reached a peak within 3 days, with relatively low bioconcentration factors that only range as high as 188 (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), again with relatively low bioconcentration factors that only ranged as high as 213 (Goodman et al. 1979).

One factor accounting for the low bioaccumulation in fish is that diazinon is rapidly metabolized and excreted. Reported half-lives for diazinon in fish tissues are typically on the order of hours to a few days (Goodman et al. 1979; Seguchi and Asaka 1981; Keizer et al. 1993). Given the relatively low bioaccumulation factors and high elimination rates coupled with the very low concentrations at which diazinon occurs, the bioaccumulation of diazinon is not expected to problematic (Howard 1991).

3.3 Degradation Processes

3.3.1 Degradation in Water and Sediments

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 waters and sediment is rapid, and 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 lower and higher pH's, 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).

As stated above (Section 3.1.4), diazinon is not expected to accumulate in sediments. However, once in sediments, diazinon is only marginally persistent, with a half-life ranging from approximately 14-21 days in aerobic sediments, and 24-32 days in anaerobic sediments (Bondarenko and Gan 2004).

3.3.2 Atmospheric Degradation
Atmospheric diazinon is subject to direct photolysis (Howard 1991), as well as reaction with photochemically-generated hydroxyl radicals (HSDP 1996), resulting in rapid atmospheric degradation, with a half-life of about 4-5 hours (Howard 1991; HSDP 1996).

4. Impairment Assessment: Current Conditions

4.1 Ambient Water and Sediment Toxicity Conditions

4.1.1 The Basin Plan Narrative Objectives 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.

Furthermore, the Basin Plan goes on to state:

> "Controllable water quality factors shall not cause a detrimental increase in the concentrations of toxic pollutants in sediment …".

While not as "definitive" as the narrative objective for aquatic toxicity, this narrative language effectively establishes that sediments must be free of pollutants in toxic amounts.

4.1.2 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 3). 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.

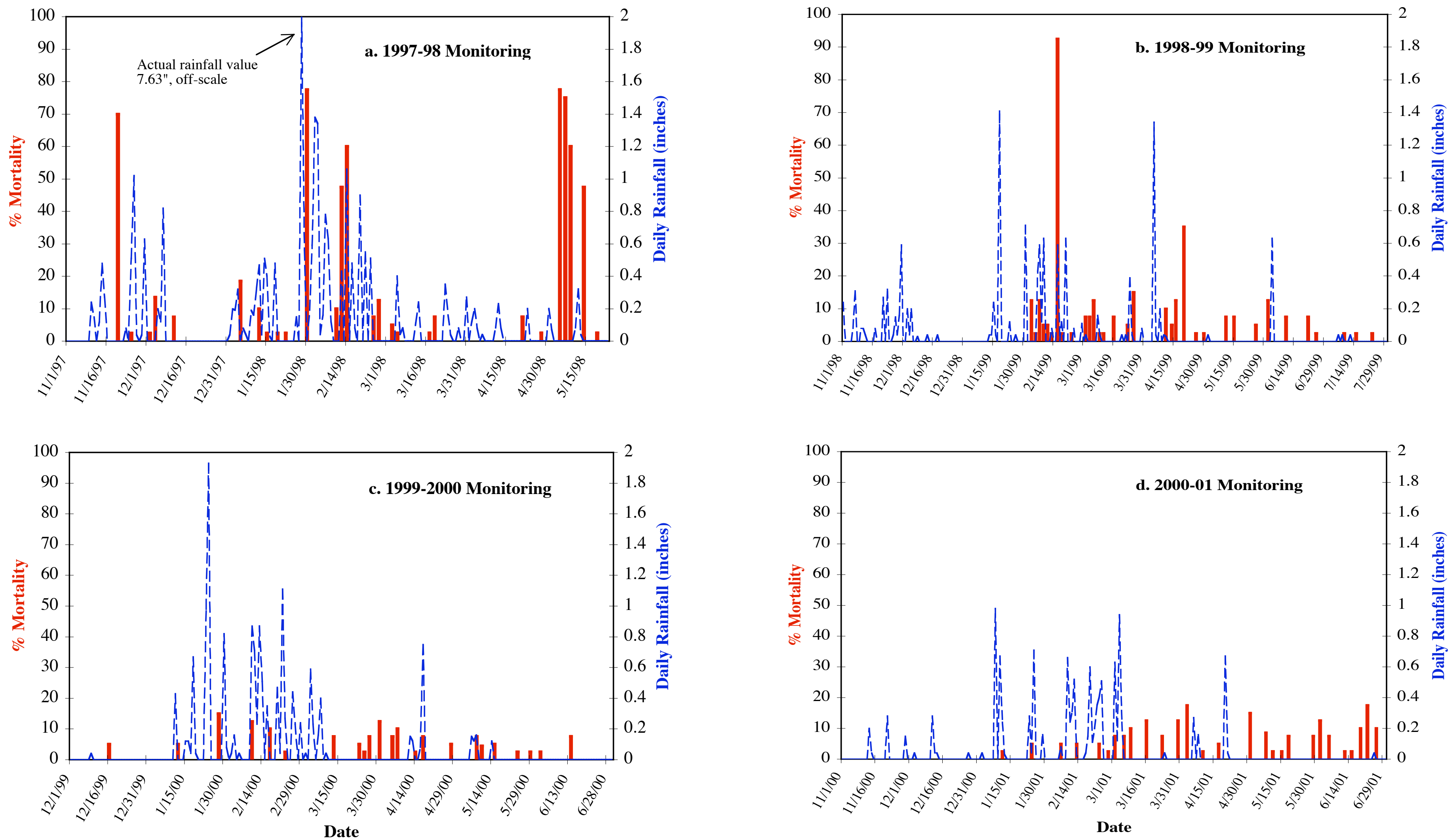
Subsequent RMP monitoring of ambient water toxicity from October, 2001 through April 2003, also indicated an absence of toxicity to the test organisms (Ogle and Gunther 2002, 2003). This trend for reduced ambient water toxicity has also been observed by similar monitoring projects taking place upstream 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.

4.1.3 Ambient Sediment Toxicity in San Francisco Bay

In addition to monitoring ambient water toxicity, the RMP has also monitored for the presence and cause of any ambient sediment toxicity since its inception. To date, the RMP sediment toxicity testing and follow-up TIEs have not observed any results that indicate or otherwise suggest potential sediment toxicity by diazinon (Thompson et al. 1999; RMP Contribution 43).

4.2 Water Quality Conditions

The RMP has monitored water and sediment chemistry in San Francisco Bay since 1993. The results of the analyses of diazinon in San Francisco Bay ambient waters are summarized in Table 4. 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 5). 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.



Figures 8a-8d. Trends in ambient water toxicity at Mallard Island, based upon RMP monitoring. Note the decrease in the frequency and magnitude of toxicity over this time period. The % mortality values have been normalized to the Control treatment response for each test.

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 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 1995). 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 may have been instances in which the true peak concentrations of diazinon (and other pesticides) in the Bay's ambient waters 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 that ambient water concentrations in the Bay are at least an order of magnitude below the water quality criteria, and data reported from studies of upstream tributary waters have also indicated a marked decline in the ambient water concentrations of diazinon (Spurlock 2002; Kuivila and Orlando 2002; Hall 2003a,b); consideration 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.

Table 4. 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
Dumbarton 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 5. 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 (draft)	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 2000b
e - U.S. EPA 1986
n.c. - not calculated.

4.2.1 Sediment Quality Conditions

There are currently no state or federal regulatory numerical criteria for sediment diazinon concentrations. 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.

Concentrations of OP pesticides in the Bay's sediments are not monitored by the RMP, or any other monitoring effort. However, as discussed previously in Section 3.1.4, based upon its low K_{oc}, significant accumulation of diazinon in sediments is not expected. Diazinon is not bound to suspended sediments entering the Bay (Domagalski and Kuivila 1993), so advective transport into the Bay's sediments is likely negligible, which is consistent with reports that ~98% of the diazinon in San Francisco Bay is in the dissolved phase (Domagalski and Kuivila 1993).

4.3 Future Water Quality Conditions: Expected Changes

4.3.1 Agency Outreach: Best Management Practices

One of the first responses by State and local agencies (e.g., RWQCBs, CDPR) to reports and observations of toxicity from agricultural and urban applications of diazinon 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 BMPs 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).

4.3.2 303(d) Listings and TMDLs in Upstream Waters

As stated previously, ambient water toxicity associated with diazinon had been observed in the Central Valley and in the urban creeks of the San Francisco Bay watershed well before such toxicity had been observed in the Bay's ambient waters. Therefore, it comes as no surprise that selected water bodies in these watersheds have previously been placed on the 303(d) list for impairment due to diazinon:

- **Sacramento and Feather Rivers –** In 1994, the Central Valley Regional Board placed the Sacramento and Feather Rivers on the CWA Section 303(d) list due to toxicity caused by diazinon. Regional Board staff have prepared a TMDL analysis and draft Basin Plan amendment that establishes the following water quality objectives:
  - 50 ng/L diazinon, measured as 4-day average;
  - 80 ng/L diazinon, measured as 1-hr average;
  - neither objective to be exceeded more than once every three years, on average.

  This draft Basin Plan amendment has been adopted by the Central Valley Regional Board, and forwarded to the State Board for approval.

- **Lower San Joaquin River -** In 1996, the Central Valley Regional Board placed the Lower San Joaquin River on the CWA Section 303(d) list due to impairment caused by diazinon and chlorpyrifos. Regional Board staff have prepared a Draft TMDL Report that proposes the following water quality objectives:
  - 50 ng/L diazinon, measured as 4-day average;
  - 80 ng/L diazinon, measured as 1-hr average.

- **Sacramento San Joaquin Delta –** In 1998, the Central Valley Regional Board placed the Sacramento San Joaquin Delta on the CWA Section 303(d) list due to toxicity caused by diazinon and chlorpyrifos. A TMDL analysis for this impairment is underway.

- **"Sacramento Urban Creeks" -** In 1998, the Central Valley Regional Board placed several Sacramento urban creeks (Arcade Creek, Elder Creek, Elk Grove Creek, Morrison Creek, Chicken Ranch Slough, and Strong Ranch Slough) on the CWA Section 303(d) list due to toxicity caused by diazinon and chlorpyrifos. Regional Board staff have prepared a TMDL Report that proposes the following water quality objectives:
  - 50 ng/L diazinon, measured as 4-day average;
  - 80 ng/L diazinon, measured as 1-hr average;
  - <1.0 toxic unit (TU) for the additive effect of diazinon and chlorpyrifos.

  This TMDL Report has been adopted by the Central Valley Regional Board, and forwarded to the US EPA for approval.

- **San Francisco Bay Area Urban Creeks -** In 1998, the San Francisco Bay Regional Board placed several Bay Area urban creeks (see SFBRWQCB 2004) on the CWA Section 303(d) list due to toxicity cause by diazinon. Regional Board staff have prepared a Draft TMDL Report that proposes the following water quality "targets":
  - <1 pesticide-related acute toxic units (TUa) or chronic TUc;
  - 50 ng/L diazinon, measured as 4-day average, no more than once every three years;
  - 80 ng/L diazinon, measured as 1-hr average, no more than once every 3 years.

It seems safe to assume that these upstream TMDLs will effectively establish 80 ng/L as the maximum allowable diazinon concentration, which is at least 50-fold less than the 96-hr LC_{50} of

4200-8500 ng/L for the test species *Americamysis bahia* (see Table 3), and at least 30-fold less than the "most sensitive saltwater species" acute toxicity value of 2570 ng/L reported for the copepod *Acartia tonsa* (US EPA 2000). Given that these upstream waters will be subject to dilution upon mixing with the Bay's waters, it seems certain that the concentration of diazinon in the Bay's ambient waters will certainly be well below levels associated with toxicity and well below any promulgated water quality criteria.

4.3.3 U.S. EPA Phases Out Most Urban 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 2000a).

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."

4.3.3.1 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.

4.3.3.2 Phase-Out of Some 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.

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).

Expected Effects of Diazinon Phase Out: It seems certain that there will be additional reductions in the amount of diazinon being applied, and in the loading of diazinon into surface waters in the Bay's upstream watersheds.

4.3.4 U.S. Court Decision Banning Diazinon Applications Near Salmonid Habitat

On January 22, 2004, the U.S. District Court for the Western District of Washington ruled in the case of Washington Toxics Coalition v. EPA, establishing buffer zones around certain water bodies in California where several pesticides (including diazinon) cannot be used. This order is in effect until the EPA completes an evaluation of whether endangered Pacific salmon and steelhead are sensitive to exposure from any of the pesticides.

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. Available information suggests that little (if any) progress has been made in the establishment of buffer zones and related requirements for point-of-sale notification (Kelly Moran, personal communication). However, if the court decision stands and is implemented, then there may be additional reductions in the amount of diazinon entering surface waters in these watersheds.

4.4 Impairment Summary: Is Diazinon Impairing San Francisco Bay?

Toxicity: Based upon the observations of decreased applications of diazinon in the Bay's watersheds and the decreased concentrations and toxicity in the upstream tributary waters of the Bay that have co-occurred with the observed "disappearance" of ambient water toxicity in the Bay, it appears that any potential toxicity that might have been 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 6a).

Table 6a. Current status of compliance with water quality objectives for ambient water toxicity.

Basin Plan Narrative "No Toxicity" 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

Water Chemistry: Based upon:
- the diazinon concentrations that have been measured in San Francisco Bay for the past 10+ years (i.e., RMP monitoring),
- observations of decreased applications of diazinon in the Bay's watersheds
- observations of decreased concentrations in the upstream tributary waters of the Bay,
- the implementation of TMDLs for diazinon in the Bay's upstream watersheds, and
- the ongoing phase-out of diazinon,

the concentrations of diazinon in the Bay's ambient waters are, and should be expected to continue to be, well below the existing CA DFG and US EPA ambient water quality criteria, and well below estuarine/marine organisms toxicity thresholds (Table 6b).

Table 6b. Current status of compliance with ambient water quality criteria.

Ambient Water Quality Criteria	Current Status
CA DFG Freshwater Acute and Chronic Criteria	Water quality objectives are being met
US EPA Freshwater Acute and Chronic Criteria	Water quality objectives are being met
US EPA Saltwater Acute and Chronic Criteria	Water quality objectives are being met

Other Considerations: Significant accumulation and/or toxicity in sediments is not expected; Significant accumulation in plant and animal tissues is not expected.

4.4.1 Assessment of Impairment by Diazinon

Any assessment of impairment of the Bay's waters will by necessity be based upon a "weight of evidence" approach, with review and evaluation of all available relevant information. The Clean Estuary Partnership has proposed a set of potential conclusions and outcomes of impairment assessment that reflects the State's 303(d)-listing policy categorizations (Table 7). Based upon this current review of available information, it is this study's conclusion that:

> **Impairment of the Bay by diazinon is unlikely –** The available data that have been reviewed through this CM/IA indicate that diazinon does not cause impairment of San Francisco Bay.

Table 7. Characterizations of the impairment of San Francisco Bay	
Clean Estuary Partnership Classification	State 303(d) Listing Policy Categories[a]
No Impairment – The available data are sufficient to unequivocally demonstrate that there are no negative effect(s) on the Bay's beneficial uses caused by diazinon.	Category 1. Attaining the water quality standard and no use is threatened.
Impairment Unlikely – The available data indicate no negative effect(s) on beneficial uses of the Bay, however, there is some uncertainty due to lack of sufficient information or disagreement about how to interpret that data.	Category 2. Attaining some of the beneficial uses; no use is threatened; and insufficient or no data and information is available to determine if the remaining uses are attained or threatened.
Unable to Determine Impairment – There is insufficient information to make any determination.	Category 3. Insufficient or no data and information to determine if any designated use is attained.
Possible Impairment – The available data suggest that there may be impairment of the Bay's beneficial uses caused by diazinon, however there are some uncertainties that must be addressed with additional studies.	
	Category 4. One or more beneficial uses are threatened, but the development of a TMDL is not required.
Definite Impairment – The available data are sufficient to clearly demonstrate that there are negative effect(s) on the Bay's beneficial uses caused by diazinon.	Category 5. The water quality standard is not attained.

a – SWRCB 2004.

4.5 Recent Developments Affecting Diazinon

4.5.1 Potential Changes to Diazinon Water Quality Criteria

The acute criteria for diazinon (100 ng/L) are presented in the U. S. EPA's recently released water quality criteria document (U. S. EPA, 2000). The freshwater acute criterion is driven by the 4 lowest genus mean acute LC_{50} values: *Gammarus fasciatus* = 200 ng/L; *Ceriodaphnia dubia* = 377 ng/L; *Daphnia magna* = 902 ng/L; and *Simocephalus serrulatus* = 1,587 ng/L. The second, third and fourth most sensitive species on this list are cladocerans, and the low toxicity values for each are consistent amongst numerous studies (reviewed in Giddings et al. 2000). However, the acute toxicity value for the amphipod, *G. fasciatus*, identified as the most sensitive species, is not consistent with the acute toxicity values for other amphipod species that are much higher (2,000 to 184,000 ng/L as reported in Giddings et al., 2000). Recent testing of diazinon with *G. pseudolimnaeus* reported a 96-h LC50 of 16,820 ng/L, which again is inconsistent with the *G. fasciatus* LC_{50} (Hall and Anderson 2004). Retrieval and examination of the original 1966 test report for the *G. fasciatus* test revealed what may have been data recording mistakes, and the

US EPA is currently considering a re-evaluation of the toxicity of diazinon to *G. fasciatus*. If it is shown that the previous *G. fasciatus* are incorrect, the new toxicity data may result in “corrected” acute toxicity criteria that are higher than the current CA DFG or US EPA criteria (Hall and Anderson 2004).

4.5.2 Department of Pesticide Regulation Re-evaluation of Diazinon

In 2003, DPR initiated the re-evaluation of diazinon products labeled for use as dormant sprays based on monitoring studies conducted between 1991 and 2001 (by the U.S. Geological Survey, Dow Agrosciences, DPR, the Central Valley Regional Board, and the State Board) indicating the presence of diazinon in surface waters of the Central Valley at concentrations that exceed Department of Fish and Game's (DFG's) water quality criteria (WQC), especially during the dormant spray season.

To mitigate off-site movement of diazinon residues, supplemental labeling has been developed for dormant spray diazinon products to add mitigation measures, such as restricting application to ground equipment only, prohibiting application within 100 feet upslope of "sensitive aquatic sites," and prohibiting application to orchards when soil moisture is at field capacity, or when a storm event is likely. The supplemental labeling has been approved for use in California for 11 of the currently registered diazinon products. The remaining products are waiting for U.S. EPA approval of the amended labeling.

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). These alternative pesticides may actually pose new water quality risks, if they 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, and have begun using pyrethroid pesticides as alternatives (Epstein et al. 2000). Similar changes are taking place in urban pesticide usages. 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.

5.2 Pyrethroid Pesticides vs. OP Pesticides

The potential toxicity implications of a transition from OP pesticides to pyrethroid pesticides were evidenced in a recent investigation comparing the toxicity of diazinon to the pyrethroid pesticide esfenvalerate 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 water samples were much more toxic to *Ceriodaphnia* than were the esfenvalerate-contaminated water samples (400-800 Toxic Units for diazinon relative to 10-20 Toxic Units for esfenvalerate). 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 esfenvalerate-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 8).

Table 8. Comparative toxicity of diazinon and pyrethroid pesticides.

Pesticide	Taxa	10th percentile of LC/EC50 values (ng/L)	r^2
Diazinon[a]	arthropods	480	0.96
Cypermethrin[b]	arthropods	6.4 (~75-fold more toxic than diazinon)	0.98
Permethrin[b]	arthropods	76 (~6-fold more toxic than diazinon)	0.96
Fenvalerate[b]	arthropods	8 (~60-fold more toxic than diazinon)	0.90

a. Giddings et al. (2000)
b. Solomon et al. (2001)

The apparently anomalous results observed by Werner et al. (2002) 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 (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 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. Recent studies have, in fact, reported that agricultural runoff from pyrethroid-treated fields can result in toxicity <u>of the sediments</u> in the receiving water ecosystems (Weston et al. 2004).

6. Uncertainties and Data Gaps Associated with this Impairment Assessment

This section summarizes the uncertainties in this report's conclusions and suggests some potential future projects to obtain additional data and conduct more analysis of the sources, fate, transport, and effects of [pollutant]. In other documents or forums, the CEP will develop appropriate strategies for addressing [pollutant] in the Bay and its watersheds. These strategies may include:

- Data collection or analysis
- Implementation of corrective actions
- Formulating and refining management questions and setting priorities for the above 2 activities
- Determining an ongoing process for integrating all of the above.

There may be control measures, remediation, and regulatory actions that can and should begin now, even with existing uncertainties. CEP partners are committed to identifying these actions. Future CEP data gathering and technical analysis should focus on determining the potential effectiveness, and actual effects, of actions to reduce or eliminate impairment and to restore beneficial uses of the Bay.

6.1 Potential Sub-Lethal Toxicity of Diazinon to Fish Reproduction

Review of the available information on the toxicity of diazinon to estuarine/marine organisms indicates that the concentrations that have been measured in the Bay and that can be expected to occur in the future are well below levels associated with direct toxicity to organism survival. However, the potential sub-lethal effects of diazinon on these organisms are essentially unknown. For example, one recent study has reported that exposure of mixtures of Atlantic salmon sperm and eggs to 50 ng/L diazinon for 2 minutes resulted in slight yet statistically significant reductions in egg hatchability (Lower and Moore 2003).

Recommendation: The potential for such an impact in San Francisco Bay is uncertain. While salmonids do not spawn in the Bay's waters, there are several species of fish (e.g., Pacific herring, Delta smelt, longfin smelt) that do spawn in the Bay's waters at times that coincide with the maximum applications and runoff of diazinon (Giddings et al. 2000; Watters et al. 2004). Given the very small magnitude of the reduction in egg hatchability that was observed in the Lower and Moore study, similar fish reproduction experiments with San Francisco Bay fish species do not seem warranted at this time; however, it is recommended that the environmental scientists and managers responsible for the protection of the Bay's resources stay abreast of any new scientific information that becomes available regarding this potential adverse impact.

6.2 Pesticide Interactions May Increase the Toxicity of Diazinon

As pointed out earlier in this CM/IA, there is considerable uncertainty that diazinon ever contributed to the observed toxicity that triggered the 303(d) listing - the measured concentrations in the Bay's waters have always been well below reported diazinon toxicity levels. However, other studies have indicated that the toxicity of 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 potential for such interactions, now or in the future, is uncertain: the RMP has not monitored triazine or pyrethroid pesticide concentrations in San Francisco Bay's ambient waters, so that the likelihood of such synergistic interactions causing 'combined' pesticide toxicity cannot be assessed.

Recommendation: The potential for such an impact in San Francisco Bay is uncertain. However, given the clearly-defined mechanisms-of-action to explain the interactive effects and the number of reports of such potential interactions, it is recommended that the environmental scientists and managers responsible for the protection of the Bay's resources continue to periodically monitor the Bay's ambient waters, particularly in the northern reach of the Bay, for toxicity that might occur as the result of such interactions. While the RMP is no longer performing such monitoring under the Status and Trends program every year, it is planned that periodic monitoring (e.g., once every three years) still be maintained for such purposes.

6.3 Changing Pesticide Usage May Cause "New" Impairments

It should be noted that the observation of water toxicity observed in the Werner et al. (2002) study represents a "worst-case" scenario 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. As indicated previously, there have, in fact, been reports concluding that agricultural runoff from pyrethroid-treated fields can result in toxicity of the sediments in the receiving water ecosystems (Weston et al. 2004). 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.

Recommendation - 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. 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.

While the exact scope of work for a revised monitoring approach remains to be worked out, it seems likely that assessment of potential pyrethroid toxicity in the Bay's sediments, particularly at the mouth of tributary rivers, streams, and creeks, may comprise a key monitoring element of such a study plan.

As a first step in addressing this critical information need, the RMP has recently initiated an 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, it is important to note that the continued monitoring of the Bay's waters and sediments to ensure the absence of diazinon (and other pesticide)-related toxicity will continue to be the responsibility of those tasked with the protection of this great resource. An integral element of this continued monitoring effort will be an ongoing vigilance in keeping abreast of changing pesticide uses within the Bay's watersheds, and adaptation of the monitoring tools to reflect those changes.

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