DIAZINON IN SURFACE WATERS IN THE SAN FRANCISCO BAY AREA: OCCURRENCE AND POTENTIAL IMPACT

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June 30, 1997

ACKNOWLEDGMENTS

Preparation of this report was supported in part by EPA 104(b) and by funding provided to Woodward Clyde Consultants (WCC) by the Alameda County Flood Control and Water Conservation District (ACFCWCD) and the Alameda Countywide Clean Water Program. The authors wish to thank all the members of the Urban Pesticide Toxicity Control Strategy - Bay Area/Central Valley Coordinating Committee (Urban Pesticide Committee, UPC) who participated in determining the scope, contents, and function of this document through constructive feedback and excellent suggestions. Special thanks are due to Valerie Connor of the Central Valley Regional Water Quality Control Board (CVRWQCB), who provided data and many insightful comments. Finally, the help of WCC, ACFCWCD, and CVRWQCB staff is gratefully acknowledged.

DISCLOSURE STATEMENT

This project has been funded wholly or in part by the United States Environmental Protection Agency Assistance Agreement No. CP999179-01-0 to the State Water Resources Control Board and by Contract No. 5-103-120-0 in the amount of $51,577.00. The contents of this document do not necessarily reflect the views and policies of the Environmental Protection Agency or the State Water Resources Control Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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EXECUTIVE SUMMARY

Diazinon is a common organophosphate pesticide, one of the most widely used for insect control in urban areas. Diazinon has been confirmed through toxicity identification evaluation (TIE) procedures using *Ceriodaphnia dubia* to be a major cause of toxicity observed in urban creeks and storm water discharges, including discharges from exclusively residential watersheds. Monitoring effort found diazinon in urban creeks and storm water discharges at concentrations above levels that are both acutely and chronically toxic to aquatic organisms. Of particular concern is the extensive household use of diazinon which implies diazinon presence, and possibly toxicity, throughout most urban watersheds.

This report provides a compilation and review of water quality and aquatic toxicity data in urban creeks and storm water discharges, focusing on diazinon in the San Francisco Bay Area. Selected data related to other locations and other pesticides is also presented to provide a wider context, and the reader is referred to the original reports for comprehensive information. The review includes a discussion of the question of potential adverse impact of diazinon on aquatic ecosystems in waters receiving urban runoff, based on runoff toxicity, TIE results, diazinon concentrations in environmental samples, and toxic values of diazinon in laboratory tests. Other approaches to determine ecological significance are also discussed.

ES-1. BACKGROUND

Aquatic toxicity testing of urban storm water samples have been performed by storm water agencies in the San Francisco Bay Area (Santa Clara Valley Nonpoint Source Control Program, Alameda Countywide Clean Water Program, and Contra Costa Clean Water Program) since the late 1980s as part of their monitoring requirements. Toxicity to *C. dubia*, a small crustacean used as a test organism according to the EPA protocol (USEPA 1989), was frequently detected. Of the 130 wet weather runoff samples collected in urban creeks (stream stations), a total of 92 (71 percent) caused mortality within the test duration of 7 days, while 28 samples (22 percent) caused mortality within 48 hours (WCC 1991a,1991b,1993a, 1993b,1994a, 1995a, CCCWP 1995, 1996, SCVNPSPCP 1995).

TIE procedures were applied to identify the substances causing toxicity in runoff from various watersheds. These include the Castro Valley Creek watershed (Hansen 1994), the Crandall Creek watershed and the Demonstration Urban Stormwater Treatment (DUST) Marsh in Fremont (WCC, 1995b), and the Sunnyvale East Channel watershed in Santa Clara Valley (SCVNPSPCP 1995). Diazinon was identified as the major cause of toxicity in all three watersheds. Toxicity monitoring and TIE efforts were performed in parallel in urban watersheds in the Central Valley of California since 1993, yielding results and conclusions similar to those obtained in the Bay Area: Diazinon was the major toxicant. Chlorpyrifos, another organophosphate pesticide, also contributed to the toxicity observed. In fact, these two insecticides were responsible for more than 90% of the observed toxicity (Connor *et al.* 1997).

After diazinon was identified as a cause of observed aquatic toxicity, a study was undertaken during the winter and spring of 1995 to directly measure and determine the extent of diazinon presence in urban creeks throughout the San Francisco Bay Area and the Central Valley. The study involved a network of water quality professionals and volunteers, and utilized enzyme-linked immunosorbent assay (ELISA) kits. ELISA kits provided an inexpensive, reliable tool for measurements of diazinon at concentrations as low as 30 ng/l (parts per trillion) (Connor *et al.* 1997, Scanlin and Feng 1997). This enabled widespread storm water sampling and analysis. Results showed that diazinon was detected in most of the samples collected, sometimes at concentrations known to be toxic to *C. dubia* (see below).

These findings made it clear that pesticide toxicity is a widespread concern that no single agency could address alone and that potential solutions require coordinated activities and collaboration among agencies, industry, and the public. Consequently, the Urban Pesticide Toxicity Control Strategy - Bay Area/Central Valley Coordinating Committee (Urban Pesticide Committee) was created with the intention of addressing the finding's implications on a regional (and perhaps state) scale. The committee is comprised of scientists, managers, planners, outreach specialists, agricultural commissioners, economists, and educators, from USEPA, California Department of Pesticide Regulation, California Central Valley and San Francisco Bay Regional Water Quality Control Boards, municipal stormwater agencies, municipal wastewater treatment agencies, academia, consulting firms, and pesticide manufacturers. This committee has provided a forum for information exchange, coordination, and collaboration on the development and implementation of an urban pesticide toxicity control strategy.

This report is one of several products which will establish the basis of the strategy. Other related products include reports that discuss the use and formulation of diazinon (Cooper 1996, Scanlin and Cooper 1997) and provide a detailed characterization of diazinon use and runoff concentrations in a specific watershed (Scanlin and Feng 1997).

ES-2. WHAT DO WE KNOW?

ES-2.1 Diazinon Is Lethal To Some Aquatic Organisms At Low Concentrations.

The toxicity of diazinon has been measured in laboratories using numerous test species of different taxonomic groups. In these tests, organisms were exposed to various concentrations of diazinon in clean laboratory water for a fixed period of time, e.g., 48 or 96 hours, the number of living and dead organisms was recorded, and the concentration of diazinon that was lethal to 50% of the organisms (LC_{50}) within that exposure time was calculated. This "toxicity value" (48 h LC_{50} or 96 h LC_{50}) was very low, in the range of 300-500 ng/l, for *C. dubia*. Other cladocerans were also sensitive (e.g., *Daphnia magna* had a 48h LC_{50} of 800 ng/l) and the amphipod *Gammarus faciatus* had a 96 h LC_{50} of 200 ng/l (see Table 4-2). Some crustaceans and insect larvae appear to be more sensitive than others. On the other hand, the lower range of toxicity values for fish starts at 90,000 ng/l, and for snails at 4,800,000 ng/l (or 4.8 mg/l, ppm) (Sheipline 1993). A table showing these toxicity values for a variety of organisms is presented in Section 4 of this report (Table 4-2).

In the real world, however, diazinon toxicity may be affected by environmental factors not present in a laboratory setting. For example, organic substances, particulate matter, and bacteria may bind or degrade diazinon molecules and attenuate its toxicity. To evaluate the toxicity of diazinon *in situ*, the pesticide has been spiked at different concentrations into outdoor tanks (microcosms), ponds (mesocosms), or experimental river channels, containing natural assemblies of organisms (Arthur et al, 1983, Giddings 1992, Giddings et al 1996). In the river channel experiments, the dosing treatments were not replicated and were changed during the course of the experiment (Arthur *et al.* 1983), hampering a validation and a straightforward interpretation of the results. The microcosm and mesocosm experiments concluded that, at average concentrations of about 1000 ng/l diazinon, the densities of some cladocerans, amphipods, and insect larvae had decreased. However, the function of the ecosystems was not significantly impaired at these concentrations (Giddings 1992, Giddings et al 1996, and summary in Section 4).

ES-2.2 Diazinon Is Widely Used In Residential Areas

Diazinon is a broad spectrum insecticide that has been used effectively against a variety of pest insects both in agricultural and residential settings. Diazinon is an active ingredient in over 200 products registered by the California Department of Pesticide Regulation (DPR). The products are formulated predominantly as liquid concentrates, granules, dusts, or ready-to-use sprays. Since 1990, manufacturers have been selling about 2 million pounds of diazinon active ingredient in California each year (Data from DPR, Scanlin and Cooper 1997). A substantial portion of this amount is used for crop protection: reported use in the Central Valley of California in 1990 was about 700,000 pounds of diazinon active ingredient (Sheipline 1993).

Professional, licensed applicators (or pest control operators, PCOs) report the amount they use and the data are compiled by DPR. In the urban setting diazinon is used both indoors and outdoors by PCOs (reported use) and by individuals who buy the product in retail stores (unreported use). DPR 1994 records show that PCOs reported the use of about 340,000 pounds of active ingredient for structural and landscape pest control in California, while the 1995 DPR records for Alameda County indicate reported use of 16,000 pounds for those purposes (Scanlin and Cooper 1997). The extent of unreported use by individuals has been estimated through retail store surveys and other sources of data (Cooper 1996, English 1996, Scanlin and Cooper 1997). A retail store survey conducted in 1996 in Alameda County estimated that 15,000 pounds of diazinon active ingredient were applied outdoors by individuals (Scanlin and Cooper 1997).

The information reviewed by the authors of this report can be summarized by the following observations. However, because some of these estimates are associated with high uncertainty, the reader is referred to the original reports for detailed description of the data sources, assumptions, and rationale used to generate these approximations.

- in the mid 1990s the unreported urban use for structural and landscape pest control in California was roughly equivalent to reported use (Cooper 1996, Scanlin and Cooper 1997).
- estimated annual per capita use of diazinon active ingredient in Alameda County for structural and landscape pest control was 0.02 pounds (about 10 grams) in 1996 (Scanlin and Cooper 1997).

- about 0.3% of the amount of diazinon applied outdoors in urban areas may reach local creeks during storm events (Cooper 1996, Scanlin and Feng 1997).

ES-2.3 Diazinon Is Often Detected In The Urban Environment.

This section provides a brief summary of diazinon concentrations data reported in multiple sources, including the coordinated survey of spring 1995, monitoring by storm water agencies during 1994-1996, special studies conducted in Alameda County, and data compiled for the Central Valley. The reader is referred to Section 3 of this report for more details.

In a coordinated survey performed during February, March and April of 1995 by professional workers and volunteers, diazinon concentrations in stormwater collected from major streams and creeks in the San Francisco Bay Area during storm events ranged from non-detect (less than 30 ng/l) to about 700 ng/l. Samples from outfalls and tributaries draining small areas, e.g., tributaries of Castro Valley Creek, contained diazinon from less than 30 ng/l to over 2600 ng/l (Appendix A).

The variability in diazinon concentrations was extremely high, in agreement with the sporadic nature of runoff events and application practices. In the 167 samples collected from major streams and creeks, diazinon was not detected in 43 percent of the survey's samples, ranged between 30 and 150 ng/l (non lethal to *C. dubia*) in 29 percent, ranged between 150 and 300 ng/l (lethal after 4-7 days) in 16 percent, and ranged between 300 and 700 ng/l (lethal to *C. dubia* within 96 hours or less) in 11 percent of the samples. Details and summary tables are provided in Section 3 and Appendix A of this report. Essentially, results indicate that some of the stormwater runoff samples collected from any residential catchment in the San Francisco Bay Area will contain detectable concentrations of diazinon during the spring months.

Where is it coming from? Follow-up studies were conducted in 1996 in selected watersheds in Alameda County, designed to trace diazinon concentrations up the watershed to the sources. In San Leandro Creek, diazinon in the range of 4000-6000 ng/l was detected in runoff from a specific outfall throughout a storm event, and subsequent sampling in street gutters of that drainage revealed consistently high diazinon levels in runoff samples from specific blocks, with concentrations of up to 70,000 ng/l, while in other blocks no diazinon was detected (Section 3 and WCC 1997a). A study with similar design and results was conducted in tributaries and street gutters of the Castro Valley Creek watershed. In a preliminary experiment, runoff samples collected within a specific property two days after application of diazinon according to label directions contained up to 1,200,000 ng/l of diazinon (Scanlin and Feng 1997). In summary, detections of diazinon in street gutters tend to be sporadic, unpredictable, and independent of each other, while the range of concentrations is much wider than in creeks. It has not been determined how much diazinon runs off as a result of normal use following the label directions, and what amounts may be due to misuse (overspraying, dumping excess in storm drains, or washing application equipment down the storm drain). This information is extremely relevant to the development of a pesticide toxicity control strategy.

How long does it persist in urban creek waters? The Castro Valley study included analysis of separate grab samples collected throughout the storm event, for several events. Results showed that peak concentrations of diazinon were associated with peak flows in some events, and showed unchanging concentrations throughout the flow period in other events. In some cases, samples collected two days after a storm event still contained more than 400 ng/l of diazinon (Scanlin and Feng 1997). Diazinon was frequently detected in creeks during dry weather (see below) and may persist for several days (Section 3 and WCC 1997b). The half-life of diazinon in surface waters or in surface water samples is 7-40 days, depending on physical (light, temperature), chemical (pH, redox potential), and biological (e.g., bacterial populations) conditions (Giddings 1992, Jennings *et al.* 1996**,** Adams et al 1996, WCC 1995b, 1996a).

Where does it go? Most streams and creeks in the San Francisco Bay Area flow directly to the Bay. Diazinon concentrations in San Francisco Bay have been measured as part of the Regional Monitoring Program with results ranging from less than 0.1 to 98 ng/l (SFEI 1995). The highest value was measured at the outlet of an urban creek. However, it must be noted that the Sacramento and the San Joaquin Rivers, carrying agricultural runoff containing diazinon (Kuivila and Foe, 1995), are probably more significant sources of diazinon to the Bay than local urban creeks. In the receiving waters of the creeks, rivers, and the Bay, diazinon is broken down within the water column by chemical and biological processes. Some of the pesticide is adsorbed to suspended solids and removed through sedimentation into the creek beds even before the runoff reaches the Bay.

"The water comes and goes, but the sediment remembers". Diazinon was detected in sediments of urban creeks at concentrations of up to 50 ug/kg dry weight that persisted for many weeks (Section 3 and WCC 1996b). Sediments are probably a sink of diazinon and are important in removal of diazinon from water. However, sediments may also be a source of diazinon during low-flow period, and may be releasing substantial amounts of diazinon into the water column. All these processes have not been characterized in urban creeks.

What happens in the summer, when there is no rain to wash it off? Diazinon is often applied on outdoor areas during late spring and summer. In the semi-arid California climate, only a few streams are fed by spring water throughout the summer, and much of the water reaching urban creeks is coming from excessive irrigation and from various washing activities. Diazinon was often detected in dry weather flows in Alameda County creeks. Concentrations in October 1996 ranged from 40 ng/l to 340 ng/l in the Castro Valley Creek watershed, less than 30 ng/l to 442 ng/l in the Crandall Creek watershed, and up to 3000 ng/l in the ditches leading into Tule Pond in Fremont (but not in the pond itself) (WCC 1997b).

Diazinon in other locations Alameda County is not unique with respect to diazinon in urban streams, nor is the San Francisco Bay Area. A Coordinated survey was also conducted in urban areas in the Central Valley during the spring of 1995, with comparable results. Dry weather flows also contained diazinon. For example, concentrations in the range of 257 to 1013 ng/l were measured in Arcade Creek in Sacramento (Connor *et al.* 1997). Diazinon has also been measured during wet weather in urban creeks in San Diego Creek-Upper Newport Bay in Orange County, Southern California (G.F. Lee, personal communication).

Diazinon in rainfall The 1995 Coordinated surveys, both in the San Francisco Bay Area and in the Central Valley, included extensive analysis of diazinon in rain samples collected around the

Bay and in the Valley during the months of February through April. Several rain samples in the Central Valley contained more than 4000 ng/l diazinon (Section 3 and Connor *et al.* 1997). These samples were collected during the period of dormant spray application in orchards in the Central Valley, in which hundreds of thousands of pounds of diazinon active ingredients have been applied. A study showed that after application to trees a considerable amount (up to 9%) was found to volatilize into the atmosphere within 24 hours (Glotfelty *et al.* 1990). However, in the San Francisco Bay Area diazinon was not detected in more than half of the rain samples collected by volunteers, and the highest concentration detected was 96 ng/l. These data suggest that, in contrast to some locations in the Valley in February and March, rain is not a major source of diazinon to urban runoff in the San Francisco Bay Area (Section 3 and Appendix A). The data also indicate that, with the prevailing winds blowing from the Bay to the Valley, atmospheric transport of diazinon from the Valley to the Bay does not contribute a significant amount to runoff (relative to the amount generated in the local watersheds in the Bay Area).

Other pesticides Diazinon is not the only pesticide detected in urban runoff. Another organophosphate pesticide used outdoors, chlorpyrifos (the active ingredient in Dursban), is often detected as well. Selected samples from the coordinated survey were analyzed for chlorpyrifos; concentrations of up to 103 ng/l were found in Santa Clara Valley (Calabazas Creek) and up to 378 ng/l in the tributaries of Castro Valley Creek (Appendix A). Toxic effects of chlorpyrifos have been documented at concentrations as low as 80 ng/l for *C. dubia* (Sheipline 1993, Bailey *et al.* 1997). The mode of action of diazinon and chlorpyrifos is very similar and their effect is **additive** (Bailey *et al.* 1997). This means that if the pesticides are found together, each at sublethal concentrations, their combined action may be lethal.

Municipal wastewater discharges Although not directly related to impact on urban creeks, indoor use or disposal of diazinon and chlorpyrifos results in considerable concentrations of these pesticides in domestic sewage. During the first week of August 1996, influent concentrations reached 1426 ng/l of diazinon or 597 ng/l of chlorpyrifos in samples collected from three Bay Area Publicly Owned Treatment Works (POTWs) (Lai 1996). The problem is that the sewage treatment process is not geared to high efficiency of pesticide removal, and POTW effluents have been known to exceed levels that are toxic to some aquatic organisms. Toxicity was often attributed to diazinon and/or chlorpyrifos. The pesticide toxicity control strategy needs to address both indoor and outdoor uses in an integrated approach.

ES-3. HOW CAN WE TELL IF IT IS A PROBLEM?

To address the question of whether the toxic levels of diazinon create a problem in receiving waters of urban creeks, we need to define what constitutes a problem. Regulatory agencies such as the California water quality control boards establish water quality objectives for receiving waters that they deem necessary to protect aquatic life. A narrative objective has been established which stipulates that "all waters shall be free of toxic substances in concentrations that are lethal to, or that produce other detrimental responses in, aquatic organisms". Numerical water quality objectives have not been established for diazinon, but maximum limit values have been recommended. Recently, the California Department of Fish and Game has conducted a hazard assessment based on toxicity values and presence (concentrations, duration, and frequency) and concluded that "freshwater organisms should not be unduly affected if the four-day average does not exceed 40 ng/l and the one-hour average does not exceed 80 ng/l more often than once every three years” (Menconi and Cox 1994). These numerical recommendations are not legally binding, but may be used as guidelines.

ES-3.1 Issues Related To Problem Definition

The representativeness of the *C. dubia* chronic toxicity test as an indication of a problem has been questioned, with arguments that *C. dubia* is too sensitive and that the 7 day test is too long. If the test is not representative, it may predict a problem where there is none. The first question is related to test organisms: Do laboratory test species (that are used as surrogate and are not necessarily found in local waters) truly reflect the sensitivity of organisms that inhabit local receiving waters? Isn’t *C. dubia* more sensitive than other species tested? The answer to this is that a correlation was often found between mortality of test species in toxicity tests with effluents discharged and adverse effect on some species in the waters receiving these effluents (deVlaming 1997). *C. dubia*, the organism used most often in our testing, is among the species that are very sensitive to diazinon, but is not the most sensitive one.

The second question relates to exposure duration: Does runoff toxicity persist in the creeks after the storm for a length of time that is equivalent to test exposure duration? Long enough to cause mortality? Most of the time, acutely toxic concentrations of diazinon do not persist in the creeks of the SF Bay Area for 7 days, but persistence of 48 hours is common.

The third set of issues is related to the type and beneficial uses of receiving waters (Bay, Rivers, tributaries, creeks), and we need to identify what exactly we are trying to protect and what is considered an adverse impact: can we tolerate the loss of a few sensitive species if the function of the ecosystem is not impaired; what damage and to which trophic levels is considered an adverse impact, do we care only about threatened species of fish, amphibian or birds, or do we want to protect economically important species?

ES-3.2 The Integrated “Weight Of Evidence” Approach

The major components of the integrated approach to water-quality-based toxics control (USEPA 1991) are: toxicity of effluent (or urban runoff samples), toxicity of specific chemicals in relation to their concentrations in the environment, and bioassessments of receiving water habitats.

Evidence derived through the first component, i.e. toxicity testing, showed that urban runoff in the San Francisco Bay Area, the Central Valley, and in other locations in California was often toxic to *C. dubia*, sometimes within less than 48 hours. This toxicity was attributed to diazinon (and in some cases to diazinon and chlorpyrifos) in residential and mixed urban land-use watersheds.

Chemical-specific toxicity, i.e. laboratory toxicity tests with diazinon, shows that the pesticide was toxic to a variety of organisms at concentrations that are often detected in the environment. In fact, monitoring of diazinon concentrations in urban creeks during storm events and during dry weather shows concentrations that, in laboratory tests, cause mortality of some sensitive test organisms such as cladocerans (e.g., *C. dubia* or *Daphnia magna*) or amphipods. This may indicate a problem because some of these sensitive test organisms or closely related species inhabit urban creeks and are an important constituent of the food chain.

The third component of this approach, bioassessments of the habitat thought to be adversely impacted by a potentially toxic discharge, has been useful in the case of continuous point source discharge (such as POTW effluent) into a river where a reference site identical in all other features was available upstream. However, given the intermittent discharge pattern from multiple sources typical of urban runoff, it is practically impossible to identify reference sites for comparison. Moreover, it is impossible to separate the effect of diazinon from other potential causes of adverse impact in urban creeks. Other toxic chemicals (pesticides, heavy metals, etc.), organic matter and nutrients, water inavailability, erosion, channelization, tree canopy removal, solar radiation, introduction of exotic species - all these factors can cause a sever impact on creek habitat.

ES-3.3 The Risk Evaluation Approach

Based on our knowledge of runoff toxicity, toxic values, and diazinon concentrations found in creeks, there is no doubt that somewhere, sometime, some non-target organisms will be killed by diazinon. The question is: how much adverse impact can be tolerated? The question can be boiled down to six relevant aspects:

- **how much diazinon** - less than 150 ng/l is not expected to cause mortality;
- **for how long** - 500 ng/l for 8 hours may be harmless, but 500 ng/l for 48 hours may kill;
- **how often** - frequent exposures may eradicate some species, several weeks without exposure will allow recovery;
- **where** - pristine urban creeks have viable ecosystems that may be impacted, while concrete box culverts cannot support an ecosystem anyway;
- **which organisms are affected** - fish may not be directly poisoned but the cladoceran populations fish use as food may be diminished (while alternative food species may not be affected);
- **when (what season)** - diazinon impact on aquatic insect larvae may not be a problem in mid-winter but scarcity of aquatic insects in riparian corridors in the autumn may impair bird preparation for migration.

The ecological risk assessment process addresses these aspects for a given habitat and involves use of three groups of data: exposure data - ambient concentrations of “stressor” substances; toxicity data - results of laboratory toxicity experiments exposing various test species to known concentrations of stressors; and “receptor” data - information about important groups of biota that are at risk.

Recently, Ciba Crop Protection sponsored an ecological risk assessment of diazinon in the Sacramento and San Joaquin River basins. A panel of scientists reviewed existing data on the seasonal concentrations of diazinon in Central Valley surface waters (exposure), on the toxicity of diazinon to various organisms, and on the life histories and seasonal feeding requirements of fish and invertebrates found in these surface waters (receptors). The data were used for a probabilistic analysis of exposure and toxicity data, based on the premise that certain fish populations need to be protected. The panel concluded from this assessments that the risk of diazinon in the Sacramento-San Joaquin Rivers is limited to the most sensitive invertebrates, primarily cladocerans, and that direct toxic effect of diazinon on fish populations are highly unlikely. They also concluded that indirect effects on fish through reduction of prey species at critical time in the year is unlikely, but recommended further studies on food preference (and ability to catch alternative prey species) of young life stages that feed predominantly on cladocerans in this system (Adams et al 1996).

The probabilistic approach used for the Sacramento-San Joaquin basins by the panel Ciba has sponsored (Adams et al 1996) could be applied to urban creeks throughout the State of California, but it would probably require much better knowledge of habitat details and would need to be tailored to specific habitats. There is a variety of viable aquatic habitats in each of the San Francisco Bay Area creeks and streams, and they differ from the Central Valley rivers. Some creeks carry running water year round and provide summer refugia for many species in their upstream portions, other creeks are earthen flood control channels without shade in which pools of stagnant water are fed by turbid street waters, while others are completely dry throughout the summer. Organisms that live in the water-column in the summer are washed away during storm events, while benthic organisms adapted to fast currents thrive in winter. Some streams support cold water fisheries, while others do not. Given the variability of urban creek habitats, any risk-evaluation process would require detailed exposure (concentrations and duration) data, judicious grouping of similar creeks, and expansion to include other receptor organisms, such as birds and amphibians, that have not been included in the Central Valley's assessment.

ES-4 CONCLUSIONS AND DATA GAPS

Results indicate that many of the stormwater runoff samples collected from essentially any residential catchment in the San Francisco Bay Area and the Central Valley are likely to contain detectable concentrations of diazinon during the rainy season.

Information of runoff toxicity, TIE results, diazinon concentrations in environmental samples, and toxic values of diazinon in laboratory tests, provides evidence that diazinon in urban creeks has a potential to cause a problem under certain circumstances, yet to be defined. Even in the absence of evidence that adverse impact has already occurred due to diazinon (because bioassessments, even if they indicate impact, cannot identify the factor(s) responsible for it in our urban creeks), the weight of evidence for the Bay Area and the Central Valley creeks justifies development and implementation of a preventive based toxicity control strategy involving education and outreach as well as minor regulatory changes.

A number of uncertainties and data gaps have been identified which should be addressed to better characterize the potential adverse impact of diazinon. These include:

- Correlation of positive laboratory toxicity results with instream impact has not been confirmed in the case of organophosphate pesticides.
- The synergistic, antagonistic, and additive effects of other pesticides, especially chlorpyrifos, need to be considered.

- It is not known if diazinon persists in urban creeks during and after storm events long enough to kill sensitive species. Concentration /duration patterns need to be further characterized so that realistic exposure scenarios may be developed for urban creeks.
- Diazinon was often present in urban creeks at concentrations toxic to *C. dubia* during fall, winter, spring and summer. More information is needed to characterize how ubiquitous and how persistent diazinon is in dry weather flows.
- Diazinon accumulation in sediments has been demonstrated but not characterized. The role of urban creek sediments as a sink and a source of diazinon may be very important.
- As long as the toxicity of diazinon and chlorpyrifos in sediments is unknown, it cannot be concluded that the current use of these pesticides is not posing a risk to aquatic life.

1.0 INTRODUCTION

Diazinon is a common organophosphate pesticide, one of the most widely used for insect control in urban areas. Diazinon has been confirmed through toxicity identification evaluation (TIE) procedures using *Ceriodaphnia dubia* to be a major cause of toxicity observed in urban creeks and storm water discharges, including discharges from exclusively residential watersheds. Monitoring effort found diazinon in urban creeks and storm water discharges at concentrations above levels that are both acutely and chronically toxic to aquatic organisms. Of particular concern is the extensive household use of diazinon which implies diazinon presence, and possibly toxicity, throughout most urban watersheds.

This report provides a compilation and review of water quality and aquatic toxicity information relevant to urban creeks and storm water discharges. The review includes a discussion of the question of potential adverse impact of diazinon on aquatic ecosystems in waters receiving urban runoff, based on runoff toxicity, TIE results, diazinon concentrations in environmental samples, and toxic values of diazinon in laboratory tests. Other approaches to determine ecological significance are also discussed.

The report is focused on diazinon in freshwater habitats in the San Francisco Bay Area. The scope of work could not include a summary of the abundant information available to date regarding occurrence of diazinon and other pesticides in the Central Valley, in southern California, and in other locations. Moreover, this report does not include information on toxicity to estuarine and marine species, nor does it address potential impact to their habitats. A small selection of data related to other locations and other pesticides are presented in this report to provide a wider context, and the reader is referred to the original reports for comprehensive information.

1.1 BACKGROUND

The Santa Clara Valley Nonpoint Source Control Program and the Alameda Countywide Clean Water Program (ACCWP) were established in the late 1980's to characterize the composition and loads of storm water constituents and to implement best management practices (BMPs) that may reduce storm water pollutant loads to the San Francisco Bay. Monitoring activities included chemical analyses for various constituents (metals, PAHs, organics, TOC, TSS, and oil and grease) as well as toxicity testing. Initially, the three test species (*Selenastrum capricornutum* (algae), *Ceriodaphnia dubia* (water flea), and *Pimephales promelas* (Fathead minnow) were used to characterize toxicity of runoff samples collected in various land use stations (WCC 1991a, 1991b). Toxicity to all three species was observed in industrial catchments, and Phase I toxicity identification evaluations (TIE) pointed to heavy metals as the major cause of toxicity in these catchments. However, fish and algae were not affected in samples from residential and mixed land use catchments while *C. dubia* proved to be the most sensitive species. Phase I TIEs indicated that non-polar organic substances are associated with toxicity of runoff from these catchments. Subsequent monitoring by the Santa Clara and the Alameda Programs, as well as by the Contra Costa Clean Water Program, focused on *C. dubia* tests with samples from mixed land-use catchments, i.e., streams. The 7-day tests detected the presence of toxicity in a majority of the samples. (WCC 1993a, 1993b, 1994a, 1995a, CCCWP 1995,1996, SCVNPSPCP 1995). Toxicity was manifested in a typical survival curve: test organisms would all survive until a certain day in the test, and then succumb to the toxicant all at once. Of the 130 runoff samples collected in stream stations, 71% caused mortality within 7 days, while 28% were lethal to *C. dubia* within 48 hours.

Advanced TIE procedures (Phase II and III) were applied to identify the substances causing toxicity in the Castro Valley Creek watershed (Hansen 1994), in the Crandall Creek watershed and the Demonstration Urban Stormwater Treatment (DUST) Marsh in Fremont (WCC, 1995), and in Sunnyvale East Channel watershed in Santa Clara Valley (SCVNPSPCP 1995). Diazinon was identified as the major cause of toxicity in the three watersheds. Subsequent toxicity tests using diazinon and *C. dubia* confirmed the typical survival curve and established a concentration-toxicity relationship, revealing that the median time to lethality (LT_{50}) was proportional to diazinon concentrations: higher diazinon concentrations caused mortality after shorter exposures.

Toxicity monitoring, TIE efforts, and pesticide analyses were also performed in the Central Valley in urban watersheds. Urban runoff monitoring yielded results and conclusions similar to those obtained in the Bay Area, except that the insecticide chlorpyrifos was also identified as a major toxicant (Connor *et al.* 1997).

After diazinon was identified as a cause of observed aquatic toxicity, a study was undertaken during the winter and spring of 1995 to directly measure and determine the extent of diazinon presence in urban creeks throughout the San Francisco Bay Area and the Central Valley. The study involved a network of volunteers and water quality professionals and utilized enzyme-linked immunosorbent assay (ELISA) kits. ELISA kits provided an inexpensive, reliable tool for measurements of diazinon at concentrations as low as 30 ng/l (parts per trillion). This enabled widespread storm water sampling and analysis. Results showed that diazinon was detected in most of the samples collected, sometimes at concentrations known to be toxic to *C. dubia*.

These findings made it clear that pesticide toxicity is a widespread concern that no single agency could address alone and that potential solutions require coordinated activities and collaboration among agencies, industry, and the public. Consequently, the Urban Pesticide Toxicity Control Strategy - Bay Area/Central Valley Coordinating Committee (Urban Pesticide Committee) was created with the intention of addressing the pesticide toxicity issue on a regional (and perhaps state) scale. The committee is comprised of scientists, managers, planners, outreach specialists, agricultural commissioners, economists, and educators, from USEPA, California Department of Pesticide Regulation, California Central Valley and San Francisco Bay Regional Water Quality Control Boards, municipal stormwater agencies, municipal wastewater treatment agencies, academia, consulting firms, and pesticide manufacturers. This committee has provided a forum for information exchange, coordination, and collaboration on the development and implementation of an urban pesticide toxicity control strategy.

This report is one of several products which will establish the basis of the strategy. Other related products include reports which discuss the use and formulation of diazinon (Cooper 1996, Scanlin and Cooper 1997) and provide a detailed characterization of diazinon use and runoff concentrations in a specific watershed (Scanlin and Feng 1997).

1.2 REPORT ORGANIZATION

Section 2 summarizes information relevant to diazinon in urban and agricultural environments (physical and chemical properties, use, formulation, fate and transport mechanisms), and identifies data gaps and outstanding questions.

The third section provides "exposure" data, i.e. concentrations that have been detected in the environment and to which the local organisms may be exposed. Diazinon concentrations in rain, storm runoff, dry weather flows, Publicly Owned Treatment Works (POTWs) effluents, and sediment samples collected in the San Francisco Bay Area are summarized. Urban runoff and rain data from the Central Valley are also included. The section also provides information about chlorpyrifos concentrations and lists other pesticides that have been detected in the Bay Area in stormwater runoff.

Section 4 summarizes information related to prediction of ecological impact. The strengths and limitations of various methods and experimental approaches that have been used or could be used to evaluate the impact of diazinon on aquatic ecosystems are addressed. The section also summarizes results of field studies and the outcome of an ecological risk assessment performed for the Sacramento-San Joaquin Rivers that receive diazinon runoff from agricultural land and urban drainages. Section 4 also addresses the applicability, strengths, and limitations of direct assessment of the aquatic habitats thought to be adversely impacted by diazinon, and lists other factors that can impact the same habitats.

Section 5 provides a summary of facts used as evidence, the conclusions drawn by the weight of evidence approach, and the uncertainty and data gaps associated with the application of this approach to diazinon in urban runoff.

A selection of relevant literature is listed in section 6. The methods used in the coordinated survey of spring 1995, as well as the raw data obtained, are presented in Appendix A.

2.0 PROPERTIES, USE AND FORMULATIONS, FATE AND TRANSPORT

Synthetic insecticides were introduced in the early 1940's to provide household and agricultural pest control. The first generation of insecticides was dominated by organochlorine substances such as DDT or Chlordane, most of which were banned in the US during the late 1960's and early 1970's due to stubborn persistence in the environment and the potential for detrimental effects associated with bioaccumulation and biomagnification up the food chain.

Organophosphate pesticides such as diazinon and chlorpyrifos dominate the second generation of pesticides introduced in the 1950's and 1960's. These metabolically activated pesticides are considered safer because they do not have the tendency to accumulate in tissues or to be biomagnified in the food chain, and because they are characterized by relatively short persistence of residues in the environment.

Pesticides of the third generation are mostly pyrethrins (insecticidal substances that are synthesized naturally by plants and are isolated from them) and their synthetic derivatives, pyrethroids. The potency of insecticides has been increasing steadily, i.e., first-generation pesticides were effective at concentrations much higher than those of second generation pesticides needed to achieve the same effect, and third generation pesticides are effective at still lower concentrations.

2.1 TARGET PESTS OF DIAZINON

Diazinon is a broad spectrum pesticide that has been used effectively against a variety of insects including: cockroaches, grasshoppers, crickets, earwigs, thrips, aphids, hoppers, psyllids, whiteflies, beetles, weevils, borers, wireworms, moths, butterflies, flies, mosquitoes, midges, gnats, fleas, ants, wasps, bees, sawflies, hornets, and silverfish. Diazinon has also been used to kill a variety of other arthropods including: sowbugs, millipedes, centipedes, and scorpions as well as arachnids: mites, ticks, and spiders. Diazinon is applied indoors and outdoors and is readily available to residents, homeowners, certified professional pest control operators (PCOs), and farmers. The most common target pest in the San Francisco Bay area are ants, fleas, grubs, and spiders (Cooper 1996, Scanlin and Cooper 1997).

2.2 FORMULATIONS AND USE OF DIAZINON

Diazinon is an active ingredient in over 200 products registered by the California Department of Pesticide Regulation (DPR), some of which are restricted to agricultural use or to use by PCOs only. The pesticide is available in a variety of formulations suitable for different applications. Granules are about 1-2 mm in size and are used to cover large lawn areas or to create perimeter barriers to structures. Dusts and powders are finer particles that are applied directly to plants and can also be used as perimeter barriers. Concentrates are intended to be diluted with water before application and can be sprayed onto individual plants or over entire lawns. Ready-to-use mixtures which do not require dilution and can be sprayed directly onto plants are also available

(Cooper 1996). A recent survey in Alameda County revealed that approximately 3 times as much concentrate form as compared to granular form was sold to residents in the retail market (Scanlin and Cooper 1997).

DPR records show that the quantity of diazinon active ingredient sold by manufacturers in California has been in the range of 1,188,000 pounds to 2,660,000 pounds each year during the first half of the 1990s. These amounts include agricultural use and urban use by licensed PCOs, both of which are reported to DPR, as well as the amount bought by individuals "over the counter" in retail stores, without need to report (Cooper 1996). In the Central Valley of California, about 700,000 pounds of diazinon active ingredient were applied in 1990, primarily as dormant spray during the winter (Sheipline 1993).

In the urban setting diazinon is used both indoors and outdoors by PCOs (reported use) and by individuals who buy the product in retail stores (unreported use). DPR records show that PCOs used about 340,000 pounds of active ingredient in 1994 for structural and landscape pest control. Extent of unreported use by individuals has been estimated from several local surveys of retail stores. The authors are aware of surveys conducted in the City of Palo Alto, the City of Sacramento, and in Alameda County (Cooper 1996, English 1996, Scanlin and Cooper 1997). Retail surveys can only provide a rough approximation of the actual amount applied due to uncertainties about where (in or out of the survey area) and when (immediately or after storage) the purchased products have been used. Based on these and other sources of information, Cooper (1996) concluded that in the mid 1990s the unreported urban use in California was roughly equivalent to reported use.

DPR 1995 records for Alameda County indicate that about 16,000 pounds of diazinon active ingredient have been applied by PCOs for structural and landscape pest control (reported use). The records do not differentiate between outdoor and indoor use for structural pest control, but it was estimated that about 80% was applied outdoors (Scanlin and Cooper 1997). A retail survey conducted in 1996 estimated that additional 15,000 pounds (unreported use) were applied outdoors by individuals in Alameda County for pest control in their yards and gardens (Scanlin and Cooper 1997). Estimated annual per capita use of diazinon active ingredient in Alameda County is 0.02 pounds (about 10 grams) (Scanlin and Cooper 1997).

The relatively high solubility of diazinon (see "properties" below) could account for mobility in runoff. The watershed characterization study in Castro Valley Creek indicated that about 0.3% of the amount applied outdoors reaches the creek during storm events (Scanlin and Feng 1997). It has not been determined whether high diazinon concentrations in runoff are a result of normal use, by citizens who follow the label directions, or are due to overspraying, dumping excess in storm drains, or washing application equipment down the storm drain. The answer to this question may be critical in developing the strategy for reducing these concentrations.

A detailed report prepared for the City of Palo Alto (Cooper, 1996) contains an explanation of the pesticide registration and reregistration processes and additional details on the use and formulation of diazinon products in the San Francisco Bay Area. The reader is also referred to the reports prepared for the Urban Pesticide Toxicity Control Project for a comprehensive presentation of diazinon use (Scanlin and Cooper 1997) and for regulatory issues (Scanlin and

Gosselin 1997). More information is needed to evaluate the importance of normal use versus misuse, to characterize the spatial, seasonal, and rain-year variability, and to define the uncertainties and margins of error associated with all the values estimated.

2.3 PHYSICAL AND CHEMICAL PROPERTIES OF DIAZINON

Diazinon is an organic compound composed of carbon, hydrogen, oxygen, nitrogen, phosphorous and sulfur with a molecular weight of 304 Dalton. It is a clear colorless liquid with a boiling point of about 84^{o}C and density of 1.117 g/ml. It is not very volatile and tends to remain in solution, however, after application to trees a considerable amount (up to 9%) was found to volatilize into the atmosphere within 24 hours (Glotfelty *et al.* 1990). Diazinon solubility in water at 20^{o}C is 40 mg/l, appreciably higher than that of chlorpyrifos (2 mg/l) or pyrethrins (in the range of several microgram/liter). Solubility could account for the relatively high mobility of diazinon in runoff water, from the site of application to the storm drain and the creek.

2.4 PERSISTENCE OF DIAZINON IN THE ENVIRONMENT

Persistence of diazinon at the sites of application and in soils depends on many factors, including temperature, humidity, light, acidity, and microbial communities. The potential to cause harm to non-target terrestrial organisms on site exists (in fact several cases of bird poisoning have been reported), but is not the focus of this paper. We are predominantly concerned with the portion that dissolves in water and reaches aquatic habitats through rain or irrigation runoff. Once in these surface waters, diazinon concentrations decrease quite rapidly. The half-life of diazinon in surface waters or in surface water samples is 7-40 days (Giddings 1992, Jennings *et al.* 1996**,** WCC 1995b, 1996a). The mechanisms of diazinon removal from water are not clear, but scavenging by particulate matter may be an important one in creeks. Diazinon accumulates in creek sediments to appreciable concentrations and may persist for weeks (WCC 1996b).

3.0 SPATIAL AND TEMPORAL OCCURRENCE IN THE ENVIRONMENT

To address the question whether diazinon is a problem in receiving waters in urban creeks, the rivers, and the Bay, we need to define what constitutes a problem and characterize the concentrations of diazinon actually found in these receiving waters. The Clean Water Act, through the NPDES permit process, stipulates a narrative toxicity objective which requires that all waters be free of toxicity. In 1972, the National Academy of Sciences recommended a guideline of 9 ng/l (parts per trillion) for the protection of aquatic life in freshwater (NAS 1973). Recently, the California Department of Fish and Game has concluded that freshwater organisms should not be unduly affected if the four-day average does not exceed 40 ng/l and the one-hour average does not exceed 80 ng/l more often than once every three years (Menconi and Cox 1994). Neither of these recommendations are legally binding, and are be used as guidelines for protection of aquatic habitats. Exceedences of these water quality recommendations does not mean that diazinon causes impairment of beneficial uses of our natural resources. To put things into context, diazinon at concentrations of 160 ng/l can cause mortality of *Ceriodaphnia dubia* after several days of exposure, and the concentration that kills 50% of these organisms within 48 hours of exposure (48h-LC_{50}) is in the range of 300 to 500 ng/l.

3.1 WET WEATHER DIAZINON IN THE SAN FRANCISCO BAY AREA AND THE CENTRAL VALLEY

3.1.1. Coordinated Survey Of Urban Creeks Runoff And Rain, Winter-Spring 1995

Diazinon has been found in creeks throughout the San Francisco Bay Area, sometimes at concentrations known to be toxic to some aquatic organisms. In a survey performed during February, March and April of 1995, professional workers and volunteers collected grab stormwater samples from major creeks and tributaries and rain samples in pans placed on roofs or in yards. The samples were analyzed by Enzyme Linked ImmunoSorbent Assays (ELISA) which provided an inexpensive, reliable tool for measurements of diazinon at concentrations as low as 30 ng/l. Duplicate analyses demonstrate that ELISA results have acceptable precision. Several samples were split and sent to analytical laboratories for analysis, and there was a good agreement between the two methods (Appendix A and Connor *et al.* 1997). The reader is also referred to the Castro valley Creek characterization report (Scanlin and Feng 1997) for a comprehensive description of the ELISA methodology and QA/QC results.

A selection of diazinon concentration data in stormwater collected in the San Francisco Bay Area during storm events are shown in Figure 3-1 and in Table 3-1. The raw data of the entire data set is presented in appendix A. Concentrations in major streams and creeks ranged from non-detect (less than 30 ng/l) to about 700 ng/l. Samples from storm drain outfalls and tributaries draining small areas, e.g., tributaries of Castro Valley Creek, contained diazinon from less than 30 ng/l to over 2600 ng/l (Appendix A). These results revealed that diazinon presence is widespread in urban creeks and stormwater discharges throughout the San Francisco Bay area.

It is important to note that most of these results are based on grab samples collected at random times during storm events, and comprehensive supporting data of flow rates, sampling time within the hydrographs, or rainfall intensity are available only for the Castro Valley Creek watershed and for a small number of other samples. Consequently, the results should not be construed as representing the full extent of diazinon presence in runoff throughout entire storm events. Scanlin and Feng (1997) present results of extensive sampling efforts in Castro Valley Creek during storm events throughout the hydrographs.

Diazinon was also found in rainfall samples in the San Francisco Bay Area. Diazinon concentrations in rain collected during February and April 1995 are shown in Figure 3-2 and in Table 3-1. Detected diazinon concentrations ranged from 33 ng/l in San Francisco to 45 ng/l in Palo Alto and up to 96 ng/l in Albany. However, diazinon was not detected in more than half of the rain water samples collected.

The coordinated survey of 1995 was also conducted in the Central Valley. Detailed results are provided in a separate report (Connor *et al.*1997) and some examples are shown below. Diazinon concentrations in samples collected by trained volunteers in three creeks during storm events are shown in the top three panels of Figure 3-3. The California Department of Fish and Game (CDFG) water quality recommendation of 80 ng/l, as well as the *C. dubia* 48 h LC_{50} of 400 ng/l, have been added to these plot for reference. Diazinon concentrations in Arcade Creek, Elder Creek and Mosher Slough are comparable to diazinon concentrations found in San Francisco Bay Area creeks. However, the seasonal pattern is different: in the Bay Area, maximum runoff concentrations were detected during the fall and the spring (Scanlin and Feng 1997), while in the Central Valley diazinon in runoff peaks in February. This is attributed to diazinon in the rain itself during the period of dormant spray application in these regions (Figure 3-3, bottom panel).

The concentrations of diazinon in rain samples collected throughout Northern California on February 8, 1995 are shown in Figure 3-4. Diazinon in rain ranged from 418 ng/L in Colusa to 5463 ng/L in Patterson. Peak concentrations were detected in areas where the density of almond orchards is high. However, these concentrations were 1 to 2 orders of magnitude higher than diazinon concentrations found in San Francisco Bay Area rain. This means that atmospheric diazinon has not been transported in large quantities from the Valley westward to the Bay during this period (when prevailing winds blow from the Bay Area to the Valley).

3.1.2 Diazinon Inputs From Different Drainages Within A Watershed

Follow-up studies to the coordinated surveys were conducted in 1996 in selected watersheds in Alameda County, designed to trace diazinon concentrations up the watershed to the sources. The watershed of San Leandro Creek was characterized during the storm of April 1, 1996. Runoff from eleven storm drain outfalls, as well as creek samples, were collected in grab samples by trained volunteers and professional workers repeatedly during the event. Figure 3-5 shows the location of the outfalls and the concentrations of diazinon in the two or three samples collected at each outfall during this 4-hour event. Diazinon concentrations in runoff from the different outfalls ranged between from 30 ng/l to 6800 ng/l. Diazinon concentrations in the creek itself did not exceed 400 ng/l (not shown). One drainage produced runoff with exceptionally high concentrations of diazinon. Subsequent “block by block” sampling of street gutters in this drainage during April and May 1996 (Figure 3-6) revealed consistently high diazinon levels in street gutter runoff samples from specific blocks, with concentrations of up to 70,000 ng/l (WCC 1997a). It must be noted that each sampling point represented a separate, independent drainage.

Similar results were obtained in the Castro Valley Creek watershed: sporadic, independent peaks of diazinon were detected in street gutter samples from some city blocks but not from others. In a preliminary experiment, diazinon was applied to control ants in a specific property. Runoff samples, collected within that property during a small rain event that occurred two days after application, contained up to 1,200,000 ng/l of diazinon. These results are included in a separate report which summarizes the Castro Valley Creek watershed characterization effort (Scanlin and Feng 1997).

3.2 DIAZINON IN DRY WEATHER FLOWS

A summary of diazinon concentrations in dry weather flows for Alameda County creeks is presented in Table 3-2. Diazinon concentrations ranged from 40 ng/l to 340 ng/l in the Castro Valley Creek watershed, from less than 30 ng/l to 442 ng/l in the Crandall Creek watershed, and from less than 25 ng/l to 3000 ng/l in the Tule Pond catchment area in Fremont. At the end of summer 1996, the inlets to the pond (consisting of ditches that are separate from the pond itself) contained diazinon at concentrations as high as 2200 and 3000 ng/l. However, all Tule Pond outlet samples had non-detectable levels of diazinon (<30 ng/l). Diazinon concentrations in creeks can change dramatically over a few days. For example, samples of water from Castro Valley Creek at Castro Valley Blvd. contained 340 ng/l of diazinon on October 4, 1996 and 60 ng/l on October 11, 1996 (Table 3-2, WCC 1997b) .

Samples collected in urban creeks in the Central Valley during dry weather also contained diazinon. For example, concentrations in the range of 257 to 1013 ng/l were measured in Arcade Creek in Sacramento.

3.3 DIAZINON IN SEDIMENTS OF URBAN CREEKS

Sediment diazinon concentrations found in Alameda County creeks in 1995 and 1996 are summarized in Table 3-3. The muddy banks, which consisted of fine particles (silts and clays), were sampled and analyzed separately from the streambed samples, which consisted of sands, silts, and clays in varying proportions. Diazinon concentrations found in muddy banks ranged from 4.1 μg/kg dry weight to 59 μg/kg dry weight, while concentrations in streambeds ranged from less than 1.1 μg/kg dry weight to 35.9 μg/kg dry weight. Size-fractionation of a sediment sample and analysis of the separate fractions showed that diazinon was associated with fine sediment particles at specific concentrations that were much higher than those found for coarse sediment particles (WCC 1996b, WCC 1997c).

Attempts to compile sediment data from other counties were not successful, possibly because diazinon has not been measured in sediment in other locations in the Bay Area or in the Central Valley. Similarly, attempts to obtain data on the toxicity of diazinon in sediment through a literature search and in toxicological forums suggest that the toxicity of diazinon to benthic organisms has not been determined in bulk sediment tests.

3.4 CONCENTRATIONS OF DIAZINON IN SAN FRANCISCO BAY

The San Francisco Bay Regional Monitoring Program (RMP) included analysis of diazinon in Bay waters in 1994 and 1995 using extremely sensitive methods with detection levels of 0.1 ng/l. Sampling was performed by pumping 100 liters of Bay water (from a depth of 1 foot below the surface) through a paper filter (for determination of particulate diazinon) and then through a polyurethane plug (which adsorbed the dissolved diazinon). In the laboratory, the pesticide was recovered and quantified. Dissolved diazinon concentrations in the Bay are summarized in Table 3-4, and sample station locations are mapped in Figure 3-7. Except for one sampling event, diazinon concentrations in San Francisco Bay were in the range of less than 0.1 to 11 ng/l, i.e., one to three orders of magnitude lower than in local creeks (SFEI 1995).

Diazinon levels were an order of magnitude higher in February 1994 than at any other time measured (SFEI 1995). This sampling period was during a runoff event following a winter rain storm that occurred during the period of dormant spray applications on orchards in the Central Valley. These data suggest that agricultural runoff in the Sacramento and San Joaquin Rivers may be a significant source of diazinon in San Francisco Bay. However, a systematic sampling of the Bay during storm runoff flow periods, which has not been performed yet, could help define the importance of the different sources of diazinon to the Bay. It should also be noted that an episodic high level of 98 ng/l of diazinon was measured near the mouth of Coyote Creek, an urban creek that drains out of the Santa Clara Valley into South San Francisco Bay.

3.5 CHLORPYRIFOS SUMMARY

Diazinon is not the only pesticide detected in urban runoff. Chlorpyrifos is another organophosphate pesticide used outdoors for insect control and often co-found (detected as well) with diazinon, albeit less frequently than diazinon. Use information indicates that chlorpyrifos is applied as much as diazinon, perhaps slightly more (Scanlin and Cooper 1997). It is found less frequently because the detection limits of both ELISA and the analytical methods are higher for chlorpyrifos and because chlorpyrifos has higher tendency to adsorb to solid surfaces, resulting in reduced migration into runoff (compared with diazinon). Chlorpyrifos is more potent than diazinon: in laboratory water, the 48h LC_{50} for *C. dubia* is about 80 ng/l (Sheipline 1993, Bailey et al. 1997).

Conventional TIE procedures cannot separate the effect of chlorpyrifos from the effect of diazinon when the two insecticides are present in the same sample. Recently, the relative toxicity of the two insecticides was estimated using a new methodology that allows selective removal of one or the other with specific antibodies, and chlorpyrifos was implicated as contributing to toxicity of several POTW effluent samples and urban runoff samples from the Central Valley (Miller et al. 1997). The study also concluded that the toxicity of both insecticides was attenuated in environmental samples (in comparison to laboratory water), suggesting that natural substances found in these samples decrease the bioavailability of the insecticides. Being closely related metabolically activated cholinesterase inhibitors, the mode of action of diazinon and chlorpyrifos is very similar and their effect is **additive**. (Bailey *et al.* 1997). This means that if the pesticides are found together at sublethal concentrations, their combined action may be lethal indeed. It also means that substituting diazinon with chlorpyrifos as the residential insecticide of choice is not likely to eliminate the toxicity of urban runoff, and that the toxicity control strategy should address both insecticides (and other pesticides as well).

Chlorpyrifos analyses using ELISA were performed with selected Bay Area runoff and rain samples within the coordinated survey of winter-spring 1995. The detection limit of these ELISA tests corresponds to the lowest chlorpyrifos calibrator of 80 ng/l. Concentrations of up to 103 ng/l were found in Calabazas Creek, Santa Clara Valley. Tributaries of Castro Valley Creek in Alameda County contained up to 378 ng/l chlorpyrifos, and samples collected in Solano County creeks contained up to 89 ng/l chlorpyrifos. All other creeks sampled and all Bay Area rain samples analyzed for chlorpyrifos in the same survey contained less than 80 ng/l chlorpyrifos (Appendix A). Central Valley samples also contained chlorpyrifos, often at concentrations known to be toxic (Connor *et al.* 1997).

Selected sediment samples from Alameda County were analyzed for chlorpyrifos in 1996. Muddy bank samples had chlorpyrifos concentrations ranging from 21 µg/kg dry weight to 85 µg/kg dry weight, while streambed samples had concentrations ranging from 2.4 µg/kg dry weight to 47.5 µg/kg dry weight. As with diazinon, there are no data about the ecological meaning of these concentrations because the appropriate bulk sediment toxicity tests have not been done or, if done, have not been published (WCC 1997c).

3.6 DIAZINON AND CHLORPYRIFOS IN MUNICIPAL WASTEWATER DISCHARGES

Significant concentrations of diazinon and chlorpyrifos have been measured in municipal wastewater discharges. The cause of toxicity in some municipal wastewater discharges has also been attributed to diazinon and chlorpyrifos. Table 3-5 summarizes diazinon and chlorpyrifos concentrations in influent and effluent samples collected from three wastewater treatment facilities (Publicly Owned Treatment Works, POTWs) during the first week of August 1996 and analyzed using ELISA. Influent concentrations reached 1426 ng/l of diazinon and 597 ng/l of chlorpyrifos, while effluent concentrations ranged from less than 30 ng/l to 809 ng/l diazinon and less than 50 ng/l to 190 ng/l chlorpyrifos (Lai 1996). Diazinon and chlorpyrifos were also detected at high concentrations in samples collected in sanitary sewers within the service area of the Central Contra Costa Sanitary District during various seasons (Singhasemanon *et al.* 1997).

POTWs are not designed to remove pesticides from their waste streams. Measured diazinon removal efficiency, 7-day average, ranged from a low of 24% to a high of 82%, while 7-day average chlorpyrifos removal was 49% to 71% (Table 3-5). This means that these insecticides may reach the environment as a result of indoor application and disposal as well (in addition to runoff resulting from outdoor use), and that the pesticide toxicity control strategy needs to address both indoor and outdoor use and disposal as an integrated problem.

3.7 OTHER PESTICIDES

Additional pesticides including herbicides and insecticides are commonly used and occasionally detected in environmental samples. In the San Francisco Bay Area monitoring efforts, many samples showed non-detect when analyzed using high detection limits. Very few stormwater samples have been analyzed using sensitive methods (detection limit of less than 1 ug/l). DDT and its derivatives, chlordane, aldrin, malathion, carbaryl, and diuron were detected in Castro Valley Creek during the first rain event in the fall of 1996 (Scanlin and Feng 1997, Appendix B). These pesticides are often detected in sediment samples (WCC 1997c). In the Central Valley, insecticides and herbicides (malathion, diuron, simazine, glyphosate (Roundup), prowl, and pounce) have been detected in urban runoff samples (Connor *et al.* 1997).

4.0 EVALUATION OF POTENTIAL ECOLOGICAL IMPACT

Diazinon has been detected and implicated in causing acute *Ceriodaphnia dubia* toxicity in urban runoff samples and in receiving creek waters in the Bay Area (WCC 1996c), the Central Valley (Connor *et al.*. 1997), and Orange County (G.F. Lee, personal communication). The USEPA recommends use of an integrated approach to evaluate, prevent and/or control the potential adverse impact of waterborne toxic substances. Table 4-1 provides a summary of capabilities and limitations of the three major components of this approach: toxicity of whole effluent (or urban runoff samples), toxicity of specific chemicals in relation to their concentrations in the environment, and bioassessments of receiving water habitats. The table was taken from USEPA's technical support document (USEPA 1991) which provides a detailed discussion of each component. In the sections below, several of the items mentioned in Table 4-1 that are particularly relevant to the purpose of adverse impact evaluation are discussed and additional components are presented.

4.1 TOXICITY MONITORING (WHOLE EFFLUENT TOXICITY)

Toxicity testing is the most cost-effective tool for assessment of the potential impact of complex mixtures of unknown pollutants, such as wastewater effluent discharge or urban runoff, on receiving waters. This approach has been used successfully as a regulatory tool for treated wastewater discharge by POTW and other point source discharges and has also been applied to storm water monitoring.

The USEPA protocols for chronic toxicity testing using three freshwater species have been widely used in the whole effluent toxicity (WET) testing program required of point-source dischargers. However, use of WET testing on urban runoff raises two fundamental issues: whether laboratory test species (that are used as surrogate and are not necessarily found in local waters) truly reflect the sensitivity of organisms that inhabit local receiving waters to the complex mixture of substances discharged into it; and whether runoff toxicity persists in the creeks after the storm for a length of time that is equivalent to test exposure duration. A third issue pertains to the type of effect, lethal or sublethal, that is relevant to impact prediction.

<u>Issue # 1: Use of surrogate test species</u>

Research has been conducted to compare and/or correlate the response of surrogate test organisms with other measures of impact in the receiving waters. For example, Birge *et al.* (1989) reported that toxicity of treated municipal wastewater (secondary effluent) discharged into a river in Kentucky correlated with species richness at locations downstream of the outfall. Other studies (e.g., Dickson *et al.* 1992, Eagleson *et al.* 1990) reported similar results. De Vlaming (1997) summarizes the 49 studies he reviewed with the conclusion that *C. dubia* test results provided either reliable predictors or an underestimation of biological community responses. Test results never overestimated impairment . Recently, a group of environmental toxicologists convened in Pellston, concluded that "it is unmistakable and clear that WET procedures, when used properly and for the intended purpose, are reliable predictors of environmental impacts" (Grothe *et al.*. 1996). However, correlation of positive *C. dubia* WET results with instream impact has not been confirmed in the case of organophosphate pesticides (Adams *et al..* 1996), and is practically impossible to confirm in the case of non-point discharge in habitats that are subject to so many other adverse factors.

Issue # 2: Exposure duration

It must be emphasized that, initially, WET testing was applied to point-source discharges that are continuous in nature and potential toxicants are released sporadically or constantly with the effluent. Application of WET testing to urban stormwater runoff raised another question: does runoff toxicity persist in the creeks after the storm for a length of time that is equivalent to the chronic test exposure duration of 7 days?

The duration of exposure to diazinon is extremely important. In the storm water toxicity testing in the Crandall Creek and the DUST Marsh, an interesting feature was observed: mortality of all individual *C. dubia* in one sample occurred at roughly the same day of the test, whether it was day 2 or day 5 (WCC 1994b). The length of time to mortality of 50 percent of the animals (LT50) proved a useful measure of the intensity of toxicity (Katznelson *et al.* 1995). Toxicity in this watershed was attributed to diazinon in two independent TIE efforts (WCC 1995b). Subsequent toxicity tests of storm water samples collected in the San Francisco Bay Area during 1994/5 and 1995/6 indicated that concentrations of 150 ng/l diazinon or less were not lethal to *C. dubia* within 7 days, 150 to 300 ng/l were lethal after 4 to 7 days of exposure, and 300 to 500 ng/l were usually lethal to *C. dubia* within 48 hours of exposure (WCC 1996a, WCC 1996d, CCCWP 1996). Consequently, the fact that high concentrations are very transient in creeks after storms could mean that measuring toxicity of the original stormwater sample for 7 days overestimates the potential impact. In reality, about 20% of the runoff samples collected in Bay Area creeks (and 80% of the samples collected in Sacramento and Stockton) caused mortality of *C. dubia* within 48 hours (WCC 1996c, Connor *et al..* 1997).

The **environmental renewal** design was used to test the survival of *C. dubia* exposed to levels of stormwater toxicants that are actually present in a stream in the six days following a storm event. Two toxicity tests were performed in parallel: In the first, the organisms were first exposed to storm water collected during the storm, but the daily renewal of test solution was done with samples that were collected in the creek every day (or two days) and shipped to the laboratory. This protocol was run in parallel to the second test in which the original storm water sample was used for renewal throughout the 7 days of the test. In November 1991, original stormwater samples collected at Crandall Creek immediately after a storm event caused *C. dubia* mortality within 48 hours, and original DUST Marsh samples caused death after 4-5 days; environmental renewal of DUST samples resulted in complete survival (Katznelson and Anderson, LBL, unpublished). The environmental renewal design was also tested at Walnut Creek in the spring of 1995: In the original sample, 90% of the organisms died within 7 days. On the other hand, all the organisms survived when exposed to samples brought from the creek each day (CCCWP 1995). These preliminary experiments indicate that 7 day exposure to the original sample did not mimic the transient conditions in the creek in the case of moderate toxicity, but the results cannot be extrapolated to predict effect of acute toxicity.

Flow-through systems are commonly used for real-time toxicity monitoring of point-source discharges to provide timely warning of any toxicant that might be present in the effluent. Behavior changes are recorded as early warning signs, so steps can be taken even before mortality occurs. Although logistically complicated, this design may be suitable to monitor toxicity of storm water during and after a storm event, particularly if it is coupled with discrete sampling and analysis for storm water toxicants such as diazinon. Results would provide better understanding of the potential impacts of transient peaks in diazinon concentrations. As mentioned earlier, the question of exposure duration is especially relevant in the case of diazinon. The median time to lethality (LT50) of *C. dubia* and other organisms exposed to diazinon exhibits close correlation with the different concentrations: the organisms die rather quickly at high diazinon concentrations and live for a few days before dying at lower concentrations (WCC 1996a).

***In Situ* exposures** are useful in evaluating the combined effect of all environmental factors in a given habitat at a given time. However, they usually do not permit linking adverse effects to a specific factor, such as the presence of a pesticide during a storm event, because it does not allow separation of factors. There is a considerable challenge in constructing cages for small test organisms in urban creeks, particularly when flows are fierce. In addition, organisms trapped in cages cannot seek temporary refugia in protected niches when environmental conditions are harsh. Preliminary tests in Crandall Creek, where local crustaceans, insect larvae, gastropods and fish were exposed in plastic cages for 3 weeks after a spring storm, indicated that temperatures (rather than chemicals) were the crucial factor causing the observed mortality (Kitting 1994).

Issue # 3: Sublethal effects:

In the chronic toxicity test, reproduction of *C. dubia* is carefully documented through the 7-day test according to the EPA protocol. The first brood of offspring usually appears when the organisms are 3 to 4 days old, and additional broods are found on subsequent days. An interesting feature was observed in *C. dubia* exposed to urban runoff samples from residential and mixed land use catchments (where diazinon was implicated as a major cause of toxicity): the organisms produced numerous offspring before they died when exposed to samples with moderate toxicity (causing mortality after 5-7 days). Statistical analyses based on the number of offspring per female per reproductive day showed that reproduction was not inhibited in these runoff samples. A very minor inhibition of reproduction by diazinon was documented in laboratory water experiments (Hansen 1994, WCC 1996c). This may mean that diazinon will not have any effect on population growth at sublethal concentrations.

4.2 EXPERIMENTAL APPROACHES TO RISK CHARACTERIZATION

The possibility of a potential problem in California watersheds emerged through toxicity monitoring. Mortality of laboratory test organisms, exposed to storm water samples in the static renewal test design, was observed. Subsequent TIE showed that diazinon was the major cause of toxicity. Analysis of storm water and dry weather flows reveal that diazinon is ubiquitous in these waters. The following sections consider the emerging question: Does diazinon actually impact the receiving water ecosystems in a way that impairs the beneficial uses of these waters?

4.2.1 Chemical-Specific Toxicity Testing

The most straightforward way of predicting impact of a substance is to test the sensitivity of various organisms to known concentrations of this substance under controlled laboratory exposure conditions. The toxicity of diazinon to aquatic organisms has been measured by several workers who used numerous test organisms, and the data were compiled in several databases of "toxicity values". Many of these organisms were raised in cultures for that purpose, and some were collected from wild populations. Table 4-2 provides diazinon toxicity values for selected organisms. Data were selected from a summary (Menconi and Cox 1994) to show the range of sensitivities and the variability, even within closely related species. The cladocerans *C. dubia* and *D. Magna* are among the more sensitive species that have been tested with diazinon.

These toxicity values can be used to predict adverse impact to organisms that inhabit given receiving waters, but caution is needed for four major reasons:

- The values are highly variable due to differences in water chemistry and the use of different life stages and different populations of a given test species;
- The reliability of some database entries is questionable (particularly if the original publication has not been peer-reviewed);
- Many values are based on nominal (calculated from dilution of stock solution) rather than measured concentrations, and potential matrix effects have not been characterized;
- There are several endpoints and point-estimates (e.g., LC_{50}, EC_{50}) and various exposure durations (e.g., 48h, 96h) associated with "Toxicity values", and not all values are comparable and/or useful for prediction of impact.

A number of standardized test protocols with defined test conditions have been developed for specific test species to allow comparisons of responses as measured by different laboratories. The protocols specify the test designs, life stage, exposure conditions, test duration, endpoints and point-estimates, reference toxicant requirements, and other relevant aspects. In time, this will improve the quality of toxicity databases.

It must be noted that chemical-specific toxicity testing needs to rely on laboratory test organisms. The option of collecting local **(indigenous)** organisms from a given waterbody and testing their sensitivity to diazinon directly is valid, but laden with drawbacks. Many creatures die shortly after transfer from the habitat and extensive research is needed just to keep them alive in control solutions. For the survivors it is necessary to develop specific protocols; this is costly too. The response to diazinon of wild populations is expected to be highly variable, so it is necessary to collect organisms from each receiving waters separately. In the polluted site, the really sensitive species that could be impacted are probably no longer there, and reference sites are not always available. The final obstacle, which indigenous species share with surrogates, is our limited ability to mimic the transient nature of exposure to runoff diazinon in urban creeks.

Sediment diazinon toxicity data are sparse and incomplete. Solid-phase (bulk sediment) toxicity tests with spiked diazinon, if performed, have not been published. Preliminary testing by the Alameda Countywide Clean Water Program is in progress.

In summary, chemical-specific toxicity testing can provide a range of concentrations, probably reliable within half an order of magnitude, in which a specific chemical is predicted to cause adverse effect to members of certain taxonomic groups.

4.2.2 Field Experiments With Specific Chemicals

Chemical-specific toxicity testing in the laboratory utilizes an approach that separates the effect of a toxicant from all other factors. In the real world, however, diazinon toxicity may be affected by environmental factors not present in a laboratory setting. To evaluate the toxicity of diazinon *in situ*, the pesticide has been spiked at different concentrations into outdoor tanks (microcosms), ponds (mesocosms), or river channels, containing natural assemblies of organisms. The following paragraphs describe these experiments.

Diazinon was synthesized in 1952, registered for insect control use by Ciba Geigy Corp. in 1954, and rapidly became widely used (Adams *et al.* 1996). Due to concerns that diazinon carried in storm runoff will reach aquatic habitats, USEPA sponsored a study to evaluate the effect of diazinon in riparian systems. The study was performed for a period of 18 weeks during the summer of 1980 in three experimental channels diverted off the Mississippi River at the Monticello Ecological Research Station of the USEPA Environmental Research Laboratory - Duluth, Minnesota. Monitoring included general water quality parameters, diazinon concentrations, benthic macroinvertebrate analyses, and collection of drift and emergence data.

The study showed that total macroinvertebrate abundance and species diversity indices were not consistently different from the control channel, both in the channel that was dosed with 300 ng/l for 12 weeks followed by 5000 ng/l for 4 weeks, and in the channel that was dosed with 3000 ng/l for 12 weeks followed by about 8000 ng/l for 4 weeks followed by about 20,000 ng/l for 2 weeks. However, certain groups (amphipods and insects) were affected at the lowest concentration. At higher concentrations, pronounced changes in community structure were observed. Mayflies, caddisflies, damselflies, and the amphipod Hyalella were not found in the treated channels after 12 weeks of exposure. Emergence of mayflies and damselflies was reduced, and drift (dislodging from the substrate) of amphipods and snails was elevated in the two treated channels (Arthur *et al.* 1983). The treatment regimes were not replicated.

Other major studies were sponsored by Ciba Geigy Corp. (the major manufacturer of diazinon in the U.S.) in 1990 and 1991. The microcosm study utilized outdoor fiberglass tanks of 11.2 cubic meter that were dosed with eight loading rates in replicates (Giddings *et al.* 1996). The mesocosm study used 0.1-acre earthen ponds that were dosed with five loading rates in replicates (Giddings *et al.* 1992). Diazinon was added in a manner that simulated aerial deposition of sprayed material or introduction through runoff, and was maintained in the water at the dozed concentrations for several weeks. Both systems were established with sediments, water and a local assemblage of biota from a nearby pristine pond, and were stocked with bluegill sunfish. Monitoring included water quality parameters and diazinon concentrations as well as periodic assessments of all major groups of biota.

The results indicate that the functional integrity of the system was not impaired at lower treatment levels, but many individual species were severely affected. The system's lowest observed adverse effect levels was 8,400 and 19,500 ng/l in the mesocosms and the microcosms, respectively. Specific observations indicate that at 1000-2000 ng/l cladocerans were severely reduced, while trichoptera and some diptera were reduced as well; at 10,000-20,000 ng/l ephemeroptera, some chironomidae, rotifers, and copepods were reduced; and at concentrations above 100,000 ng/l most insects as well as fish were affected (Giddings *et al.* 1992, Giddings *et al.* 1996). After diazinon dozing was terminated, biota populations recovered from low-level impacts within several weeks (Giddings *et al.* 1992).

In summary, these experiments concluded that, at concentrations maintained at 1000 ng/l for several weeks, some cladocerans, amphipods, and insect larvae were affected, but the function of the ecosystems was not impaired and recovery was observed within weeks of diazinon concentration decline. For comparison, diazinon concentrations in Bay Area and Central Valley receiving waters seldom exceed 1000 ng/l and usually decrease rapidly, but pulses of diazinon at higher concentrations do occur and need to be characterized.

Controlled field experiments with specific chemicals can provide direct evidence that a chemical at a given concentration will not impair the function of given ecosystem. Conclusions of such studies may be extrapolated to predict effects in similar ecosystems. However, the certainty that such extrapolation is valid decreases when different ecosystems are considered.

4.3 ECOLOGICAL RISK ASSESSMENT

Several workers reviewed and addressed the potential hazards of diazinon to terrestrial or aquatic life (Eisler 1986, Menconi and Cox 1994, Foe 1995), but these did not include a full ecological risk assessment. The ecological risk assessment process for a given habitat involves use of three types of data: exposure data - ambient concentrations of "stressor" substances; toxicity data - results of laboratory toxicity experiments exposing various test species to known concentrations of stressors; and "receptor" data - information about important groups of biota that are at risk. Recently, Ciba Crop Protection (an affiliate of Ciba Geigy) sponsored an ecological risk assessment of diazinon in the Sacramento and San Joaquin river basins (Adams *et al.*, 1996). The following paragraphs summarize this effort.

A panel of scientists compiled all pertinent data, arguments, and justifications for regulatory actions related to the use of whole effluent toxicity testing (see above, section 4.1). The panel concurred with the conclusion that *C. dubia* is a suitable surrogate of median sensitivity to pollutants found in point source discharges from "municipal treatment plants, refineries, coke plants, chemical manufacturing plants, fertilizer plants, steel mills, and other industrial sources", where convincing correlation between *C. dubia* response and instream biological response were demonstrated. (Adams *et al.*, 1996). However, the panel argued that such correlations were not demonstrated for organophosphate pesticides (OPs) and that *C. dubia* is among the most sensitive species to OPs. Given the lack of correlation and the extreme sensitivity of *C. dubia* to OPs, the panel concluded that the results of toxicity tests and TIEs in the Sacramento-San Joaquin Basins cannot be interpreted as evidence of actual pesticide impact on the regional ecology, and advocated following the screening tests with a more detailed analyses (Adams *et al.*, 1996).

The panel reviewed existing data on the seasonal concentrations of diazinon in Central Valley surface waters, on the toxicity of diazinon to various organisms, and on the life histories and seasonal feeding requirements of fish and invertebrates found in these surface waters. This information was used in a probabilistic analysis of exposure and toxicity data, based on the premise that certain fish populations need to be protected. The panel concluded from this assessment that the risks posed by diazinon in the Sacramento-San Joaquin Basins are limited to the most sensitive invertebrates, primarily cladocerans, and that direct toxic effects of diazinon on fish populations are highly unlikely. They also concluded that indirect effects on fish through reduction of prey species at critical time in the year is unlikely, but recommended further studies on food preference (and ability to catch alternative prey species) of young life stages that feed predominantly on cladocerans in this system (Adams *et al.*, 1996).

This effort to assess the ecological risk of diazinon was focused on one of the major beneficial uses of the Sacramento-San Joaquin River Basins, i.e., fisheries, and concluded that all life-stages of the various fish populations in the rivers are not at risk under the present conditions as far as diazinon is concerned. The risk assessment draft document was reviewed by local scientists, and their questions concerning data and assumptions used in the analysis will be discussed in an open forum in the fall of 1997 (D. Kelly, Novartis, personal communication).

4.4 APPLICATION OF RISK ASSESSMENTS TO URBAN CREEKS

The probabilistic approach used for the Sacramento -San Joaquin Rivers (Adams *et al.* 1996) could be applied to urban creeks in the San Francisco Bay Area (and possibly throughout the State of California), but it will probably require much better knowledge of the details and will need to be tailored to specific habitats. Each creek and stream in the Bay Area has a list of beneficial uses assigned to it, based on available or desirable natural resources it can offer. Some creeks carry running water year round and provide summer refugia for many species in their upstream portions, other creeks are earthen flood control channels without shade in which pools of stagnant water are fed by turbid street waters, while still others are completely dry throughout the summer.

Table 4-3 shows an example of beneficial uses assigned to two watersheds in the Bay Area. An ecological risk assessment focused on diazinon should address potential ecological impacts, namely impairment of beneficial uses for aquatic (warm freshwater and cold freshwater) habitat, fish spawning, and possibly freshwater replenishment. Wildlife habitat may be affected indirectly (through reduction of food). It is anticipated that groundwater recharge is not expected to carry diazinon through the soil with it. Potential impact of diazinon on the other beneficial uses listed in Table 4-3 is not related to the ecological risk assessment.

Given the variability of urban creek habitats and beneficial uses, any ecological risk-evaluation process for diazinon would need to define a specific ecosystem and will require detailed exposure (concentrations and duration) data, judicious grouping of similar creeks, consideration of habitat value for threatened or endangered species, and expansion to include other receptor organisms, such as birds and amphibians, that are important in securing the beneficial use of that system.

4.5 DIRECT ASSESSMENT OF HABITAT AT RISK

As mentioned above, documented impairment of habitats have been correlated with toxicity of point-source discharges into these habitats (deVlaming 1997). These data were collected in habitats that could be compared to a reference site subject to the same environmental conditions, so that the effect of the discharge could be separated from other effects. When we ask the question: “Is there any connection between diazinon presence and adverse impacts on urban creeks, in terms of community indices derived from bioassessments?” we need a selection of reference sites for comparisons. This is extremely difficult in the case of urban runoff emanating from multiple sources.

In reality, it is practically impossible to separate the effect of diazinon from other causes of impairment. Urban creeks are subject to a myriad of factors that can cause adverse impact. The presence of other pesticides, heavy metals, and other toxic chemicals, sometimes at concentrations that are likely to cause harm, have been recorded (although the bioavailability of these substances in local waters and sediments has not been characterized). Urban creeks receive and accumulate organic matter and nutrients from runoff and dumping; eutrophication-related toxicity (ammonia, sulfide, oxygen depletion) is prevalent in sediments and, during low flow periods, in water as well. Water projects in the watershed alter the availability of water. Physical disturbance of habitat, erosion, channelization, etc. destroy ecological niches and seldom create alternative niches of any value. Removal of trees and loss of canopy cover enables solar radiation at intensities that elevate temperature to lethal degree, promote growth of nuisance algae, support photosynthesis to oxygen supersaturation and extremely high pH values, and increase ultraviolet exposure of creek biota. Another problem is the introduction of exotic species - plants, fish, insects - that may alter the community indices used in bioassessments.

In summary, bioassessments of the habitat thought to be adversely impacted by a potentially toxic discharge has been useful in the case of continuous point source discharge (such as POTW effluent) into a river where a reference site identical in all other features was available upstream. However, given the intermittent discharge pattern from multiple sources typical of urban runoff, it is practically impossible to identify reference sites for comparison. Moreover, it is impossible to separate the effect of diazinon from other factors potentially causing adverse impact in urban creeks. Each of these factors may affect biota independently, but it is also likely that they have a cumulative or even synergistic effect in urban creeks.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 WEIGHT OF EVIDENCE

Data provided in this report and in numerous other sources indicate that 1) Urban runoff in the San Francisco Bay Area, the Central Valley, and in other locations in California was often toxic to *Ceriodaphnia dubia*; 2) Toxicity Identification Evaluations (TIEs) point to diazinon as one of the major causes of toxicity to *C. dubia*, at least in residential and mixed land-use watersheds; 3) Diazinon concentrations measured in urban creeks during storm events and during dry weather periods often exceed concentrations that, in laboratory tests, have caused mortality in *C. dubia* and in other sensitive test organisms. Some of these organisms or closely related species inhabit urban creeks, and are assumed to be used as food by fish, birds, and possibly amphibians at critical times.

Based on this information of runoff toxicity, TIE results, diazinon concentrations in environmental samples, and toxic values of diazinon in laboratory tests, there is no doubt that some non-target organisms in some receiving waters will be affected by diazinon at one time or another. Because adverse impact of diazinon will depend on the specific circumstances of a receiving water, it is impossible to draw a general conclusion that diazinon presence in our urban creeks constitutes an ecological problem. On the other hand, at this point there is no evidence that diazinon presence is not a problem in urban creeks in California.

Unfortunately it is practically impossible to separate the effect of diazinon from the effect of other potential stress factors in urban creeks, so decisions must be made in the absence of supporting bioassessments.

5.2 JUSTIFICATION FOR ACTION

Is there a sufficient threat of a problem to justify action? Although existing data cannot prove that there is an ecological risk, waiting for such proof before taking action may be a risk, particularly when there are so many data gaps. For example, it is not known if diazinon persists in urban creeks long enough to kill sensitive species. There is little information about diazinon in sediments and no information about the bioavailibility and toxicity of diazinon in sediments. Severe action such as banning the use of diazinon is certainly not called for, but directing resources towards more judicious use of the pesticide cannot be a waste of resources. The preventive based toxicity control strategy currently under development by the Urban Pesticide Toxicity Control Strategy - Bay Area/Central Valley Coordinating Committee (Urban Pesticide Committee, or UPC) addresses the different options and means to achieve better understanding of the risk and to reduce the risk. The current version of this evolving document (Scanlin and Gosselin 1997) outlines action in three major fields:

- public education and outreach
- provision of additional information
- minor regulatory changes.

5.3 DATA GAPS AND OUTSTANDING ISSUES

Toxicity of diazinon and chlorpyrifos: The environmental effect of diazinon may often be augmented by chlorpyrifos, another organophosphate pesticide which is also detected in runoff and implicated as causing toxicity to *C. dubia*. Chlorpyrifos shares the same mode of action with diazinon and the toxic effect of the two insecticides is additive. The new methodology to estimate the relative contribution of each pesticide (using selective antibodies) should be further applied to questions related to potency, bioavailibility, additivity, and sample matrix effects. However, even at this point in time it is clear that substituting diazinon with chlorpyrifos for outdoor pest control is not likely to eliminate the toxicity of urban runoff, and that the toxicity control strategy should address both insecticides (as well as other pesticides). Discussion of the following issues is focused on diazinon but is relevant to chlorpyrifos as well.

Lethal and sublethal effects: Diazinon concentrations correlated well with the median time to lethality (LT_{50}) of *C. dubia* in the 7-day static renewal test: concentrations of 150 ng/l diazinon or less were not lethal to *C. dubia* within 7 days, 150 to 300 ng/l were lethal after 4 to 7 days of exposure, and 300 to 500 ng/l were usually lethal to *C. dubia* within 48 hours of exposure. This was observed in laboratory tests of storm water samples collected in the San Francisco Bay Area during 1994/5 and 1995/6. However, *C. dubia* exposed to runoff samples with moderate toxicity (causing mortality after 5-7 days) produced numerous offspring before they died. Statistical analyses based on the number of offspring per female per reproductive day showed that reproduction was at normal levels, i.e., not inhibited, in these moderately toxic runoff samples. A very minor inhibition of reproduction by diazinon was documented in laboratory water experiments. This may mean that diazinon will not have any effect on population growth at sublethal concentrations. More information is needed on sublethal effects of urban insecticides.

Use and formulation: It has not been determined whether high diazinon concentrations in runoff are a result of normal use, by citizens who follow the label directions, or are due to misuse (overspraying, dumping excess in storm drains, or washing application equipment down the storm drain). Results of street gutter sampling indicate that peaks of diazinon concentration in runoff are independent of each other and can be numerous in some neighborhoods; does it mean that all these peaks are a result of misuse? More controlled experiments involving application according to label followed by focused sampling and analyses may elucidate this question. However, raising public awareness of the fate and effects of outdoor insecticides may achieve reduction of runoff concentrations that are due both to normal use and misuse, because it is believed that misuse is associated with lack of awareness rather than intent. In addition, more data are needed on the potential of diazinon and chlorpyrifos to run off following application of different formulations onto different surfaces (turf and garden plants versus paved areas around the perimeter of buildings).

Persistence in the environment:

- High concentrations (>500 ng/l) of diazinon in creeks during storm events are usually transient. Concentration/duration patterns vary for each storm event and for each watershed;

very few of these variations have been carefully documented. Concentration /duration patterns need to be further characterized so that realistic exposure scenarios may be developed for urban creeks. Scenarios developed for benthic organisms or for organisms strongly associated with aquatic vegetation (i.e., organisms that are not swept by currents) may be different from exposure scenarios developed for water column organisms.

- Recent measurements of diazinon concentrations in creeks during dry weather provide indication of a diazinon problem that is potentially more significant than that associated with rain runoff: diazinon was often present at concentrations toxic to *C. dubia* during fall, winter, spring and summer. Diazinon could persist longer during dry weather due to very slow flows which result in very limited flushing, and due to less dilution (as compared to rain runoff events).

- Diazinon accumulation in sediments has been demonstrated. Sediments are probably a sink of diazinon and are important in removal of diazinon from water. However, sediments may also be a source of diazinon during low-flow period, and may be releasing substantial amounts of diazinon into the water column. All these processes have not been characterized in urban creeks. Moreover, as long as the toxicity of diazinon and chlorpyrifos in sediments is unknown, it cannot be concluded that the current use of these pesticides is not posing a risk to aquatic life.

- Fate and transport studies on diazinon and chlorpyrifos should address the differences in their solubility and in their differential stability under acid or basic conditions.

- Seasonal pulses of insecticides, sometimes linked to toxicity in laboratory tests with estuarine and marine species, have been detected in the Delta, in Suisun Bay, and in sloughs draining into the South Bay. More information is needed to assess the relative contribution of different sources (i.e., agricultural runoff, urban runoff, and POTW discharges) to these pulses. Additional studies are needed to provide understanding of transport mechanisms, persistence, and fate of insecticides from the different sources, as well as their potential to cause toxicity in these Delta and Bay habitats.

Evaluation of risk: Whole effluent toxicity (WET) testing results are considered a good predictor of impact to receiving waters, at least in the case of point source discharges. However, correlation of positive WET results with instream impact has not been confirmed in the case of organophosphate pesticides, and is practically impossible to confirm in the case of non-point discharge in habitats that are subject to so many other adverse factors. Application of the ecological risk assessment process on a pilot study scale, using specific details of diazinon concentration and receptor data for a well characterized watershed, could illuminate the usefulness of this approach in generating information that is relevant to decision makers.

Disposal in sanitary sewers: Diazinon and chlorpyrifos concentrations in influent and effluent samples collected from Publicly Owned Treatment Works (POTWs) have been known to exceed levels that are toxic to some aquatic organisms. POTWs are not designed to remove pesticides from their waste streams. Practically it means that the pesticide toxicity control strategy needs to address the "environmental results" of both indoor and outdoor use and disposal as an integrated problem. In service areas where POTW effluent toxicity has been attributed to organophosphate pesticides, further monitoring need to be done to determine the sources within the POTW collection system so that the outreach efforts may be targeted to the types of dischargers (e.g., pet grooming, restaurants, PCOs, residents) that contribute significant amounts.

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APPENDIX A

DIAZINON COORDINATED SURVEY (SPRING 1995)

SAMPLING PROCEDURES

Grab samples were collected by professional workers and volunteers directly into clean glass containers, either 1-liter amber bottles or 20 ml scintillation vials. Rain samples were collected in glass pans that had been precleaned (scrubbed with dishwashing liquid, rinsed, soaked in 10% bleach solution, rinsed and dried). Pans were set on roofs or decks when rain was predicted and retrieved at the end of the storm. The rain samples were transferred to scintillation vials. All samples were kept on ice or in a refrigerator throughout the storage, shipping and holding period. A "chain of custody" form including sampling and rain information was attached to each sample.

LABORATORY PROCEDURES

ELISA kits were purchased from Millipore Corp. and run according to manufacture's instructions. Full details are provided by Connor et al. (1997). Quality assurance/quality control (QAQC) measures included testing of replicates within run, testing of the same samples in consecutive runs, testing a laboratory reference material (diazinon solution in methanol) with each ELISA run throughout the study period, and splitting samples for parallel analysis using a GCMS method. Table I below shows diazinon concentrations measured in the reference material in 21 consecutive ELISA runs. Figure 1 shows the correlation between ELISA results and GCMS analytical results, and Figure 2 shows the distribution of relative percent difference, or RPD (the difference between the two results divided by the average of the two results, and multiplied by 100) between the methods. RPD values of 30-40% are common in analytical work with organic materials in environmental samples. The reader is also refereed to comprehensive appendices on ELISA methodology in the Sediment Diazinon Special Study report (WCC 1996b) and the Castro Valley report (Scanlin and Feng 1997).