

Report of the Pesticide Workgroup

Prepared by
The Pesticide Workgroup
San Francisco Estuary Institute
1325 S. 46th Street
Richmond, CA 94804

Introduction

The goal for the Pesticides Workgroup (PWG) was to make recommendations to the Program's Technical Review Committee (TRC) for improving the manner in which the Regional Monitoring Program for Trace Substances in the San Francisco Estuary (RMP) monitors the abundance, distribution, and effects of pesticides in the Estuary. The results of the Five-Year Review (Bernstein and O'Connor, 1997), and the data generated by the RMP and other programs, were used as guidance for developing these recommendations.

As part of the results of the Five-Year Review, the Steering Committee adopted a revised set of program objectives (finalized on April 15, 1998). The PWG was asked to craft recommended changes to the RMP pesticide monitoring effort to more effectively achieve the new objectives.

The revised objectives for the RMP indicate that the overall goal of the program is to provide data and interpretation that helps to address identified information needs of the San Francisco Bay Regional Water Quality Control Board (Regional Board). In general, these needs have been summarized in five major objectives:

- Describe patterns and trends in contaminant concentration and distribution.
- Describe general sources and loading of contamination to the Estuary.
- Measure contaminant effects on selected parts of the Estuary ecosystem.
- Compare monitoring information to relevant water quality objectives and other guidelines.
- Synthesize and distribute information from a range of sources to present a more complete picture of the sources, distribution, fates, and effects of contaminants in the Estuary ecosystem.

The mailing list for the PWG is found in Table 1, though not all of the individuals on this list attended the three meetings. The basic approach taken by the PWG was to produce a conceptual model of the sources, fates, and effects of pesticides in the Estuary. The group then considered recent monitoring and research results to develop a set of recommendations to apply to the 1999 RMP (see Appendix 1). The group also developed a conceptual model for ecological assessment and restoration with respect to pesticides in the San Francisco Estuary. Considering the weight of evidence of the impact of pesticides on the Estuary, the PWG developed a set of findings and recommendations for consideration by the TRC for inclusion in the reconfiguration of the RMP in the year 2000 and beyond.

Conceptual Models

In order to organize the review and assessment conducted by the PWG; the first step was to establish a conceptual model of the fate and effects of pesticides in the Estuary (Figure 1). This model allowed the PWG to reach consensus regarding the key pathways and points of impact for pesticides in the ecosystem. This model also helped the group identify important gaps in knowledge for which special studies or other monitoring activities are required. The RMP will be able to update and revise this model as our knowledge of the sources, fates, and effects of pesticides in the Estuary expands.

The PWG also developed a conceptual model that integrates RMP measurements with regulatory actions for assessing impacts upon beneficial uses and designing programs to protect and restore these uses (Figure 2). This model was particularly useful for purposes of identifying how the Regional Board could make use of existing data or the results of recommended special studies.

Findings

After consideration of the available information regarding pesticides in the Estuary, the PWG developed a set of findings that represent the consensus opinion of the group. These findings form the basis for the changes that the group recommends for the RMP in the year 2000 and beyond.

Finding 1: Chemical and toxicological measurements demonstrate that registered pesticides are adversely impacting beneficial uses in the Estuary.

The current indicators of impacts of pesticides on beneficial uses are (1) chemical concentrations of pesticides in surface water, or (2) toxicity in standardized aquatic toxicity tests that followed accepted quality assurance/quality control protocols. The present benchmarks by which the indicators are used to judge impairment are (1) U.S. EPA Water Quality Criteria or California Department of Fish and Game Hazard Assessment Criteria, or (2) toxicity in laboratory tests that is 20% greater than controls. By these standards, the weight of evidence suggests that San Francisco Bay and many local creeks are impaired, with the qualification that many toxicity tests have not had accompanying toxicity identification evaluations (TIEs) to verify pesticides as the causative agent. Registered pesticides are thus adversely affecting beneficial uses in the Estuary, which has led to the listing of the Estuary and other receiving waters in the region as impaired pursuant to §303(d) of the Clean Water Act.

A large body of data has been developed over the past decade regarding the impact of pesticides on beneficial uses in the San Francisco Estuary and the Sacramento and San Joaquin rivers. Investigations of ambient water toxicity in areas receiving agricultural drainage using U.S. Environmental Protection Agency (U.S. EPA) standardized tests have indicated a relatively high frequency and duration of toxicity in some of these waters (Foe and Connor, 1991a; Foe, 1995; Ogle *et al.*, 1998). Toxicity testing of stormwater runoff from urban areas has also revealed frequent toxicity to aquatic organisms (Connor, 1995; BASMAA, 1996).

In 1988, the Central Valley Regional Water Quality Control Board began conducting monitoring studies of ambient water toxicity in the San Joaquin River basin. They found that a 43 mile reach of the San Joaquin River between the confluence of the Merced and Stanislaus rivers was toxic to *Ceriodaphnia dubia*, the invertebrate component of the standard U.S. EPA freshwater bioassays, in 40-50% of the samples (Foe and Connor, 1991a). Follow-up monitoring in 1991-1992 documented that 22% of the water samples collected from the San Joaquin Basin were toxic to *Ceriodaphnia*. Four insecticides—chlorpyrifos, diazinon, fonofos, and carbaryl—appear responsible for most of the toxicity (Foe, 1995).

More recent ambient water toxicity monitoring along the Sacramento River and in the Sacramento-San Joaquin Delta demonstrated frequent and significant toxicity to *Ceriodaphnia* (Deanovic *et al.*, 1996; Deanovic *et al.*, 1998). TIEs, including several Phase III TIEs, indicated that organophosphate (OP) pesticides are responsible for most of the ambient water toxicity to *Ceriodaphnia* (Bailey *et al.*, 1996; Deanovic *et al.*, 1996; Deanovic *et al.*, 1998; Foe *et al.*, 1998), although other pesticides are also suspected of contributing some toxicity.

In over half of the stormwater runoff samples collected from Sacramento, Stockton, and several urban basins in San Francisco Bay, the OP pesticides diazinon and chlorpyrifos have been measured at toxic concentrations, and toxicity tests with *Ceriodaphnia* have indicated that most of these samples have caused complete mortality of the test organisms. TIE studies, including some with TIE fractionations using antibodies that are chemical-specific to chlorpyrifos or diazinon, have identified these OP pesticides as causes of much of the toxicity (S.R. Hansen & Associates, 1995; Bailey *et al.*, 1996; Bailey *et al.*, 1997).

In the winter of 1996, RMP sampling for aquatic toxicity coincided for the first time with stormwater inflows to the Estuary, and significant toxicity (using the U.S. EPA standard

saltwater toxicity test with the shrimp *Mysidopsis bahia*) was detected in Grizzly Bay and the Sacramento and San Joaquin rivers (Table 2). This was followed by detection of toxicity at the San Joaquin River site in July of 1996 (SFEI, 1998), and at the Napa River, Grizzly Bay, Sacramento River, and San Joaquin River sites in January of 1997 during high outflow that followed major storms (Ogle *et al.*, 1998).

In addition to toxicity in the Estuary apparently associated with storm runoff, dry season toxicity to mysids has also been detected as part of the RMP base program sampling. This includes the previously mentioned toxicity in July 1996 at the San Joaquin site, and also toxicity at Redwood Creek, Dumbarton Bridge, Coyote Creek, San Jose (site C-1-3), and Sunnyvale (site C-3-0) in July of 1997 (SFEI, 1999). These samples represent the first detection of toxicity in the South Bay as part of the RMP base program. Toxicity results from the RMP base program are summarized in Table 2.

Table 3 summarizes the exceedances of water quality guidelines for pesticides in RMP water samples between 1993-1996. The guidelines listed are either those promulgated by U.S. EPA in the National Toxics Rule (57 FR 60848) or the Hazard Assessment Criteria established by the California Department of Fish and (Menconi and Paul, 1994a; Menconi and Paul, 1994b). Water chemistry measurements by the RMP have clearly documented concentrations of registered pesticides that exceed established water quality standards, although the RMP measures individual samples and the standards are 4-day average concentrations. When reviewing these data, it is essential to remember that not all pesticides are being measured by the RMP, and that criteria do not exist for all pesticides found in surface waters of the Estuary.

Finding 2: Event-based sampling strategies will improve the ability to detect aquatic toxicity in the Estuary.

Results from the RMP have indicated that sampling for aquatic toxicity when runoff events occur increases the likelihood of detecting aquatic toxicity. This has been shown when base program sampling has fortuitously coincided with runoff events, and by the Episodic Toxicity Pilot Project sampling in sloughs with urbanized watersheds.

In 1994-1995, the RMP sampled aquatic toxicity twice annually during sampling cruises at 13 sites, using the *Mysidopsis bahia* toxicity test. Significant toxicity was detected in only 2 of 52 samples (toxic events indicated in Table 2). This sampling was conducted based upon a schedule that was completely independent of runoff events. An earlier survey using silverside minnow, fathead minnow, bivalve larvae development, and echinoderm fertilization tests found very little evidence of toxicity with the exception of one cruise that documented widespread toxicity in the echinoderm test. The investigators note that while they were unable to rule out certain interferences (interactions between algal cells and echinoderm gametes), their data were consistent with the concept of episodes of toxicity in the Estuary (Anderson *et al.*, 1990; Katznelson *et al.*, 1993).

As mentioned previously, in the winter of 1996 RMP sampling for aquatic toxicity coincided for the first time with stormwater inflows to the Estuary, and significant toxicity was detected in Grizzly Bay and the Sacramento and San Joaquin rivers (Table 2). This was followed in January 1997 by detection of significant toxicity at the Napa River, Grizzly Bay, Sacramento River, and San Joaquin River sites (Ogle *et al.*, 1998).

The Episodic Toxicity Pilot Project was established in 1996 to further test the apparent link between aquatic toxicity and runoff events. This project sampled only in regions of the Estuary influenced by runoff, with sampling occurring during or after storm events. The frequency of detection of toxicity in this project was high compared to 1994-1995. Table 4 provides a summary of results for this program from 1996-1998.

Finding 3: Monitoring at the mouths of urbanized watersheds demonstrates toxicity associated with urban runoff.

Sampling at Guadalupe Slough, Alviso Slough, and Pacheco Slough has documented toxicity associated with runoff events. The toxicity frequently occurs when diazinon or chlorpyrifos are present, although no TIE work has been performed by the RMP to prove these pesticides are the toxic agents. In addition, toxicity has been detected in Pacheco Slough with no detectable diazinon or chlorpyrifos. The PWG considers it likely that further sampling will document such episodic toxicity during runoff events in other sloughs with urbanized watersheds.

The first episodic sampling at the mouth of an urban watershed was at Guadalupe Slough and Alviso Slough during the winter of 1996-1997. Significant toxicity was detected three times in Guadalupe Slough (Table 5). The toxic samples from Guadalupe Slough contained the pesticide chlorpyrifos above 70 ng/L. Additional chemical measurements taken during the sampling events in the South Bay indicate that chemical concentrations vary on a small spatial scale, suggesting that it is quite easy to miss the “peak” concentration of toxicants. This, in combination with a weather pattern that produced few of the spring runoff events in 1997 that were expected to be the most toxic (due to patterns of pesticide use by homeowners), led the principal investigators to conclude that the 1996-1997 results underestimated the temporal and spatial scale of the problem (Ogle and Gunther, 1997).

In the winter of 1997-1998, another sampling site was added at Pacheco Slough, which receives runoff from Walnut, Grayson, and Pacheco creeks. A total of 12 storm events were sampled at Pacheco Slough in 1997-1998 (Table 4), with 2 of the 12 storms demonstrating significant mortality (Table 5). Of the 12 water samples collected, 10 had measurable concentrations of diazinon and/or chlorpyrifos. Both of the toxic samples contained diazinon at concentrations of about 350 ng/L, but only one of the samples had detectable quantities of chlorpyrifos. Although chemical measurements of diazinon and chlorpyrifos indicate that these OPs are normally present in toxic samples, this is not always the case, nor are samples containing these contaminants always toxic.

In one of the toxic Pacheco Slough water samples, the measured chlorpyrifos concentration exceeded a reported 96-hr LC₅₀ for *Mysidopsis bahia* of 35 ng/L (Schimmel *et al.*, 1983). However, in the other four toxic samples, the measured concentrations of diazinon and chlorpyrifos were below toxic concentrations (Ogle *et al.*, 1998), and in none of the samples did the chlorpyrifos concentration exceed the LC₅₀ of about 150 ng/L suggested by the California Department of Fish and Game (CDFG) for the resident mysid *Neomysis mercedis* (Menconi and Paul, 1994a). This suggests that other contaminants could be contributing some of the observed toxicity, or that the two OP pesticides were producing additive toxicity (Bailey *et al.*, 1997).

Finding 4: Sampling in the Northern Reach indicates that toxic episodes, probably associated with pesticides, occur on broad enough temporal and spatial scales to have the potential to cause adverse impacts to CALFED priority fish species and other organisms in the Estuary.

During the winter of 1997-1998 episodes of toxicity to *M. bahia* were detected at Mallard Island. Sampling at this site is conducted every 2-3 days, and two episodes in 1998 spanned several consecutive sampling days (Figure 3). If one interpolates between these individual samples, the period of toxicity in the Estuary exceeded the time to lethality (6 days maximum) in the bioassays. Other RMP sampling events have documented toxicity from sites at the mouths of the Sacramento and San Joaquin rivers west to the Napa River. These results are strongly suggestive of the potential for effects on sensitive organisms (such as crustaceans), or the sensitive life-stages of fishes, which are known to inhabit this portion of the Estuary during the period when sampling occurred.

While maintaining healthy, viable invertebrate communities in our natural waters is an objective *in and of itself*, these invertebrates are also ecologically important as food for priority fish populations. Numerous studies have documented that virtually all of the priority fish populations in the Sacramento-San Joaquin River basins and the San Francisco Estuary rely upon these invertebrates, particularly during their vulnerable early life stages (Heubach *et al.*, 1963; Eldridge *et al.*, 1982; Schaffter *et al.*, 1982; Brown, 1992; Moyle *et al.*, 1992; Meng and Moyle, 1995; Lott, 1998; Nobriga, 1998). If pulses of pesticides through these aquatic ecosystems diminish the available invertebrate resources at critical periods, such as when fish fry are obligatory users of the invertebrates for food, adverse effects on the fish populations can be expected. The period when toxicity in these waters occurs (January-June) coincides with the presence of early life stages of most of the fish populations currently in decline, including delta smelt, chinook salmon, longfin smelt, splittail, steelhead trout, and green sturgeon, all of which have been identified as “Priority Species” by the CALFED Bay-Delta program. In fact, recent studies have indicated that there is evidence of food limitation for Delta smelt (Nobriga, 1998), although no evidence of food limitation on striped bass was documented from 1988-1991 (Bennett *et al.*, 1995). The latter study also found evidence of pollutant-induced liver damage in striped bass larvae, and the investigators make the important point that it is unlikely a single factor is responsible for the noted declines in fish populations.

Finding 5: It is likely that agricultural discharge and runoff are the major contributors to toxicity detected at Mallard Island.

As noted previously, the Central Valley Regional Water Quality Control Board found that in 1988 a 43 mile reach of the San Joaquin River between the confluence of the Merced and Stanislaus rivers was toxic to *Ceriodaphnia dubia*, and it was hypothesized that pesticides in agricultural runoff were causing the observed toxicity. Concurrent monitoring of agriculturally-dominated tributaries of the river revealed similar toxicity problems (Foe and Connor, 1991b). Follow-up monitoring in 1991-1992 documented that 22% of the water samples collected from the San Joaquin Basin were toxic to *Ceriodaphnia* (Foe, 1995). Subsequent TIEs, including some phase III TIEs, indicate that most of the observed toxicity could be attributed to the concentrations of four pesticides: diazinon, chlorpyrifos, fonofos, and carbaryl, although other pesticides were also detected in the water samples (Foe *et al.*, 1998). When the pesticide concentrations were normalized to their toxicity to *Ceriodaphnia* (in a Toxic Units approach), it was found that diazinon, chlorpyrifos, and parathion accounted for over 90% of the toxic units measured. Kuivila and Foe (1995) documented the movement of toxic, pesticide-laden water from the Delta into Suisun Bay. Finally, staff of the Central Valley Regional Board have demonstrated, by using TIEs, that diazinon was the major cause of toxicity in Orestimba Creek, the San Joaquin River, and Sacramento Slough in storm runoff in January and February of 1996 and 1997 (Foe *et al.*, 1998).

Other recent ambient water toxicity monitoring along the Sacramento River and in the Sacramento-San Joaquin Delta demonstrated frequent and significant toxicity to *Ceriodaphnia*. TIEs, including some phase III TIEs, indicated that OP pesticides are responsible for the detected toxicity (Bailey *et al.*, 1996; Deanovic *et al.*, 1996; Deanovic *et al.*, 1998).

Kuivila and Foe (1995) documented episodic increases in OP pesticide concentrations in the San Joaquin River and Suisun Bay that were associated with the use of these chemicals during the winter in stone fruit orchards. Schemel and Hager (1986) concluded that agricultural discharge into the Sacramento River has a major influence on dissolved water quality in the Delta region, accounting for 30-40% of the dissolved ions measured at Rio Vista. Toxicity in the Sacramento River has also been linked to pesticide use and discharge from rice fields (Fox and Archibald, 1997). No studies have been conducted that would link other pesticide use practices,

especially in the Delta region, to the episodic toxicity events that have been detected in the Estuary by the RMP.

Developing stronger links between agricultural pesticide use and toxicity might be possible if the Pesticide Use Report (PUR) database was more easily accessed by scientists conducting monitoring programs. It would be particularly helpful if pesticide use information was available in a more timely manner, and standard practices relating to use by crop type or region were more readily available. PUR data must be sorted manually from information available from County Agricultural Commissioners, or investigators must obtain the PUR database for the entire state and develop their own electronic sorting procedures (Kuivila, 1998).

Finding 6: The current episodic toxicity program generates insufficient information regarding the substances that are causing detected toxicity.

While the findings of toxicity are important for determining impairment of beneficial uses, the RMP has done very little to identify the causative agent of the toxicity. Previously, some preliminary TIE work was conducted for samples from regional stations in the Estuary, but this work utilized the echinoderm fertilization assay (Anderson *et al.*, 1990). Identification of causative agents of toxicity in the *Mysidopsis bahia* test is a prerequisite for the Regional Board to implement a program to mitigate the impairment. TIEs have been implemented extensively by the Central Valley Regional Board (Bailey *et al.*, 1996; Deanovic *et al.*, 1996; Foe *et al.*, 1998). These studies have allowed the Central Valley Regional Board to clarify that pesticides, especially the OP pesticides diazinon and chlorpyrifos, are responsible for most of the toxicity they have detected.

It is interesting to note, however, that a program to mitigate the impairment apparently created by diazinon has not been established, despite the placement of the San Joaquin River, the Sacramento River, and the Delta on the §303(d) list by the Central Valley Regional Board. This is because the Department of Pesticide Regulation (DPR), which has been given the authority for regulating the impact of pesticides on surface waters in California, appears unwilling to accept evidence from laboratory toxicity tests as indicators of impairment. This suggests that TIEs will need to be accompanied by studies designed to prove ecological effects in the field if they are to trigger regulatory action. Due to the myriad of confounding factors, field studies frequently do not provide the type of conclusive evidence apparently desired by DPR. CALFED's recent solicitation package includes a call for proposals to determine the ecological significance of pesticide loads to the Bay-Delta (CALFED, 1999); perhaps this will lead to more direct evidence of ecological effects.

Finding 7: Current indicators used to determine adverse impacts of pesticides on beneficial uses should be improved.

The current indicators of impacts of registered pesticides on beneficial uses are (1) concentrations of pesticides in receiving waters, and (2) toxicity in standardized aquatic toxicity tests. Both these chemical and toxicological indicators could be improved. Chemical indicators could be improved by increasing the number of pesticides measured, regularly comparing measurements to all relevant state and federal criteria, further developing an understanding of synergistic, antagonistic, or additive effects, and identifying unknown substances that are detected on gas chromatographs or mass spectrometers. In addition, Enzyme-Linked Immunosorbant Assay (ELISA) analyses for OP pesticides need to be considered in the RMP Quality Assurance Program Plan.

Expansion of the list of pesticides analyzed will have to be considered carefully, as there are many more pesticides in the waters of the Estuary than the RMP is likely to be able to measure without a significant increase in the analytical budget. For example, a recent study by the U.S.

Geological Survey (USGS) at four sites in the San Joaquin basin detected 49 different pesticides. Only one sample contained none of the 83 pesticides for which they tested, and 50% of the samples contained seven or more pesticides. The herbicides dacthal, EPTC, metolachlor, and simazine and the insecticides diazinon and chlorpyrifos were found in more than 50% of the samples. While no drinking water criteria were exceeded, criteria for the protection of aquatic life were exceeded in 68% of all samples analyzed (Panshin *et al.*, 1998).

Toxicological indicators could be improved by validating the *Mysidopsis bahia* toxicity test as a model for environmental conditions and resident species in the Estuary, and conducting TIEs to identify toxic agents in laboratory tests. The U.S. EPA-standard static-renewal toxicity test using *Mysidopsis bahia* at 25°C may under- or overestimate toxicity to estuarine organisms. Work conducted by the National Marine Fisheries Service at their Tiburon Laboratory (Earnest, 1970) indicates that the resident Korean Shrimp (*Palaemon macrondactylus*) is three to ten times more sensitive to chlorpyrifos than *Mysidopsis*, with an LC₅₀ of 10 ng/L. If this is true, “non-toxic” samples in RMP tests could be having toxic effects in the field. Invertebrate test organisms are very sensitive to OP pesticides; a recent study documented that three invertebrate test species were 200 times more sensitive to chlorpyrifos than the fathead minnow (Moore *et al.*, 1998). It must be noted, however, that these tests with *P. macrondactylus* were preliminary, and lacked sufficient documentation regarding control conditions to be included in the California Department of Fish and Game’s Hazard Assessment for chlorpyrifos (Menconi and Paul, 1994a).

Conversely, there is the potential of the mysid test overestimating the risk of effects. Standard tests are conducted at temperatures and salinities that are normally higher than ambient waters, and it is possible that altering the physical properties of the water could produce more toxic conditions due to physicochemical processes such as hydrolysis, flocculation, or adsorption. A recent study examining *Daphnia magna* concluded that when exposure to the pesticide fenoxycarb occurs as pulses, instead of a constant exposure regime, toxicity is significantly reduced (Hosmer *et al.*, 1998). The same might be true for mysids exposed to OPs. We might also find that other resident species are less sensitive than *Mysidopsis bahia*. Well documented tests using the resident mysid *Neomysis mercedis* indicate a 96-hour LC₅₀ for chlorpyrifos of 150 ng/L (Menconi and Paul, 1994a), well above the 96-hour LC₅₀ reported for *P. macrondactylus* (Earnest, 1970) and *Mysidopsis bahia* (Schimmel *et al.*, 1983).

Finally, as noted above under Finding 6, laboratory toxicity tests are only indicators of the potential for effects in the field. Actual field studies that document ecological effects, although difficult to conduct in a conclusive manner, would strengthen the weight-of-evidence for effects of pesticides in the environment.

Recommendations

Based upon the findings above, the PWG makes the following recommendations to the RMP to improve the value of the measurements of pesticide toxicology and chemistry.

Recommendation 1: Incorporate episodic monitoring of aquatic toxicity into the RMP base program.

The methodological approach of the Episodic Toxicity Pilot Project, basing the aquatic toxicity sampling on the assumption that particular locations will demonstrate toxicity over short time scales, should be incorporated into the RMP base program for aquatic toxicity monitoring. This should be done in a cost-effective manner, and must be integrated with the other RMP redesign recommendations. One possibility would be to alter the “declining hydrograph” sampling cruise of the RMP by using a faster vessel to make weekly trips through the northern reach during the ecologically critical February–April time period.

Recommendation 2: Develop joint strategies with other organizations making chemical measurements of pesticides in the Estuary. These strategies should include efforts to increase understanding of agricultural practices, and urban pesticide use, to help link specific practices to toxic events.

The RMP should approach the DPR and the USGS to ascertain whether they would be willing to conduct pesticide analysis on all samples collected by the RMP for bioassay, as such a recommendation was provided by DPR on the draft of this report. Given that the Central Valley Regional Board has placed the western delta on the 303(d) list for probable diazinon impairments, DPR could help collect data to resolve whether this was appropriate. The Central Valley Regional Board has developed considerable expertise and experience with pesticides and should be regularly consulted by RMP staff as pesticide monitoring plans develop.

Increasing understanding of pesticide use and discharge in agriculture might identify relatively easy ways to minimize impacts. The alteration of practices associated with rice farming is an example of how joint strategies can be effective in reducing beneficial use impacts. In the mid 1980s evidence of toxicity in the Sacramento River was linked to discharge of carbofuran, methyl parathion and malathion from flooded rice fields (Foe and Connor, 1991b). It was determined that holding water on the rice fields longer greatly reduced the concentration of these pesticides, and the Regional Board prohibited discharge in 1990 unless a 28-day holding period was adopted. The result has been significant reductions in toxicity and contaminant concentrations (Fox and Archibald, 1997). Some farmers have adopted water conservation and pesticide use reduction measures (Cohen and Curtis, 1998) that if more widespread could have a positive influence on restoration and protection of beneficial uses.

Finally, the Regional Board and the DPR must reach agreement regarding the indicators of beneficial uses in the Estuary, and the benchmarks for these indicators that represent impairment (Figure 2). If the RMP is measuring indicators that are not accepted by DPR, then impairment identified by the RMP will not result in corrective action by DPR.

Recommendation 3: Conduct experiments, in coordination with planned ecological field studies, to determine the sensitivity of resident crustaceans to organophosphate pesticides at ambient concentrations and environmental conditions.

Experiments should be conducted to validate the *Mysidopsis bahia* toxicity model for the Estuary. Two high priority experiments are an assessment of the relative sensitivity of *M. bahia* compared to important resident crustaceans such as *Palaemon macrondactylus* and *Crangon franciscorum* (Seigfried, 1980). Similar experiments could be conducted to validate the *Ceriodaphnia* results in freshwater using resident species.

In addition, consideration should be given to having the RMP participate in a larger effort to document ecological effects in the northern reach of the Bay and the Delta. While the cost of conducting such a large-scale field effort would be beyond the means of the RMP alone, the recent solicitation from CALFED (CALFED, 1999) indicates that they could be a partner in such a program. The special studies proposed above using resident species in the laboratory would be extremely valuable if coordinated with a larger-scale program looking at impacts on resident organisms in the field.

Additional indicators should be investigated, especially those that might relate pesticide toxicity to the important potential effects on the sensitive life-stages of resident or migratory fishes, including impacts on their prey species. For example, histopathological abnormalities in striped bass larvae might be a candidate indicator of pesticide impacts. These indications of

disease decreased during 1988-1991, a time during which rice herbicide concentrations were declining in the Sacramento River (Bennett *et al.*, 1995).

A measure of the intensity of toxicity in RMP bioassays should also be reported. Presently, a sample that kills test organisms in 24 hours is not differentiated from a sample that kills test organisms in six days. The standard method for assessing the intensity of toxicity is to perform toxicity tests on a dilution series, calculating an LC₅₀, and then expressing the toxicity in terms of toxic units. This provides a measure of the strength of the toxicity in the sample using a standard toxicological method.

The time-to-lethality in toxicity tests could also be reported to assist in interpreting toxicological data (Katznelson and Cooke, 1993; Katznelson *et al.*, 1995). Reporting an LT₅₀ would allow an assessment of how long it takes to achieve a significant toxic response in a sample, which could be used to interpret the data from Mallard Island. If sampling at Mallard Island documents toxicity over a time period that is greater than the time-to-lethality in the bioassays, it strengthens the argument for potential effects in the field. Conversely, if the duration of toxicity detected at Mallard Island does not exceed the time-to-lethality in bioassays, then it can be argued that the duration of exposure in the field may not be long enough to produce a toxic response.

Recommendation 4: Expand the QAPP to include Enzyme-Linked Immunosorbant Assay (ELISA) measurements.

Most measurements of diazinon and chlorpyrifos are being made using ELISA test kits. Many investigators have determined that these kits produce acceptable precision and accuracy when compared to standard methods such as HPLC and GC/MS (Bushway *et al.*, 1991; VanEmon and Lopez-Avila, 1992; Ferguson *et al.*, 1993). SFEI should prepare an update to the Quality Assurance Project Plan (QAPP) that addresses the accuracy of ELISA kits (especially with relation to saltwater measurements, and the reactivity of the antibodies with particulates), and any necessary methodological steps to take when conducting analyses. The RMP is in an excellent position to conduct ELISA and GC/MS measurements on the same water mass as part of the QA program.

This effort can be most efficiently implemented by coordinating work with the Monitoring and Science Subcommittee of the Urban Pesticide Committee, which has recently published an ELISA quality assurance document *Recommended Method Validation And Continuous Quality Assurance Practices and Performance Specifications For The Analyses Of Water Samples Using Enzyme-Linked Immunosorbant Assay (ELISA) Techniques*.

Recommendation 5: The list of pesticides analyzed by the RMP should be expanded.

Many frequently used pesticides are not measured by the RMP. These include the organophosphate pesticides malathion, methyl parathion, and fonofos, and the carbamate pesticides carbaryl and carbofuran. Other frequently used pesticides from the PUR should also be considered for analysis. The herbicides EPTC, simazine, and metolachlor, which were frequently detected in the San Joaquin Basin by the USGS (Panshin *et al.*, 1998), should also be considered for analysis.

Recommendation 6: The benchmarks for determining impairment should be periodically reviewed.

The present benchmarks used to judge impairment are (1) U.S. EPA Water Quality Criteria or CDFG Hazard Assessment Criteria or (2) toxicity in laboratory tests that is at least 20% greater

than controls. These benchmarks or standards should be regularly reconsidered by the Regional Board, DPR, and the RMP Technical Review Committee for use in interpreting data produced by the RMP. At present, the lack of consensus between the Regional Board and DPR regarding what constitutes impairment of receiving waters by registered pesticides is likely to frustrate any attempt at mitigation.

Recommendation 7: Toxicity identification evaluations should be an integral component of any RMP program element that monitors aquatic toxicity.

The TIE approach was developed to help identify which specific contaminant(s) from among a complex mixture of contaminants is responsible for observed toxicity. The fundamental concept of the TIE is to remove specific classes of contaminants and determine if the altered water remains toxic. If the toxicity is no longer present, then the group of contaminants that were removed must be responsible for the toxicity. This step is essential if the impairment to beneficial uses represented by toxicity is to be mitigated by regulatory action to control pesticide sources.

Based upon previous observations of pesticide toxicity in the upper watershed surface waters (Foe and Connor, 1991; Foe, 1995; Ogle *et al.*, 1998), it is strongly suspected that most of the toxicity being observed in the *Mysidopsis bahia* test is caused by pesticides. This contention is supported by the fact that OP pesticides are frequently detected in toxic water samples. In light of these results, and in order to conserve funds, the initial TIEs to be performed as part of the RMP should use a selected set of the fractionations recommended by the U.S. EPA (U.S. EPA, 1991). Briefly, a toxic water sample should be split into aliquots for specific TIE treatments (Phase I): filtration, C8 solid-phase-extraction chromatography (to remove non-polar organics; Borburgh and Hammers, 1992), and PBO addition (to prevent activation of OP pesticides). Observation of toxicity removal by these treatments may justify follow-up TIE methods (Phase II) to further characterize and identify the contaminant(s) causing the toxicity, and Phase III TIEs in which extracted toxicity is reintroduced. All TIEs for pesticides must be sensitive to the fact that the solubility of specific pesticides must be well understood in order to properly interpret TIE results (Kuivila and Crepeau, 1999).

Finally, it must be kept in mind that TIEs are not always conclusive, and there can remain unexplained toxicity even after TIEs are completed. One cause of such unexplained toxicity is additive or synergistic effects of different chemicals. This is a very complex subject, and there is currently no scientific consensus regarding the appropriate regulatory response to dealing with such effects (Gimme *et al.*, 1996).

Recommendation 8: Our knowledge regarding the relative importance of various pesticides sources to the Estuary must be improved.

Given that pesticide inputs to the Estuary are having an adverse impact upon beneficial uses, we must develop a more thorough understanding of the importance of various sources of pesticides to the Estuary. A recent assessment of publicly owned treatment works loadings of diazinon and chlorpyrifos (Chew *et al.*, 1998) is a beginning of this assessment. This information will be essential to prioritize efforts to control pesticide discharges to mitigate the impact. (It is expected that the Sources, Pathways, and Loadings Workgroup will address this issue in some detail. Determining the loads of pesticides will have to be prioritized along with the need to determine the loading of other substances.

Table 1: Mailing list for the Pesticide Work Group

Name	Organization	Address	Voice	Fax	E-mail
Andrew Gunther, Chair	Applied Marine Sciences	4749 Bennett Dr., Suite L Livermore, CA 94550	(510) 451-7936	(510) 451-3631	gunther@amarine.com
Bruce Abelli-Amen	Baseline Environmental	101 H Street Suite L Petaluma CA 94952	(707) 762-5233	(707) 762-5271	baseline@crl.com
Ray Arnold	Exxon Biomedical Sciences	Mettlers Road, CN 2350 East Millstone, NJ 08875-2350	(908) 873-6305	(908) 873-6009	wrarnol@fpe.erenj.com
Bart Brandenburg	Central Contra Costa County Sanitary District	5019 Imhoff Place Martinez CA 94553	(925) 229-7361	(925) 372-7635	bbranden@centralsan. dst.ca.us
Valerie Connor	Central Valley Board	3443 Routier Rd Sacramento CA 95827-3098	(916) 255-3113	(916) 255-3015	connorv@rb5s.swrcb.c a.gov
Jay Davis	San Francisco Estuary Institute	1325 S. 46th Street Richmond CA 94804	(510) 231-9539	(510) 231-9414	jay@sfei.org
Jason Donchin	Chevron Products Company	Jason Donchin, , PO Box 1272, Richmond, 94802,	(510) 242-2183	(510) 242-5353	jasd@chevron.com
Linus Farias	Contra Costa Clean Water Program	255 Glacier Dr Martinez, CA 94553-4897	(925) 313-2364	(925) 313-2301	lfarias@pw.co.contra- costa.ca.us
Christopher Foe	Central Valley Board	3443 Routier Rd Sacramento CA 95827-3098	(916) 255-3113	(916) 255-3015	foec@gwgate.swrcb.ca .gov
Rainer Hoenicke	San Francisco Estuary Institute	1325 S. 46th Street Richmond CA 94804	(510) 231-9539	(510) 231-9414	rainer@sfei.org
Revital Katznelson	Woodward-Clyde URS Greiner	500 12th St, Ste 200 Oakland CA 94607-4014	(510) 874-3048	(510) 874-3268	revital_katznelson@urs corp.com
Kathryn Kuivila	U.S. Geological Survey	6000 J Street , Placer Hall Sacramento CA 95819-6129	(916) 278-3054	(916) 278-3071	kkuivila@usgs.gov
Candace Miller	Dept. of Pesticide Regulation, EM&PM Branch	830 K St. Mall Sacramento, CA 95814-3510	(916) 324-4188	(916) 342-4088	cmiller@dpr.ca.gov
Tom Mumley	San Francisco Bay Regional Board	1515 Clay St., Suite 1400 Oakland CA 94612	(510) 622-2395	(510) 622-2460	tem@rb2.swrcb.ca.gov
Scott Ogle	Pacific Eco-Risk Laboratories	827 Arnold Way, Suite 100 Martinez CA 94553	(510) 313-8080	(510) 313-8089	scottogle@eco- risk.com
Paul Salop	Applied Marine Sciences	4749 Bennett Dr., Suite L Livermore, CA 94550	(925) 373-7142	(925) 373-7834	gunther@amarine.com
James Scanlin	Alameda County Clean Water Program	951 Turner Court, Room 300 Hayward CA 94544	(510) 670-6548	(510) 670-5262	jims@acpwa.mai.co.al ameda.ca.us
Kim Taylor	S.F. Bay Regional Water Quality Control Board	1515 Clay St., Suite 1400 Oakland CA 94612	(510) 622-2426	(510) 622-2460	kat@rb2.swrcb.ca.gov
Bruce Thompson	San Francisco Estuary Institute	1325 S. 46th Street Richmond CA 94804	(510) 231-9539	(510) 231-9414	brucet@sfei.org
Charles Wier	East Bay Dischargers Authority	2651 Grant Avenue, San Lorenzo, CA 94580,	(510) 278-5910	(510) 278-6547	ebdacvw@flash.net

Table 2: RMP Samples demonstrating significant toxicity, with associated chemical measurements (ng/L, total) of pesticides for which water quality criteria exist. ND=not detected; NA=not analyzed; Q=outside quality assurance limits.

Date	Site	Mysid mortality above controls (%)	Diazinon	Chlorpyrifos	Dieldrin	Heptachlor epoxide	DDT	Total chlordanes
2/7/94	Red Rock	22.5	NA	0.231	0.042	ND	ND	0.061
2/8/94	Napa	25	5.05	0.618	0.130	Q	ND	0.089
2/15/95	San Joaquin R	17	7.6	0.17	ND	0.170	ND	0.246
2/13/96	Napa River	84	39	0.68	0.007	0.058	0.062	0.183
2/13/96	Grizzly Bay	28	58	0.360	ND	0.009	0.018	0.091
2/14/96	Sacramento R	80	26	0.3	NA	0.014	0.016	0.078
2/14/96	San Joaquin R	88	25	0.440	ND	0.011	ND	0.095
7/23/96	Grizzly Bay	22	6.4	ND	0.027	0.019	0.013	0.091
7/22/96	Sacramento R	20	4.5	0.004	0.062	0.039	0.021	0.200
7/22/96	San Joaquin R	22	3.2	0.006	0.012	0.018	0.022	0.165
1/29/97	Sacramento R	57	37.0	0.358	0.275	0.029	0.349	0.256
1/29/97	San Joaquin R	80	31.0	0.604	0.246	0.039	0.277	0.249
1/28/97	Grizzly Bay	17	Q	0.481	0.280	0.269	0.375	0.254
1/28/97	Napa River	22	17.4	0.294	0.218	0.093	0.580	0.540
1/22/97	Sunnyvale	50	NA	NA	NA	NA	NA	NA
7/29/97	Redwood Ck	67	0.75	0.068	0.037	0.018	ND	0.094
7/29/97	Coyote Ck	100	3.1	NA	NA	NA	0.011	0.007
7/29/97	San Jose	100	11	0.578	0.102	0.206	0.052	0.618
7/29/97	Sunnyvale	100	NA	NA	NA	NA	NA	NA

Table 3. Summary of chemical measurements of pesticides in RMP samples from 1993-1996 that exceed available water quality standards. Data from (SFEI, 1996; SFEI, 1997; SFEI, 1998). Water Quality Standards taken from National Toxics Rule, 57 FR 60848, as quoted in (SFEI, 1998), except diazinon (Menconi and Paul, 1994b) and chlorpyrifos (Menconi and Paul, 1994a).

Pesticide (N)	Standard	Number of Exceedences 1993-1996	Samples Exceeding Standard (%)
Diazinon (130)	40 ng/l, 4-day average	4	3.1
Chlorpyrifos (116)	5.6 ng/L, 4 day average	0	0
Dieldrin (146)	1.9 ng/L, 4-day average	11	7.5
Heptachlor Epoxide (146)	3.6 ng/L, 4 day average	19	13
DDT (146)	1 ng/L, 4-day average	3	2
Total Chlordanes (146)	4 ng/L, 4-day average	5	3.4

Table 4: Toxicity and ELISA results from sampling by the Episodic Toxicity Project in 1996-1998. Data from Ogle and Gunther (1997; 1999)

Site (N)	Toxic Samples (%)	Samples containing Diazinon (%)	Samples containing Chlorpyrifos (%)
1996-97			
Guadalupe Slough (9)	30	30	30
Alviso Slough (7)	0	30	60
1997-98			
Pacheco Slough (12)	33	90	20
Guadalupe Slough (13)	15	80	20

Table 5: Summary of toxic samples from sloughs sampled in the Episodic Toxicity Pilot Project, 1996-98. GS=Guadalupe Slough, PS=Pacheco Slough, ND=not detected

Date	Site	Mysid mortality above controls (%)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
10/29/96	GS	97.5	392	145
4/19/97	GS	97.5	ND	78
5/23/97	GS	50	ND	70
12/7/97	PS	17.5	278	ND
4/3/98	GS	70	345	50
5/4/98	PS	90	54	73
5/12/98	GS	47.5	342	ND
5/13/98	PS	37.5	ND	ND

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Appendix 1: Draft Recommendations from the Pesticide Work Group for the 1999 Episodic Toxicity Project

Findings

The Pesticides Work Group (PWG) discussed the results of the Episodic Toxicity Pilot Project at their meeting on August 7, 1999. There were several consensus findings that emerged from the discussion.

1. The Pilot Project clearly achieved its objectives. By basing the aquatic toxicity sampling on the assumption that particular locations will demonstrate toxicity over short time scales, the RMP has greatly improved its ability to detect aquatic toxicity in the Estuary. This contributes directly to the ability of the Regional Board to refine its listing of the Estuary as impaired for toxicity pursuant to §303(d) of the Clean Water Act.
2. Sampling at Guadalupe Slough, Alviso Slough, and Pacheco Slough, has documented toxicity associated with runoff events. The toxicity is correlated with the presence of diazinon or chlorpyrifos, although no toxicity identification evaluation work has been done to prove these pesticides are the toxic agents. The PWG considers it likely that further sampling will document such episodic toxicity in sloughs with urbanized watersheds.
3. ELISA analyses for diazinon and chlorpyrifos in samples collected on transects from Guadalupe Slough into the South Bay documents quick dilution of pesticide concentrations.
4. The pilot project also documented episodic toxicity to *Mysidopsis bahia* at the head of the Estuary. Two episodes lasted several days, exceeding the time to lethality in the bioassays. These results are strongly suggestive of the potential for effects on sensitive life stages. However, it is important to consider whether the tri-weekly sampling at Mallard Island is actually sampling the same water mass repeatedly as it cycles with the tide, or new water entering the estuary.

Unanswered Questions

The Work Group identified three important unanswered questions:

1. **What is causing the toxicity that has been documented by the RMP?**
While TIEs have clearly implicated diazinon (and probably chlorpyrifos when it is present) as the causative agent for toxicity to *Ceriodaphnia* in creeks, no TIEs have been conducted for toxicity observed in RMP samples. When toxicity has been present in episodic sampling, OPs have been present (especially chlorpyrifos, to which *Mysidopsis bahia* is very sensitive). However, toxicity has been identified in Mallard Island samples when neither chlorpyrifos or diazinon were detected. TIEs are essential to the development of all source control strategies.
2. **How representative is the static-renewal toxicity test using *Mysidopsis bahia* at 25°C of potential effects on resident organisms?**
Work by CDFG indicates that the resident Korean Shrimp (*Palaemon macrodactylus*) is an order of magnitude more sensitive to chlorpyrifos than *Mysidopsis*. If this is true, “non-toxic” samples in our tests could be having toxic effects in the field. Conversely, there is the potential of the mysid test overestimating the risk of effects. Tests with *Ceriodaphnia* suggest that at ambient temperatures (as opposed to test temperatures of 25°C) the test organisms are much less sensitive to diazinon, and the duration of exposure to a given

concentrations of a toxic substance in the field are generally shorter than in laboratory tests (except for a few cases encountered at Mallard Island last year)

3. Are there other sites where toxicity is occurring in the Estuary?

Given the results from Guadalupe Slough, Alviso Slough, and Pacheco Slough, in combination with the earlier work of Anderson *et al.* at marsh stations around the Estuary, it seems clear that when the contaminated plume from major urban creeks enters the Estuary, toxicity is present. However, these same studies also indicate that the toxicity is quickly diluted by Bay waters (the only exception being the detection of toxicity in July 1997 at BA40 and points south; chemistry of these samples needs to be examined). Would the toxicity from north bay watersheds such as Napa River or Sonoma Creek demonstrate different toxicity characteristics due to prevalence of agricultural land uses in these drainages?

Recommendations

Based upon the findings and unanswered questions described above, the PWG makes the following recommendations to the RMP Program Technical Review Committee.

1. The episodic toxicity project should be funded in 1999, with modifications as described below.
2. Toxicity Identification Evaluations (at least Phase I and II) should be conducted on toxic samples collected by the project. This should include at least one sample taken from a Slough station, and several from the Mallard Island site.
3. Given the results so far, it seems likely that runoff from urbanized watersheds will be toxic. Rather than expend further resources testing the mouths of other urbanized watersheds, it is more important to characterize the north bay watersheds that have not yet been studied and include large agricultural land uses. It is therefore recommended that the resources directed toward sampling at Guadalupe Slough be reallocated to sampling on the Napa River. Prior to commencing sampling, however, the records of the Napa County Agricultural Commissioner should be reviewed in order to obtain a characterization of the nature and timing of pesticide use in the watershed of the Napa River. This information should be used to devise a sampling plan for assessing episodic toxicity in the Napa River.
4. The sampling at Mallard Island could be conducted in a more cost-effective manner. Hydrologic information should be used to modify the sampling schedule to make sure that the same water mass is not sampled on a continuous basis. Instead, each “new” water mass (operationally defined based on delta outflow characteristics) should be sampled. When toxicity is found, its temporal and spatial characteristics should be determined.
5. The RMP should approach the Department of Pesticide Regulation to ascertain whether they would be willing to conduct pesticide analysis on all samples collected for bioassay analysis. Given that the Central Valley Regional Board has placed the western delta on the 303(d) list for probable diazinon impairments, DPR could help collect data to resolve whether this was appropriate.
6. Finally, experiments should be conducted to validate the *Mysidopsis bahia* toxicity model for the estuary. Two experiments to conduct immediately are an assessment of the relative sensitivity of *M. bahia* compared to important resident crustaceans, and to determine the response of *M. bahia* to toxic samples under conditions of salinity and temperature more representative of actual environmental conditions in the estuary. One problem in developing a consensus regarding adverse effects of pesticides in natural waters is the extension of toxicity to *Ceriodaphnia* in the laboratory to toxicity of resident

invertebrates in the field. A recent risk assessment of diazinon in the Sacramento and San Joaquin basins (Adams, 1996) concluded that while cladocera (such as *Ceriodaphnia*) are sensitive invertebrates to organophosphate pesticides, other important invertebrate groups, including copepods, mysids, amphipods, insects, and rotifers, are less sensitive and are likely not being affected by the existing organophosphate pesticide concentrations.