EXECUTIVE SUMMARY
of Report EH01-01 Entitled

Analysis of chlorpyrifos and diazinon surface water monitoring and acute toxicity bioassay data, 1991 - 2001

California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Hazards Assessment Program

PURPOSE

The Department of Pesticide Regulation (DPR) Environmental Hazards Assessment Program (EHAP) analyzed chemical analytical data for two organophosphate (OP) pesticides, chlorpyrifos and diazinon, from 22 surface water sampling studies conducted from 1991- 2001. This report presents where, how often, and at what concentration these pesticides were detected, either singly or in combination, and then specifically focuses on the most recent data collected, 10 dormant spray studies conducted by EHAP from 1997-2001. EHAP compared concentrations detected with water quality criteria based on human and aquatic toxicity of these pesticides, and with 96-hour *Ceriodaphnia dubia* (*C. dubia*) toxicity tests to determine the relationship between *C. dubia* toxicity and analytical chemistry data. The report also discusses trends in frequency and concentrations of detections of chlorpyrifos and diazinon.

BACKGROUND

Chlorpyrifos and diazinon are pesticides each reportedly used to control pests on more than 100 agricultural commodities and on nonagricultural sites, such as buildings and structures and landscape maintenance in California. Applications are made throughout California and at various times during the year.

There have been numerous reports of detections of chlorpyrifos and diazinon in California surface water since the 1980s. They have been detected by various chemical analytical methods and are reported to be sources of aquatic toxicity in toxicity tests conducted in surface water.

MAJOR USES

Most of the California surface water monitoring data for chlorpyrifos and diazinon from 1991-2001 was collected in the San Joaquin and Sacramento river basins. Based on 1991-2000 pesticide use report data, chlorpyrifos and diazinon were used up to 5 times more and 1.5-2.5 times more annually, respectively, in counties composing the San Joaquin River Basin than in counties composing the Sacramento River Basin. Overall chlorpyrifos use was much greater than diazinon use but annual applications of both pesticides have declined since the mid-1990s.

The greatest current use of chlorpyrifos in these basins occurs in cotton during August and September, with other substantial uses in May through August in nut crops and March in alfalfa. There has been no consistent trend in wintertime pesticide use on crops in these areas over the decade, but since 1997 use on alfalfa has declined while use on fruit and vine crops has increased.

The greatest use of diazinon in these basins is in January on fruit and nut crops, although total winter diazinon applications have decreased on these crops since the early 1990's.

METHODS

Sampling data for chlorpyrifos and diazinon were analyzed from 22 studies conducted from 1991-2001. These studies were conducted by the Central Valley Regional Water Quality Control Board, the U.S. Geological Survey, Dow Agrosciences, and DPR. This report does not include sampling data from the following: urban storm water drain sampling, because there were so little data; studies with undocumented or unreported analytical methods or where data reported to DPR did not include accompanying quality assurance/quality control information, because the quality of those data cannot be assessed; and data based solely on Enzyme-linked Immunosorbent Assay, because of a possible systematic bias in those data that is still under investigation.

The chlorpyrifos and diazinon data analyzed were collected from 3901 samples at 82 sites, and 3954 samples at 95 sites, respectively. The concentrations of both pesticides were measured in most (3716) samples. In addition, 488 acute 96-hour *C.dubia* toxicity tests were conducted in a number of the analyzed studies.

The most recent of the 22 surface water monitoring studies conducted for chlorpyrifos and diazinon were 10 studies conducted by EHAP during five dormant seasons (1997-2001) in the Sacramento and San Joaquin river basins. In a separate section, these results are analyzed and compared to the entire data set.

STATISTICAL CONSIDERATIONS

Some subsets of the data discussed in this report are amenable to quantitative analysis. However, the combined data from the 22 studies cannot be analyzed quantitatively because they are not equally representative of geographic areas where, or of years when, the samples were collected. In addition, different analytical methods were used that were able to detect very low concentrations in some studies but only relatively higher concentrations in other studies. As a result, this report describes the overall data using qualitative measures, such as the relative magnitudes, locations and seasonality of observed chlorpyrifos and diazinon concentrations in specific surface water bodies.

<u>Limit of quantification (LOQ)</u>. LOQ is the lower limit of the detectable concentration of a chemical that an analytical method can detect. If chemicals are present in water at levels below the LOQ, they will not be detected. So, as LOQs rise, detection frequencies can decrease. . In addition, detection frequencies from studies with different LOQs cannot be fairly compared. For example, the results of study A with a high LOQ would not be comparable to study B with a low LOQ where chemicals were detected at levels below the LOQ of study A.

The LOQs for chlorpyrifos and diazinon ranged over two orders of magnitude (100x) in the studies analyzed. Since detection frequencies of different groups of data cannot be meaningfully compared without accounting for the effect of LOQ, a “censoring” threshold of 0.04 ppb (ug/L) was used for those comparisons. This means that samples with concentrations of less than 0.04 ppb were defined as non-detections when detection frequencies were analyzed.

High LOQs can also mean that sometimes concentrations are not detected that could be causing aquatic toxicity. Since the lethal chlorpyrifos concentration for 50 percent of the aquatic test organism *C. dubia* is 0.038 ppb and most LOQs for chlorpyrifos were at 0.04 ppb and above, the intermediate chlorpyrifos concentrations between 0.038 and 0.04 ppb that cause toxicity in the test organism may not have been detected. In contrast, the lethal diazinon concentration for 50 percent of the aquatic test organism *C. dubia* is 0.436 ppb, which is well above the LOQs for all diazinon data collected. Thus, all diazinon concentrations that caused toxicity in the test organism would have been detected in the studies reported.

RESULTS AND DISCUSSION

ANALYTICAL CHEMICAL DATA

Chlorpyrifos

Overall, chlorpyrifos was detected most frequently in March – May (35-40 percent of all samples) and in August and September (each at 19 percent of all samples), mostly in tributaries. Chlorpyrifos was also detected at higher concentrations in tributaries than in rivers. In tributaries, most samples and detections were from one study in Orestimba Creek in 1996-1997.

Very little chlorpyrifos was detected in rivers. All of the chlorpyrifos detections in rivers during September to November occurred in the Alamo River in Imperial County, where the eight percent detected in October was the highest detection frequency in any month and any river. Chlorpyrifos was detected relatively infrequently in January and February because little chlorpyrifos is applied during those months. Chlorpyrifos has not been detected at any river sites in the Sacramento Valley, or at any river sites since 1995, probably due to decreased sampling, higher LOQs, and reduced chlorpyrifos sampling in recent years. Overall, chlorpyrifos was detected much less frequently in rivers than diazinon.

Most of the highest chlorpyrifos detections were measured in the early 1990s when sampling was most frequent.

Subject to the statistical considerations mentioned above, chlorpyrifos exceeded the chronic toxicity criterion for chlorpyrifos of 0.014 ppb in 16.8 percent of all samples, 2.9 percent of river samples and 32.9 percent of tributary samples from 1991-2001. However, these exceedances are probably biased toward the low side because the censoring threshold, and the LOQs of most chlorpyrifos studies, are somewhat higher than the chronic toxicity criterion. So some chlorpyrifos concentrations exceeding the chronic toxicity criterion were probably either classified as nondetections or could not be measured by the analytical method used.

Diazinon

Like chlorpyrifos, diazinon was detected more frequently and at higher concentrations in tributaries than rivers from 1991-2001. In tributaries, it was detected most frequently in January to May (30 – 53 percent of samples) and in August (27 percent of samples). In rivers, the most frequent detections (32-42 percent of all samples) occurred during January – February, with lesser amounts (9-12 percent) detected in March, August and October. Similar to chlorpyrifos, most of the diazinon detections in rivers during September to November occurred in the Alamo River; no diazinon was detected in the Sacramento and San Joaquin rivers during that period. Diazinon's more frequent detection than chlorpyrifos is not due to its persistence, which is less than that of chlorpyrifos, but may be explained by its lower soil adsorption coefficient (less likely to bind to soil) and its greater use during the rainy season when more sampling was conducted.

The highest concentrations of diazinon in rivers were observed in the early 1990's when sampling was most frequent; in recent years sampling frequency was very low. In contrast, high diazinon concentrations have been detected in tributaries in both the early 1990s and in recent years.

Subject to the statistical considerations mentioned above, diazinon exceeded the chronic toxicity criterion of 0.05 ppb, the lowest water quality criterion for diazinon, in 21.7 percent of all samples, 16.9 percent of river samples and 27.2 percent of tributary samples from 1991-2001. The diazinon exceedances are relatively unaffected by the censoring threshold and the LOQs of most studies because they are less than the chronic toxicity criterion of 0.05 ppb.

DPR dormant spray monitoring results from 1997-2001

Of 560 samples collected from seven sites in the Sacramento and San Joaquin basins, chlorpyrifos was detected in only one sample at 0.093 ppb, which exceeds the *C. dubia* LC_{50} (0.038 ppb) for chlorpyrifos.

Diazinon was found more frequently and at higher concentrations at two tributary sites in the Sacramento River basin than at the river sites. Detection frequencies were 74 percent at the Wadsworth Canal tributary and 34 percent at the Sutter Bypass tributary compared to 13 percent at the river sites. The highest concentrations at the Wadsworth Canal ranged up to 2.74 ppb with 11 samples (17 percent) exceeding 0.5 ppb, all of which are greater than 0.436 ppb, the highest water quality criterion for diazinon. The maximum concentration at the Sutter Bypass was 0.132 ppb, which exceeds both the chronic (0.05 ppb) and acute (0.08 ppb) water quality criteria for diazinon, but not the *C. dubia* LC_{50} (0.436 ppb). The maximum river concentration of 0.171 ppb was found at the Alamar Marina, 9 miles below the confluence of the Feather and Sacramento rivers.

Detection frequencies at the San Joaquin River basin tributary site (Orestimba Creek) and river site (Vernalis) were similar, at 13 and 12 percent, respectively, as were the maximum concentrations, 0.161 ppb and 0.144 ppb, both of which exceeded the chronic and acute criteria, but not the *C. dubia* LC_{50}.

Overall, the percent samples exceeding the criteria for chronic aquatic toxicity, acute aquatic toxicity, and the *C. dubia* LC_{50}, respectively, were 12, 3, and 0 in the Sacramento River; 65, 55, and 17 in the Wadsworth Canal; 24, 9, and 0 in the Sutter Bypass; 12, 5, and 0 at Vernalis on the San Joaquin River; and 8, 4, and 0 at Orestimba Creek.

Co-Occurrence and Toxicity

Since OP pesticides display a common mechanism of toxicity, their separate toxicities should be additive. Thus the detection of chlorpyrifos and diazinon, the major OP pesticides detected in these studies, in the same sample is of interest. While 54 percent of the samples positive for diazinon also were positive for chlorpyrifos, more than 90 percent of samples positive for chlorpyrifos were also positive for diazinon.

C. dubia acute aquatic toxicity was determined on 488 surface water samples collected between 1991 and 2000. EHAP compared the observed *C. dubia* acute aquatic toxicity measured in a water sample with the predicted toxicity based only on concentrations of chlorpyrifos and diazinon (other factors can also contribute to toxicity). Predicted toxicity is calculated by adding the individual toxic units (TU) of chlorpyrifos and/or diazinon detected in the sample. TU is the ratio of the concentration detected of each pesticide divided by the laboratory-determined LC_{50} of that pesticide, and the sum of TUs of chlorpyrifos and diazinon represents their theoretical combined acute toxicity.

"Significant toxicity" is defined as a difference of 30 or more percent survival between the control and the sample. Of 301 toxicity tests conducted on tributary samples, 29 percent showed significant toxicity to *C. dubia*, and of 187 river sites, seven percent showed significant toxicity. Samples classified as "significantly toxic" and "not significantly toxic" displayed significantly different median TUs. In addition, significant toxicity was consistently observed in those samples with a calculated TU of greater than 0.5.

However, the following were also noted. Other constituents were present in amounts sufficient to either cause or significantly contribute to toxicity in approximately half of the 30 samples with a TU of greater than 0.5 but less than 1.0. In addition, for 12 samples where observed toxicity was 100 percent, no toxicity was predicted to occur based on chlorpyrifos and diazinon concentrations. And for 7 samples with predicted TU > 0.5 (4 of which with a predicted TU > 1.0), no toxicity was observed.

Detection Frequency/Concentration Trends

The San Joaquin River at Vernalis and Orestimba Creek at River Road were the only two sites sampled both before 1995 and between 1996 and 2001, and at the same time of year. Data from these sites were both concentration-censored and season–censored (to include only the dormant season) before analysis to assess frequency and concentration trends. Both detection frequencies and concentrations of diazinon at these two sites were higher before 1995 than after 1995. Significant reductions in diazinon wintertime use after 1995 largely accounts for this trend; there was a significant correlation between winter detection frequencies and the amount of diazinon applied in winter.

No trend analysis was possible for chlorpyrifos because only one sample exceeded the concentration censoring threshold at Vernalis and because the seasonal distribution of the concentration-censored data at the Orestimba Creek site for the 1997-2001 period was skewed.

CONCLUSIONS

Use of chlorpyrifos and diazinon in the Sacramento and San Joaquin basins has steadily decreased in recent years.

Detections of chlorpyrifos and diazinon and acute aquatic toxicity have been more frequent in tributaries than in rivers.

The highest river concentrations of chlorpyrifos and diazinon were reported during the early 1990's, when much more river sampling was conducted than in the late 1990's.

Acute toxicity to *C. dubia* was strongly related to TU calculated solely from measured chlorpyrifos and diazinon concentrations. However calculated TU for chlorpyrifos and diazinon should be used cautiously as an indicator of toxicity form the two pesticides. Although more than 90 percent of samples with a calculated TU > 0.5 based on concentrations of both chlorpyrifos and diazinon were significantly toxic, approximately half of the samples with 0.5<TU<1.0 contained other constituents present in amounts sufficient to either cause or significantly contribute to toxicity. In addition, for 12 samples where observed toxicity was 100 percent, no toxicity was predicted to occur based solely on chlorpyrifos and diazinon concentrations. And for 7 samples with predicted TU > 0.5 (4 of which with a predicted TU > 1.0), no toxicity was observed.

Chlorpyrifos

Chlorpyrifos has not been detected in rivers since 1995. It was detected in only one of 263 tributary samples during 1997-2001 winter monitoring, when dormant sprays deposited on soil can be carried by rainfall to surface water. However, recent sampling has been conducted with a relatively high LOQ of 0.04 ppb, which is slightly higher than the chlorpyrifos *C. dubia* LC_{50} and double the water criterion for acute aquatic toxicity. Thus, chlorpyrifos would not be detected at the lowest concentrations capable of causing acute toxicity. In addition, no recent monitoring has been conducted during the summer, the major season of chlorpyrifos use.

Diazinon

Winter diazinon concentrations and detection frequencies in the San Joaquin River at Vernalis were significantly lower in 1997-2001 than in 1991-1995.

Winter diazinon detection frequencies at Vernalis are significantly correlated with diazinon use. Lower diazinon wintertime use largely explains lower concentrations and detection frequencies in recent years.

Regular winter dormant season exceedances of the diazinon *C. dubia* LC_{50} have been recently observed in Sacramento River tributaries. Recent diazinon concentrations at Wadsworth Canal have ranged up to approximately six times the *C. dubia* LC_{50}.

In recent winter dormant season monitoring, diazinon was associated with toxicity measured in Wadsworth Canal but not with toxicity measured in Orestimba Creek.

During the last five years of winter monitoring, diazinon has not exceeded the *C. dubia* diazinon LC_{50} in the San Joaquin River at Vernalis or the Sacramento River near Sacramento. However, the diazinon acute toxicity criterion was exceeded in five and three percent of the samples taken at Vernalis and the Sacramento River, respectively.

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