# TEMPORAL DISTRIBUTION OF INSECTICIDE RESIDUES IN FOUR

**CALIFORNIA RIVERS** 

by

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and

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### **Russian River**

#### **Russian River Watershed**

The Russian River watershed resides mostly in Sonoma and Mendocino Counties (Figure 46). The river's head waters are in Lake County, but less than 1% of the watershed lies in that county. The watershed is about 80 miles long and from 10 to 30 miles wide. The drainage area of the watershed upstream of the sampling site located near Guerneville, is about 1,202 mi<sup>2</sup>. The river is about 110 miles long and flows primarily south, running parallel to the coastline. The last section of the river flows westward for almost 20 miles through the coastal hills to the Pacific Ocean. The Russian River has many beneficial uses including wildlife habitat, recreation, and municipal and domestic water supplies (NCRWQCB, 1993).

Generally, the highest flow of the Russian River occurs from October to May. Flow is continuous throughout the year and is controlled by releases from Coyote Dam at Lake Mendocino, and Warm Springs Dam at Lake Sonoma (Figure 46) (NCRWQCB, 1993). In addition, there is a hydropower project that diverts water from the Eel River into the Russian River above Lake Mendocino at an average annual rate of 330 cfs (SWRCB, 1994). Most of the tributaries flow during the wet-weather season, but flows dwindle by mid to late summer. There are greater than 40 tributaries to the mainstem of the Russian River. Most of the tributaries are intermittent and some are perennial (Goodwin, NCRWQCB). The principal tributaries are Big Sulphur Creek, Dry Creek, Mark West Creek and Austin creeks (NCRWQCB, 1993). The tributary farthest downstream that contributes agricultural runoff to the Russian River is Green Valley Creek (Klamt, NCRWQCB) which flows from south of Sebastopol to the Russian River near Rio Dell. Most tributaries entering the river upstream of Green Valley Creek carry some crop runoff while those downstream contribute less runoff from crops. Practically all insecticide use occurs upstream from the sampling site chosen (Figure 51 through 58). The major crops grown in the watershed include wine grapes, alfalfa, pears, hay, walnuts, apples and a variety of row crops.

The Russian River sampling site was located at a private residence on the Russian River approximately 1 mile upstream of the Highway 116 Bridge, in Guerneville (Figure 46). The site is 5 miles downstream of Green Valley Creek and about 17 miles upstream of the mouth of the river. Discharge data were obtained from the DWR

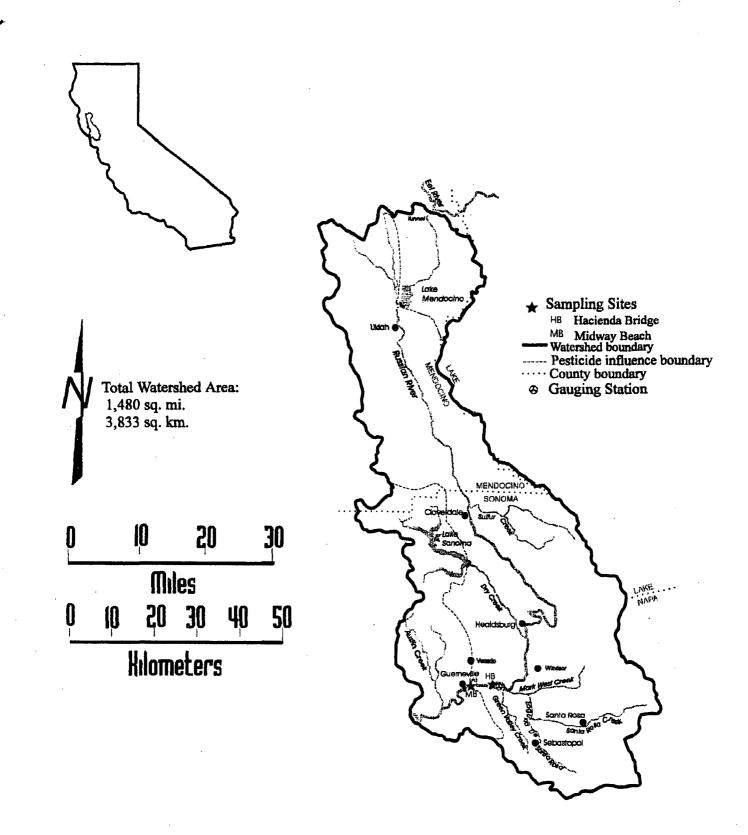


Figure 46. Map of the Russian River watershed.

gauging station located 4 miles upstream of the sampling site at Hacienda Bridge. At this location the river is impounded for recreational purposes during the summer months. During this period there is a chance that the river at this site may not be mixed adequately. Pesticides that tend to adhere to sediment have potential to settle and pesticides entering the river locally, within the impounded area, may not be completely mixed across the cross section. The environmental measurements would be affected the most during this period, and would be more accurate if taken across the river's cross section.

Weekly sample collection began on August 8, 1994, using the automatic sampler. Due to heavy rains that resulted in regional flooding in the sampling area, the automatic sampler was removed from its location on January 5. Subsequent samples were collected weekly from January 17 through May 1 from the Hacienda Bridge located 4 miles upstream of the original sampling site using two methods; a grab sample collected with a bucket at center-stream and the equal-width depth-integration method (Guy and Norman, 1970). From May 8 to August 8, samples were again to be collected using the automatic sampler that was returned to the site near Guerneville.

#### **Environmental Measurements**

Water samples taken during the year-long study had pH values ranging from 7.1 to 8.3 and DO ranging from 6.1 to 13 mg/L (72% to109% saturation, respectively, Table 8). The pH met the objectives set by the NCRWQCB in the Water Quality Control Plan for the North Coast Region (1994)(Table 3). The Water Quality Control Plan lists the pH objectives as a minimum of 6.5 and a maximum of 8.5. The DO values met the water quality minimum objective set specifically for the Russian River of 7.0 mg/L for all but one sample collected July 17, 1995. However, the DO values were at or above the 90% lower limit 88.6% of the time and at or above the 50% lower limit only 15.9% of the time. Water temperature on sample pick up days varied from 8 to 30°C and the air temperatures ranged from 7 to 37°C.

Besides parameters measured by DPR, discharge data were obtained from the DWR gauging station at Hacienda Bridge. Daily rainfall measurements were obtained from the DWR weather station at Venado, 6 miles north of the sampling site. During the first quarter there were 1.6 inches of rain recorded at the Venado weather station and the Russian River discharge rate fluctuated between 91 and 285 cfs (Figure 47). August

Start Sample	End Sample	Air	Water	Dissolved	% saturation	рН	pH	Detections
Date	Date	Temperature	Temperature	Oxygen (mg/L)		(in situ)	(lab)	
Midway Beac	h							
8/12/94	8/15/94	NT	30	NT	NT	NT	7.8	
8/19/94	8/22/94	37	24	8.0	95	NT	7.8	
8/26/94	8/29/94	33	22	8.0	<b>9</b> 2	NT	7.8	
9/2/94	9/5/94	24	21	7.6	85	NT	7.7	
9/9/94	9/12/94	22	20	7.6	84	NT	7.6	
9/16/94	8/19/84	NT	21	NT	NT	NT	7.9	
9/23/94	9/26/94	NT	21	7.9	89	NT	7.9	
9/30/94	10/3/94	22	22	NT	NT .	NT	8.1	
10/8/94	10/11/94	25	17	8.3	85	NT	7.8	
10/15/94	10/18/94	NT	15	9.6	95	NT	7.9	
10/22/94	10/25/94	NT	16	9.0	91	NT	7.8	
10/29/94	11/1/94	21	14	8.8	85	NT	7.8	
11/5/94	11/8/94	12	13	7.3	68	NT	7.7	Diszinon (0.076)
11/12/94	11/15/94	11	11 8	8.4	76	NT	7.8	+
11/19/94	11/22/94	8		9.6		NT 7.7	7.8	
11/26/94	11/29/94	10	11 9	9.4	85 83	7.7	8.0	+
12/2/94	12/5/94	7	9	9.7 10.8	92	7.1 NT	7.1	
12/9/94	12/12/94	9 11	8	9.7	87	7.3	7.7	+
12/17/94	12/20/94	11	10	9.2	85	7.5	8.1	+
	1/3/95	11	10	10.1	89	7.3	7.7	+
	looding in Guerr							+
Hacienda Bri							·····	1
The second s	Grab sample	NT	11	10.4	92	7.4	7.8	
	Grab sample	NT	11	10.9	99	7.6	7.7	
1/30/95	Grab sample	16	13	9.4	89	7.8	7.3	1
2/6/95	Grab sample	16	12	9.6	89	7.5	7.6	
2/14/95	Grab sample	14	12	10.4	96	7.3	7.3	
2/21/95	Grab sample	23	13	8.4	79	7.8	7.6	
2/27/95	Grab sample	14	17	7.4	76	7.9	7.6	
3/6/96	Grab sample	16	9	12.6	109	7.9	7.8	
3/13/05	Grab sample	13	16	NT	NT	7.5	7.3	
3/20/95	Grab sample	15	NT	NT	NT	7.6	7.3	Dimethoate (0.11
وماجات ويستعده فتحت والبادعا	Grab sample	12	18	NT	NT	7.4	7.5	
a spin a sub	Grab sample	20	13	10,4	91	7.6	NT	<u></u>
the second s	Grab sample	13	18	9.2	96	7.6	7.7	<u></u>
	Grab sample	14	13	9.4	85	7.8	7.5	
4/24/95	Grab sample		18	9.3	97	7.8	7.8	
5/1/95	Grab sample	14	18	9.2	92	7.6	7.5	
Midway Beac	h							
	Grab sample	NT	18	9.6	96	8.0	7.4	
	15-May	NT	15	9.4	93	7.8	7.6	
	5/22/95	14	18	8.3	87	7.8	7.1	
	5/30/95	8	20	9.0	83	7.8	7.8	
the second s	8/5/96	20	22	9.4	105	8.2	7.8	+
	8/12/95	25	20	9.2	103	8.2	7.7	+
	8/19/95 Grah tampia	23	19	9.1	96 89	8.0	7.9 7.9	
and the second	Grab sample	22	25	7.4 NT	NT	7.8	7.8	
the second s	7/3/95 7/10/95	19 NT	21 23	7.6	89	8.1	8.0	+
	7/17/95	23	23	6.1	73	8.3	7.6	<u> </u>
	7/24/95	23	24	6.1 8.6	100	7.8	1.0	1
	7/31/95	31	23	7.5	92	7.7	7.5	
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## Table 8. Russian River Water Quality Data and Pesticide Detections

NT=measurement not taken

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## **Russian River**

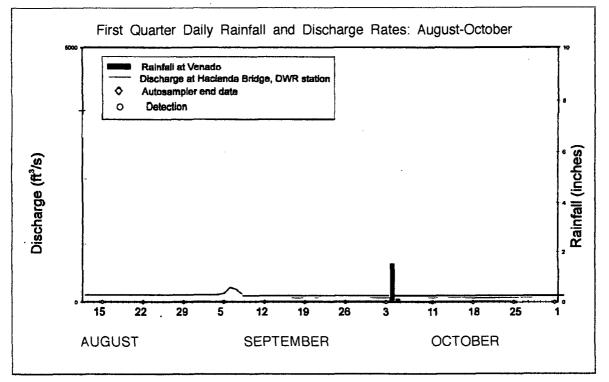


Figure 47. Daily rainfall and Russian River discharge (river flow) for August 12, 1994 through November 1,1994.

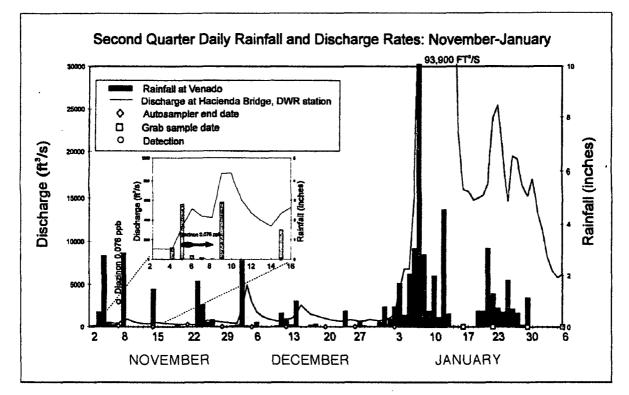


Figure 48. Daily rainfall and Russian River discharge for November 2, 1994 through February 6,1995.

through December discharges were lower than the historical monthly averages (Ayers et al., 1995; Friebel et al., 1996). However, during the second quarter rainfall totaled 59.8 inches at Venado and the discharge ranged from 107 to 93,900 cfs (Figure 48). In mid-January heavy rain and flooding occurred in the watershed. The river gage height during January reached 48.0 feet, close to the record stage height of 48.6 feet during the 1986 flood (Friebel et al., 1996). Total annual runoff for the 1995 water year was greater than 200% of the historical average.

During the third quarter 38.1 inches of rain were recorded at the Venado weather station and the Russian River discharge rate fluctuated between 1,241 and 61,274 cfs (Figure 49). The highest discharge during the third quarter came in March, coinciding with heavy rain and flooding in the watershed for the second time that year. The stage height during the March flood reached 42.0 feet, 6 feet less than the flood in January. During the fourth quarter, rainfall totaled 2.08 inches at Venado and the discharge ranged from 188 to approximately 9,000 cfs (Figure 50).

#### **Pesticide detections**

During the **12-month** sampling period, two of the 52 samples (3.8%) had a pesticide concentration above the reporting limits (Table 8). Diazinon was detected in a sample collected in November 1994, and dimethoate was detected in a equal-width increment depth integrated sample collected in March 1995. There were no detections reported from the six quality control rinse blanks of the splitting equipment.

Diazinon was detected at a concentration of 0.076 ppb in the sample collected November 5-8, 1994. According to CDFG, freshwater organisms should not be affected unacceptably if the average concentration of diazinon does not exceed 0.04 ppb in a 4day period more than once every 3-years (Menconi and Cox, 1994; **Stephan** et al., 1985, Table 4). Our results are not directly comparable to these criteria since the duration of sampling does not match the exposure period for which the criteria were developed. However, the detection indicates that additional, more intensive sampling for diazinon may be warranted.

Diazinon was applied throughout the year in the Russian River Watershed with a peak in April. More than 2,200 lb a.i. of diazinon were used on a variety of crops and the use was scattered throughout the watershed (Figure 51). November was the month when the least diazinon was applied to crops, the same month in which diazinon was

## **Russian River**

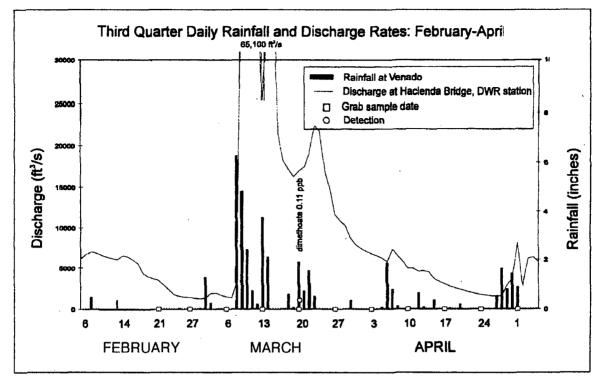
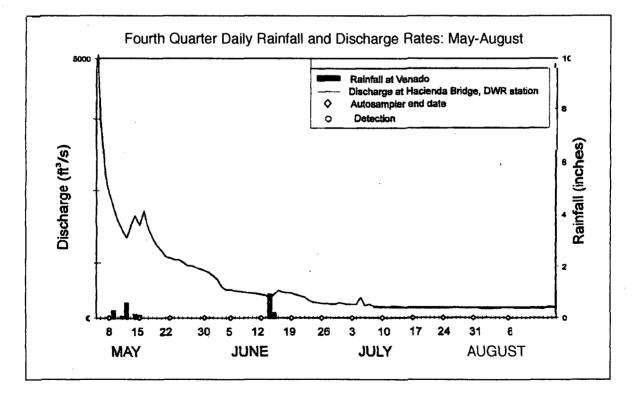


Figure 49. Daily rainfall and Russian River discharge for February 6,1995 through May 5, 1995.





#### DIAZINON USE IN THE RUSSIAN RIVER WATERSHED

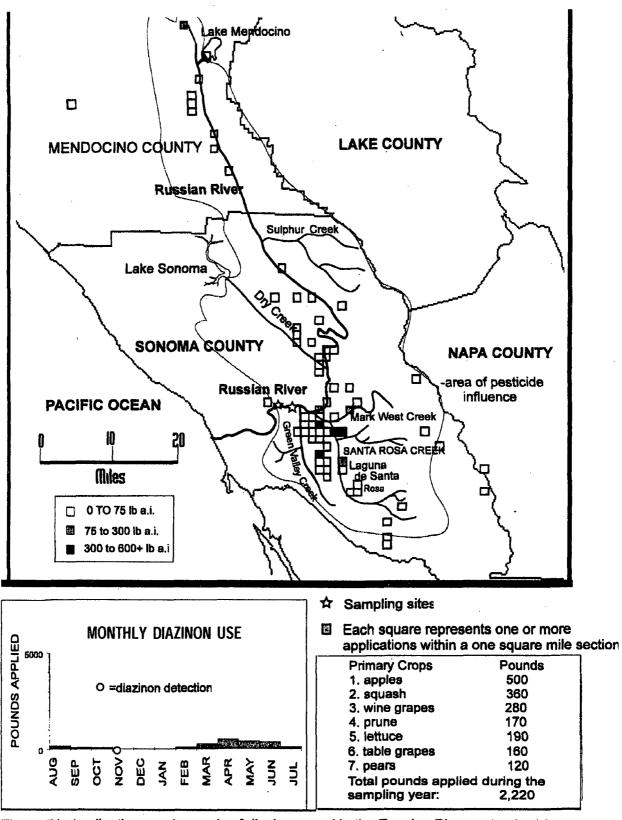


Figure 51. Applications and pounds of diazinon used in the Russian River watershed from August 1994 through July 1995.

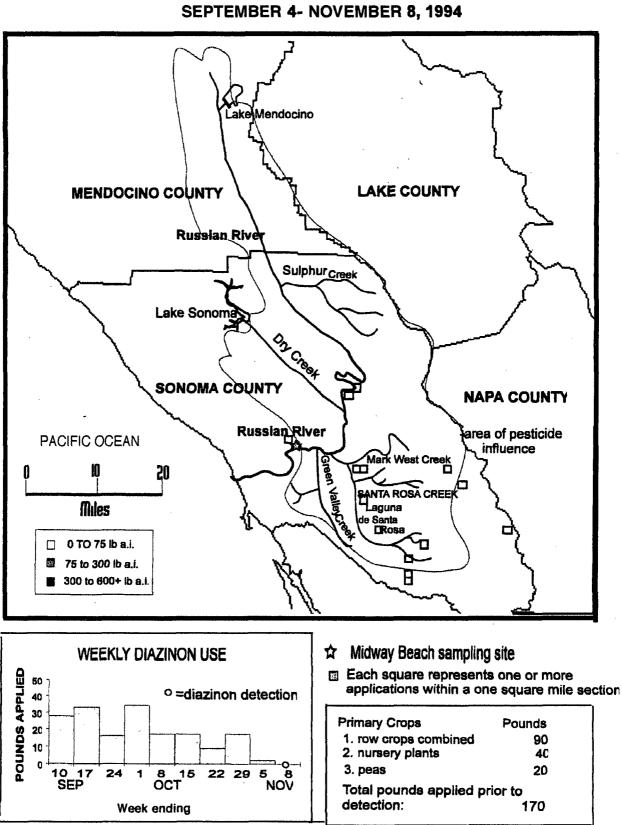
detected in the river sample. During the 10 weeks before the November 8 diazinon detection, a total of 174 lb a.i. of diazinon was used in the watershed (Figure 52). The use was mostly in Sonoma County on row crops such as lettuce, mustard, broccoli, and Swiss chard at less than 20 lb a.i. per crop. Some was used on nursery plants. In the 3-weeks before the detection, only about 30 lb a.i. of diazinon were used for agriculture and no diazinon use was reported for the week prior to the detection. The application that was made closest to the sampling site in the highlighted section in figure 52, happened 58 days prior to the detection and was located downstream of the site.

Due to the low agricultural use of diazinon in the watershed, there is a possibility that the detection resulted from landscape, structural or home and garden use. Diazinon is commonly used for home and garden applications to control pests such as ants, lawn grubs, and flies. Home and garden use is not reported to DPR and is not included in figures 51 and 52. In addition, diazinon has been detected in other parts of the United States and California in urban runoff (Schueler, 1995). Most of the urban runoff in Sonoma County is untreated. For instance, the Laguna de Santa Rosa receives discharges from street and stormwater drain systems which eventually flow to the Russian River (NCRWQCB, 1992). Typical of most diazinon detections in surface water, the detection came during rainfall and during a period of increased river discharge. The river flow increased about 309% by November 8 and greater than 700% at the peak 2 days later. This was the first storm of the season resulting in a significant increase in discharge.

Diazinon has been detected in a previous study. Thirteen clam samples were collected and analyzed for Diazinon for the SMWP. Diazinon was detected once out of 13 samples collected from the Russian River and some of the tributaries, at 70 ppb at the Laguna de Santa Rosa (Rasmussen, 1995a).

Dimethoate was detected in the sample collected on March 20, 1995 at 0.11 ppb. There is no current U.S. EPA water quality criterion for the protection of freshwater aquatic organisms (Table 4).

Dimethoate was used throughout the watershed primarily from March through August with peak use in June and July (Figure 53). Dimethoate is a systemic insecticide and acaricide used mostly on wine grapes and some was used on table grapes and apples. About 6,200 lb a.i. were applied during the I-year study period. A total of 51 lb a.i. of dimethoate were applied on grapes and apples during the 3-week period prior to the



DIAZINON USE IN THE RUSSIAN RIVER WATERSHED

Figure 52. Applications and pounds of diazinon used in the Russian River watershed from September 4 through November 8, 1994.

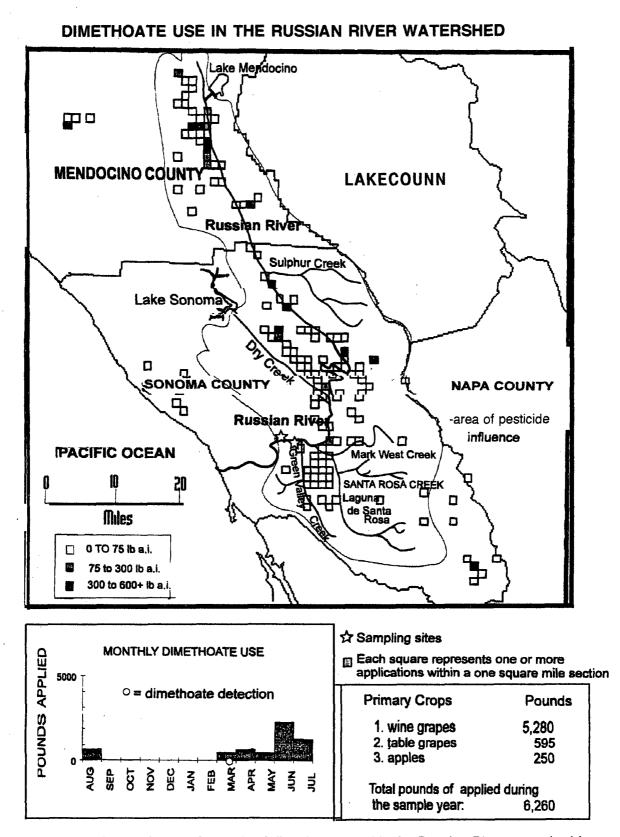


Figure 53. Applications and pounds of dimethoate used in the Russian River watershed from August 1994 through July 1995.

March 20 detection, at a time when the season for dimethoate applications was just beginning (Figure 54). Applications were made on March 16, 18 and 19, which were days when there was no rain. Rain occurred every week during the month prior to the detection with flooding occurring March 9 though March 15. From March 7, before the storm to the peak discharge on March IO, there was greater than a 5000% increase in flow. The detection occurred as discharge was declining but during a minor increase due to another storm. Despite a short half-life, dimethoate can reach surface water due to its high solubility (Table 5). Therefore, it is likely that the dimethoate entered the Russian River in rain runoff from fields treated between the storms. The use of dimethoate increased significantly after March 20. However, despite applications in excess of 700 lb a.i. in April and with rainfall still occurring, dimethoate was not detected again. During February, March and April equal-width increment samples were collected instead of using the autosampler, and thus only a very small portion of the weekly discharge in the Russian River was examined.

#### **Toxicity Results**

Only one of the 23 split samples analyzed by DFG for toxicity caused significant mortality to cladocerans. Mortality was not correlated with any pesticide detections. Tests showed no significant mortality to fathead minnows (Appendix V).

#### **Other Pesticides Used in the Watershed**

Chlorpyrifos was used primarily on apple orchards mainly in the area between Green Valley Creek and the Laguna de Santa Rosa from February through June at about 5,600 lb a.i. (Figure 55). Due to a longer half-life and a use period corresponding with the last half of the rainy period, chlorpyrifos had potential for being found in the river, but it was not detected. Since chlorpyrifos tends to bind with sediment and to move offsite with soil erosion, it may have moved offsite during periods of greatest rainfall, which may not have coincided with our sampling. Also these periods may have corresponded with flow discharges that diluted chlorpyrifos residue and made it undetectable. Chlorpyrifos was detected in the SMWP. Of the 21 clam samples taken at several locations in the watershed, IO had detectable levels of chlorpyrifos ranging from 4.4 to 290 ppb. The chlorpyrifos detection of 290 ppb was from mussels placed in Green Valley Creek in 1993 (Rasmussen, 1995a).

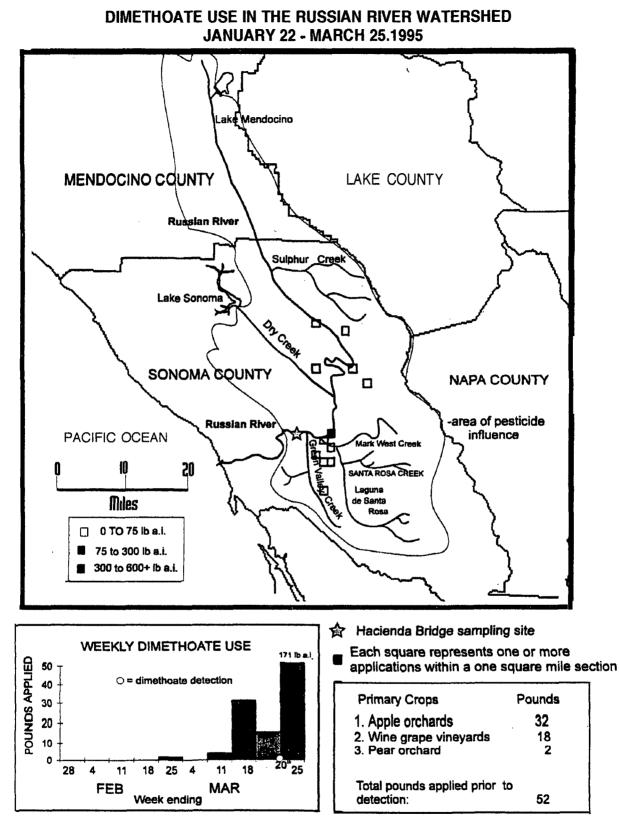


Figure 54. Applications and pounds of dimethoate used in the Russian River watershed from January 22 through March **25**, **1995**.

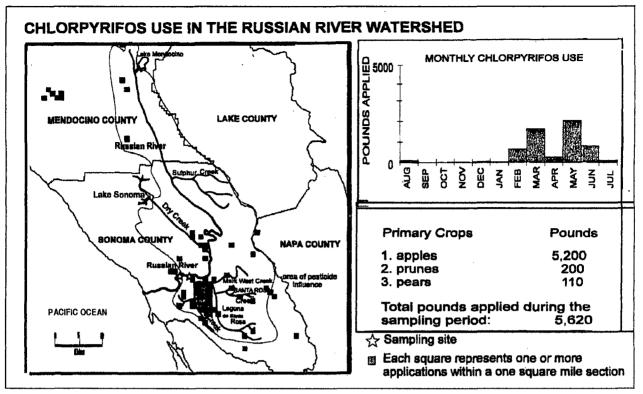


Figure 55. Applications and pounds of chlorpyrifos used in the Russian River watershed from August 1994 through July 1995.

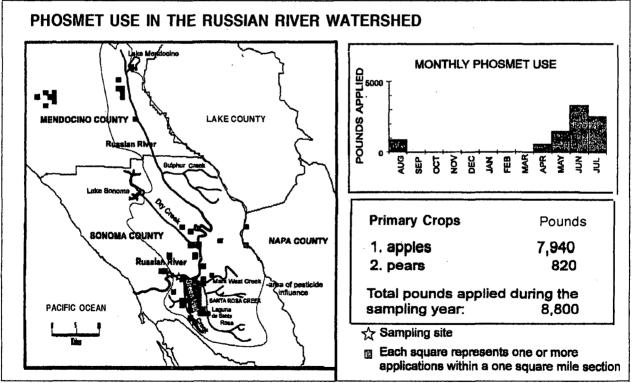


Figure 56. Applications and pounds of phosmet used in the Russian River watershed from August 1994 through July 1995.

Phosmet was applied on apple orchards in many of the same sections where Chlorpyrifos was used (Figure 56). More than 8,800 lb a.i. of phosmet was applied during the study period but it was never detected in the samples collected. Phosmet was used from April through August, with the most use occuring in June and July. Azinphos-methyl was applied on pear orchards in Mendocino and Somoma Counties and apple orchards mainly in Sonoma County. It was used at greater than 9,800 lb a.i., primarily in May and through July (Figure 57). With the exception of the use in April, these **OPs** would be expected to have less potential to reach the Russian River because each were used during the early part of the dry season and have an average field-dissipation half-life of less than 2.5 weeks (Table 5). In April 560 and 322 lb a.i. of phosmet and azinphos-methyl were used, respectively. There was no reported use of phosmet or azinphos-methyl during September, October or November, the months prior to the first significant increase in discharge.

Carbaryl is the only carbamate applied in the watershed that was analyzed in our screen. Approximately 1,000 lb a.i. of carbaryl were applied within the watershed from February through September primarily on table grapes, apples, wine grapes and squash (Figure 58). Carbaryl may be found in February, March and April in surface water within this watershed since it is used during the rainy season. However, it is still unlikely carbaryl would end up in the Russian River from agricultural use due a short half-life of under 2 weeks (Table 5) and few applications.

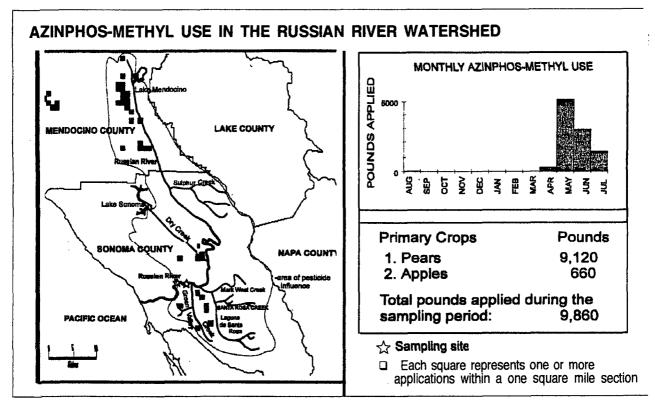


Figure 57. Applications and pounds of azinphos-methyl used in the Russian River watershed from August 1994 through July 1995.

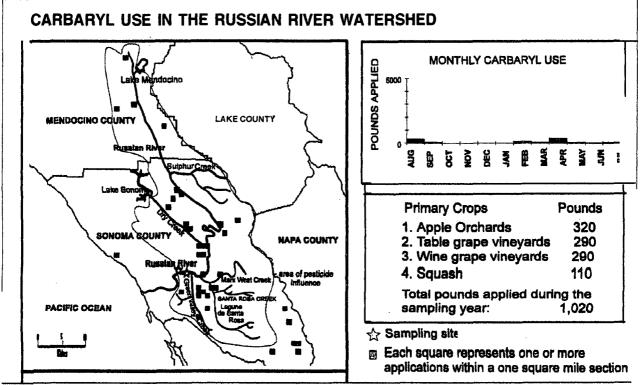


Figure 58. Applications and pounds of carbaryl used in the Russian River watershed from August 1994 through July 1995.

#### Conclusions

Overall, the DO levels and pH levels in all four rivers were good. The DO was below the minimum required levels (Regional Water Quality Control Boards) in 12 out of 157 measurements. However, the percent saturation never fell below 50% on any measurement. The pH readings taken primarily *in situ* with some taken in the lab, were below the regional board standards in only 4 of 212 measurements. Rainfall amounts during the winters included in the study were atypical. The winter of 1994 was fairly dry resulting in below normal discharge in the Sacramento River. In the winter of 1995, we experienced a tremendous amount of rainfall that produced flooding on the Merced, Russian and Salinas Rivers.

During the year-long sampling on the four rivers, the number of positive samples was 13 of 224 samples (5.8%), and pesticides were detected 17 times in the 224 samples (7.6%) due to multiple detections in some samples. Five different pesticides were detected: diazinon was detected seven times, dimethoate was detected four times, methidathion was detected four times and chlorpyrifos and 3 OH-carbofuran were each detected once. Ten samples were positive during the rainy season while there were only three positive samples during the dry season. Diazinon, methidathion, dimethoate, 3 OH-carbofuran and chlorpyrifos were detected in the wet season, while dimethoate and diazinon were detected in the dry season. Most detections occurred just after or during rainfall, and all occurred with elevated discharge except in the Salinas River Lagoon, for which we have no flow data.

During the year-long sampling period, two of the 52 samples collected at the Sacramento River had a pesticide detection. Diazinon was detected twice at 0.11 and 0.07 ppb during January and February, respectively. Since the two detections came during periods of increased discharge due to rainfall, rain runoff from dormant spray applications to nut and stone fruit trees appears to be the principal means by which diazinon reached the Sacramento River.

The most detections were found in the Merced River samples (ten), primarily during the winter dormant spray period. The most types of pesticides were also found in the Merced River (4) including the only carbamate found, 3-OH-carbofuran. We began to sample the river twice a week on January 31 and the results suggest that more intense monitoring from December through March would be useful.

Chlorpyrifos was the only pesticide detected along the middle reach of the Salinas River. Chlorpyrifos was detected at 0.12 ppb in January, just after the first major storm of the year. The greatest number of detections per number of samples collected came from the Salinas Lagoon where only 12 monthly samples were collected. Diazinon and dimethoate were detected in the same sample collected in June, at 0.20 and 0.11 ppb, respectively. These two pesticides may have entered the lagoon via irrigation runoff or drift.

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There were two detections in samples collected from the Russian River. Diazinon was detected at 0.076 ppb in November, after the first storm of the year producing significant runoff. Agricultural use of diazinon was low during the three months **preceeding** the detection. There is a possibility that the detection could be due to landscape, structural or home and garden use. Dimethoate was detected at 0.11 ppb in March, during a storm.

During the year-long study there were few detections in the Sacramento and Russian Rivers and the middle reach of the Salinas River for several possible reasons. First, there may not be much insecticide residue moving off-site into the rivers. Secondly, our sampling periods may have missed the residue pulses or diluted them. Third, the Salinas River had one and the Russian River had two flood events during sampling. As a result, residues may have been diluted in the abnormally high flows, at a time of the year when detections occurred in studies of other rivers. However, the heavier rainfalls that occur within the Russian River watershed can result in greater flow increases than in the other three rivers. These flows may render pesticides flowing into the Russian River during storms, when detections normally occur, undetectable due to dilution. Furthermore, along the Merced River, dam releases during the spring of 1995 may have diluted residues during the last three months of monitoring. And last, there may have been residues present in these rivers in localized areas, upstream or along the tributaries that were diluted at our sampling sites.

The 3-day composite method was chosen to sample more of the weekly discharge than collecting a one-hour-long equal-width increment sample. One disadvantage of using the 3-day sampling period is possible degradation of pesticide residues during the sample collection and during transport time. The results of a storage stability study conducted on carbamates and **organophosphates** showed that only five pesticides and seven breakdown products may begin to degrade during this length of time.

Another concern of using the 3-day composite method was the dilution of residues. The USGS's single-day sampling on the Sacramento River concurrently with our monitoring provided a comparison with our 3-day composite method. USGS's diazinon detections corresponded with two of our detections. When the USGS's daily concentrations of diazinon were averaged, the quantity of diazinon residues is the same as our 3-day composite method. In addition, DPR's negative 3-day sample periods (no detections) coincided with periods when either no detections were made by USGS or detections were below our RL. Peak levels of diazinon detected by USGS seemed to coincide with peak river discharges, which in some cases did not coincide with our 3day sampling periods. USGS detections of methidation on the Sacramento River showed that levels were below our RL. According to the USGS data, our sample collection method was adequate in capturing the major pulses of diazinon.

Endosulfan was included in the analyses for this study since it is still detected in fish and clam tissues by the TSMP and SMWP. In addition, it was also included to see if changes in use permits, which are to prevent residues from moving offsite in drainage from fields beside waterways, have had an effect. Statewide use of endosulfan is declining; 475,743 lbs. used in 1994 and 229,157 lbs. in 1995. Use in Monterey County, where endosulfan has been detected in fish and clam tissues and in soil and sediment samples, was low compared with the other pesticides used, with 1,731 and 2,953 used in 1994 and 1995, respectively (PUR 1994, PUR 1995). Based on a lack of detections in this study, we have no evidence that the permits are not protecting these rivers.

The CDFG Aquatic Toxicology Laboratory tested 107 of the 212 samples collected at each of the four rivers for toxicity. The Salinas River Lagoon site was not included. DFG found no apparent relationship between the presence of pesticide residues and mortality observed in the samples tested for toxicity. Three samples caused significant mortality to either fathead minnows or cladocerans but those samples did not contain detectable concentrations of pesticides. The cause of the mortality is unknown at this time.

#### Recommendations

Since the rainfalls for both winters included in the study period were atypical, the fairly low number of pesticide detections from samples from the Sacramento and Russian Rivers and the middle reach of the Salinas River should not preclude further sampling on these rivers. There is potential, however, to increase the number of detections by optimizing the type of sampling and the timing. Monitoring during storms when the discharge is increasing, especially in periods after increased applications of these chemicals, may lead to more detections from all four rivers. Our sampling procedure was developed to survey each of these rivers for a whole year. Sampling dates were predetermined, and therefore may not have coincided with peak residue levels in these rivers. Also, pesticides might be detectable along the tributaries of all four rivers. Since we sampled at one site on each river (two on Salinas River), we have no knowledge of pesticide contamination along the tributaries that may have been diluted at the confluence of the rivers or at our sampling site.

The Merced River and Salinas River Lagoon stand out as needing further study based on the number of detections. The most detections were found in samples from the Merced River, primarily during the winter dormant spray periods. Also, the most types of pesticides, three **OPs** and the only CB found, 3-OH-carbofuran, were found there. Further sampling along the Merced River would be beneficial since the winter of 1995 was atypical and the dam releases in the spring were greater than normal. Since the lagoon is a recognized wildlife habitat area, more monitoring for pesticide residues there would be beneficial. Unlike the middle reach of the Salinas River, the stage height does not fluctuate greatly. Therefore, an autosampler and the 3-day composite method could be used at the lagoon.

The most frequently used pesticides in the Russian River Basin were herbicides and some fungicides which were not analyzed in this study. Since greater amounts of these pesticides were used in the basin rather than insecticides, those that have potential to move off-site and are toxic to aquatic organisms should be the focus of further study along with the pesticides we detected in this study. If further study is conducted on the Salinas River, chlorthal-dimethyl should be included due to the large quantity used and it has been detected numerous times in this watershed in other studies.

#### References

Anderson, S.W., T.C. Hunter, E.B. Hoffman, and J.R. Mullen. 1993. Water Resources Data, California Water Year 1992. Vol. 3. U.S. Geological Survey Water-Data Report . Report #CA-92-3. Sacramento, CA.

Ayers, W. and others. 1995. Water Resources Data, California, Water Year 1994. Vol. 2. U.S. Geological Survey Water-Data Report, CA-94-2. Sacramento, CA.

Buchanan, T.J. and W.P. Somers. 1969. Discharge measurements at gauging stations. In; Techniques of Water-Resources Investigations of the United States Geological Survey. Book 3, Chap. A8. 65p.

California Department of Food and Agriculture. 1994. 1993 County Agricultural Commissioner's Data. California Agricultural Statistics Service, California Department of Food and Agriculture joint report with The U.S. Department of Agriculture. Sacramento, California.

Central Coast Regional Water Quality Control Board. 1994. Water Quality Control Plan, Central Coast Region.

California Department of Health Services. 1990. Summary: Maximum contaminant levels (MCLs) and action levels (ALs). Office of Drinking Water. Berkeley, California.

California State Lands Commission. 1993. California's Rivers; A public trust report. Second Edition. Sacramento, CA. p. 130-I 33, 148-152.

Central Valley Regional Water Quality Control Board . 1989. Water diversion and discharge points along the Merced River: Cressey Bridge to San Joaquin River. Sacramento, CA.

Central Valley Regional Water Quality Control Board . 1995a. Insecticide concentrations and invertebrate bioassay mortality in agricultural return water from the San Joaquin Basin. Sacramento, CA.

99

Central Valley Regional Water Quality Control Board . 1995b. Water Quality Control Plan, Central Valley Region, Sacramento and San Joaquin Rivers. California Regional Water Quality Control Board, Central Valley Region and State Water Resources Control Board. Third Edition.

Domagalski, J.L. 1995. Nonpoint sources of pesticides in the San Joaquin River, California: input from Winter Storms, 1992-93. U.S. Geological Survey. Report # 95-165. Sacramento, CA.

Domagalski, J. and L.R. Brown. 1994. National Water Quality Assessment Program, Sacramento River Basin. U.S. Geological Survey. Sacramento, CA.

Department of Pesticide Regulation. 1991. Pestcide use report. Sacramento, CA.

Department of Pesticide Regulation. 1992. Pestcide use report. Sacramento, CA.

Department of Pesticide Regulation. 1993. Pestcide use report. Sacramento, CA.

Department of Pesticide Regulation. 1993. Pestcide use report. Sacramento, CA.

Department of Pesticide Regulation. 1994. Pestcide use report. Sacramento, CA.

Department of Pesticide Regulation. 1995. Pestcide use report. Sacramento, CA.

Department of Water Resources. 1993. Quality Assurance Technical Document 3. Compilation of State Drinking Water Standards and Criteria. Division of Local Assistance. Department of Water Resources. Sacramento, CA. July 1993.

Fleck, J.E., L.J. Ross, and K. Hefner. 1988. Endosulfan and chlorthal-dimethyl residues in soil and sediment of Monterey County. Report # EH 88-06. Environmental Hazards Assessment Program. Dept. of Pesticide Regulation. Sacramento, CA.

Foe, C. 1994. Letter to K. Bennett regarding pesticide detections on the Merced River. Central Valley Regional Water Quality Control Board. Letter dated January 4, 1994. Sacramento, CA. Foe, C. and R. Sheipline. 1993. Pesticides in surface water from applications on orchards and alfalfa during the winter and spring of 1991-92. California Regional Water Quality Control Board, Central Valley Region, Sacramento, CA.

Friebel, M.F., L. F. Trujillo and K.L. Markham. 1996. Water resources data, California, Water Year 1995. Vol. 2. U.S. Geological Survey Water-Data Report CA-95-2. Sacramento, CA.

Goodwin, C. 1994. Personal communication regarding Russian River watershed. North Coast Regional Water Quality Control Board. March 1994.

Goodwin, C. 1993. California Regional Water quality Control Board, North Coast Region. Letter to C. Ganapathy regarding Russian River tributaries and past monitoring of the Russian River. December 6, 1993.

Guy, H. P. and V.W. Norman. 1970. Field methods for measurement of fluvial sediment In:Techniques of water-resources investigations of the United States Geological Survey. Book 3. Chapter C2. U. S. Gov. Print. Office. Washington, D.C.

Howard, P. H. 1991. Handbook of environmental fate and exposure data for organic chemicals. Volume III, Pesticides. Lewis Publishers. Chelsea, Michigan.

Klamt, R. 1995. Personal communication regarding dissolved oxygen levels. North Coast Regional Water Quality Control Board. August 1995.

Klamt. R. 1994. Personal communication regarding Russian River watershed boundary. North Coast Regional Water Quality Control Board. April 1994.

Kollman, W., and R. Segawa, 1995. Interim report of the pesticide chemistry database. Envrionmental Hazards Assessment Program. Dept. of Pesticide Regulation. Sacramento, CA.

Kratzer, C. 1997. Personal communication in January 1997 regarding Merced River Basin. U.S. Geological Survey. Sacramento, CA.

101

Kuivila, K.M. and C.G. Foe. 1995. Concentrations, transport and biological effects of dormant spray pesticides in the San Francisco Esturary, California. Environ. Toxicol. Chem. 14(7):1141-1150.

Lee, J. M., L. J. Ross and R.G. Wang. 1993. Integrated environmental toxicology and monitoring in the development and maintenance of a water quality program: California's rice herbicide scenario. In: Effective and Safe Waste Management. Chapter 18. Lewis Publishers. p211-224.

MacCoy, D., K.L. Crepeau, and K.M.Kuivila. 1995. Dissolved pesticide data for the San Joaquin River at Vernalis and the Sacramento River at Sacramento, California, 1991-94. U.S. Geological Survey. Report# 95-I 10.

Markham, K.L., J.R. Palmer, M.F. Friebel, L. F. Trujillo. 1993. Water Resources Data, California, Water Year 1993. Vol. 2. U.S. Geological Survey Water-Data Report CA-92-2. Sacramento, CA.

Marshack, J. B. 1995. A compilation of water quality goals. Central Valley Regional Water Quality Control Board. Sacramento, CA.

Mayer, F.L. and M. R. Ellersieck. 1986. Manual of acute toxicity: Interpretation and data base for 410 chemicals and 66 species of freshwater animals. U.S. Fish and Wildlife Service, Washington, DC.

Menconi, M. and S. Seipmann, 1996. Hazard assessment of the insecticide methidation to aquatic organisms in the Sacramento-San Joaquin River system. California Dept. of Fish and Game, Rancho Cordova. Administrative Report# 96-1.

Menconi, M. and C. Cox. 1994. Hazard assessment of the insecticide diazinon to aquatic organisms in the Sacramento-San Joaquin River system. California Department of Fish and Game. Environmental Services Division. Administrative **Report#** 94-2.

Miller, J.C. and J.N. Miller. 1988. Statistics for analytical Chemistry. 2nd ed. Ellis Horwood Limited. Chichestier, West Sussex.

Mullen, J.R., M.F. Frieble, K.L. Markham and S.W. Anderson. 1994b. Water Resources Data, California, Water Year 1993. Vol. 4. U.S. Geological Survey. Water-Data Report CA-934 Sacramento, CA.

Mullen, J.R., S.W. Anderson, and P.D. Hayes. 1994a. Water Resources Data, California Water Year 1993. Vol. 3. U.S.Geological Survey. Water-Data Report CA-93-3. Sacramento, CA.

North Coast Regional Water Quality Control Board , 1992. Investigation for nonpoint source pollutants in the Laguna de Santa Rosa, Sonoma County. September 24, 1992.

North Coast Regional Water Quality Control Board . 1994. Water Quality Control Plan for the North Coast Region (Basin Plan). Revised 1997. Santa Rosa, CA.

North Coast Regional Water Quality Control Board . 1993. Interim staff report regarding Russian River water quality monitoring. Santa Rosa, CA.

Oakden, J.M. and J.S. Oliver.1988. Pesticide persistence in fields and drainages of the central Monterey Bay Area. Report prepared for the RWQCB, Central Coast Region by Moss Landing Marine Laboratories. Moss Landing, CA.

Palmer, J.R., M.F. Friebel, L. F. Trujillo and K.L. Markham. 1994. Water Resources Data, California, Water Year 1993. Vol. 2. U.S. Geological Survey Water-Data Report CA-93-2. Sacramento, CA.

Racke, K.D. 1993. Reviews of environmental contamination and toxicology. Vol. 131. Springer-Verlag. New York, NY.

Rasmussen, D. 1995b. Toxic Substances Monitoring Program, 1992-93. Report **# 95-**1WQ. California State Water Resources Control Board. Sacramento, CA.

Rasmussen, D. 1995a. State Mussel Watch **Program, 1987-1993** Data Report. Report # 94-I WQ. California State Water Resources Control Board. Sacramento, CA.

103

Rassmussen, D. 1994. Preliminary Summary of the 1994 Species Data. Toxic Substances Monitoring Program. California State Water Resources Control Board. Sacramento, CA.

Rassmussen, D. 1991 . Toxic Substances Monitoring Program, 1988-89. Report # 91-WQ. California State Water Resources Control Board. Sacramento, CA.

Rassmussen, D. **1993**. **Toxic** Substances Monitoring Program, 1991. Report # 91 -WQ. California State Water Resources Control Board. Sacramento, CA.

Ross, L.J. 1992a. Preliminary results of the San Joaquin River study; Summer 1991. Memorandum to Kean Goh, Environmental Hazards Assessment Program. Department of Pesticide Regulation. May 21, 1992.

Ross, L.J. 1993a. Preliminary results of the San Joaquin River study; Summer 1992. Memorandum to Kean Goh, Environmental Hazards Assessment Program. Department of Pesticide Regulation. September 22, 1993.

Ross, L.J., R. Stein, J. Hsu, J. White, and K. Hefner. 1996. Distribution and mass loading of insecticides in the San Joaquin River, California; Winter 1991-92 and 1992-93. Report #EH 96-02. California Department of Pesticide Regulation. Sacramento.

Ross, L.J., K.D. Bennett, K.D. Kim, K. Hefner, J. Hernandez. 1996. Reducing dormant spray runoff from orchards. Environmental Hazards Assessment Program. Report # EH 97-03. Department of Pesticide Regulation. Sacramento, CA.

Salinas River Lagoon Management and Enhancement Plan. 1992. Prepared by Habitat Restoration Group for the Salinas River Lagoon Task Force. (Draft).

Schueler, T. 1995. Urban pesticides: From the lawn to the stream. Watershed Protection Techniques. Vol.2, No.1.

Seipman, S. and T. Yargeau. 1996. Hazard assessment of the insecticide dimethoate to aquatic organisms in the Sacramento-San Joaquin River system. California Dept. of Fish and Game, Rancho Cordova. Administrative Report# 96-4.

Shelton, L.R. and L.K. Miller. 1988. Water quality data, San Joaquin valley, California. March 1985 to March 1987. U.S. Geological Survey. Open file Report 88-479. Sacramento, CA.

Stein, R.G. and J. H. White. 1993. Aerial movement and deposition of diazinon, chlorpyrifos, and Ethyl parathion. Report # EH 93-04. Dept. Pesticide Regulation. Sacramento, CA.

**Stephan,** C.E., D.I. Mount, D.J. Hansen, J.H. Gentile, G.A. Chapman, and W.A. Brungs. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. U. S. EPA. Office of Research and Development. Washington, D.C.

State Water Resources Contol Board. 1990. Sacramento River toxic chemical risk assessment project. Final Report. California State Water Resources Control Board, Division of Water Quality. Report# 90-I 1 WQ. Sacramento, CA

State Water Resources Contol Board, 1994. Notice of Public Workshop on January 4,1995. Information relating to water right issues on the Russian River. Notice date December 1, 1994. California State Water Resources Control Board. Sacramento, CA.

U.S. Environmental Protection Agency. 1986. Quality Criteria for Water. Office of Water Regulations and Standards, Washington, D.C. May 1, 1986.

U.S. Environmental Protection Agency. 1988. Health advisories for 50 pesticides. Part 1. U.S. Dept. of Commerce. National Technical Information Service. Washington D.C. p. 268-285.

U.S. Geological Survey. 1995. Water Resources Data, California, Water Year 1995. Region 3. Internet-http://wr.usgs.gov/data/index.html.

Wauchope, R.D.1978. The pesticide content of surface water draining from agricultural fields-A review. J. Envrion. Qual., Vol. 7. no. 4.

105

Wofford, P.L. and P. Lee. 1995. Results of monitoring for the herbicide MCPA in surface water of the Sacramento River Basin. Environmental Hazards Assessment Program. Report # EH 95-I 1. Dept. of Pesticide Regulation. Sacramento, CA.