

**ENVIRONMENTAL MONITORING RESULTS OF THE  
MEDITERRANEAN FRUIT FLY ERADICATION PROGRAM,  
VENTURA COUNTY, 1994-1995**

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## ABSTRACT

In October 1994, the California Department of Food and Agriculture began a series of aerial applications to eradicate an infestation of the Mediterranean fruit fly (Medfly) in Ventura County. Treatment consisted of 14 applications of a malathion-bait mixture applied over a 41 square kilometer ( $\text{km}^2$ ) area encompassing the eastern part of Camarillo and the town of Somis. Applications were made at night, at 14-to-21-day intervals from October 12, 1994, to May 23, 1995. The Environmental Hazards Assessment Program of the California Department of Pesticide Regulation monitored applications throughout the treatment program to measure the amount of malathion and malaoxon (a breakdown product of malathion) reaching the ground, and the concentration of these chemicals in air, surface water, and rain runoff. In addition, this information was compared with data from previous similar applications.

Mass deposition of malathion averaged 8.21 milligrams per square meter ( $\text{mg}/\text{m}^2$ ) for the first two sprays, which is 80% of the theoretical deposition rate of 10.19  $\text{mg}/\text{m}^2$ . During the third spray, average mass deposition was 3.23, which is 30% of the theoretical rate. Atypical weather conditions most likely contributed to the unusually low malathion deposition during the third spray. Malaoxon was not detected in the majority (75%) of the samples. The amount of malaoxon deposited on the ground ranged from none detected to 0.07  $\text{mg}/\text{m}^2$ . The laboratory reporting limit for malathion and malaoxon was 0.011  $\text{mg}/\text{m}^2$ .

Outdoor air samples were collected during the second, third, and ninth applications at five sites within a 0.8 km diameter area located near the center of the spray area. Samples were collected at each site for four consecutive periods: 24-hr immediately before the spray, during the spray plus one-half hour, and for two consecutive 24-hr periods after the spray. The highest average malathion level was measured during application at 5.0 ppt ( $0.067 \mu\text{g}/\text{m}^3$ ). The highest average malaoxon level was 0.80 ppt ( $0.010 \mu\text{g}/\text{m}^3$ ) during the first 24-hr period following the spray. These air results were not adjusted for the small fraction of malathion that oxidizes to malaoxon during sampling.

During the first three applications, water was collected before application at an inflow site upstream of the treatment boundary, and at an outflow site downstream of the treatment boundary. Immediately after the spray, water was collected at the outflow site. Malathion concentration in outflow water averaged 44 ppb and ranged from 39 to 50 ppb. Malaoxon concentrations at this site averaged 0.05 ppb and ranged from none detected to 0.083 ppb. Malathion concentrations in surface water samples were approximately two times greater than during the 1994 Medfly program; both programs used the same application rate. Malaoxon was not detected in surface water samples during any of the monitored sprays in the 1994 program.

Rain runoff water was collected during storms that occurred 3, 6, and 12 days following application at three sites immediately downstream of the treatment boundary. Malathion levels in rain runoff during the second storm were higher than expected. Therefore, three sites were added further downstream to determine if malathion and malaoxon were entering Mugu Lagoon. The Mugu Lagoon is an estuary approximately 5.5-km downstream from the treatment area. Three days after the seventh spray the maximum malathion concentration, 787.1 ppb, was found in Calleguas Creek. The highest malaoxon level was 160.2 ppb and occurred at the same site, 12 days after the second spray.

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## **DISCLAIMER**

The mention of commercial products, their source or use in connections with material reported herein is not to be construed as an actual or implied endorsement of such product.

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## INTRODUCTION

### Background

The Mediterranean fruit fly (Medfly), *Ceratitus capitata*, is one of the most destructive agricultural pests, which can infest and damage more than 260 fruits, flowers, and nuts (Foote, 1993). Medfly establishment in California represents a serious threat to produce quality and export, and its presence is considered an emergency situation. Consequently, the California Department of Food and Agriculture (CDFA) maintains an extensive trapping program, and eradication measures are initiated as soon as an infestation is detected. A detailed description of this program is provided in the technical report from the 1994 eradication effort in Corona, Riverside County (Ando 1995).

In September 1994, an infestation of Medfly was detected in a citrus orchard located in Camarillo in southern Ventura County. The decision was made to conduct an aerial spray program to protect the agricultural industry in California.

### Aerial Treatment Program

The aerial eradication program consisted of 14 applications of malathion bait spray applied at 14- to 21-day intervals from October 12, 1994, to May 23, 1995. The malathion and bait mixture was applied over a 41 square kilometer (km<sup>2</sup>) area encompassing the eastern part of Camarillo and the town of Somis. The mixture was applied using three Bell 204 helicopters flying north-south at approximately 100 meters above ground level and at a speed of 130 km/hr. Each helicopter discharged the mixture through six Tee Jet 8010 flat fan nozzles resulting in a nominal swath width of 61 meters (m). The applications occurred at night beginning at approximately 9:00 p.m. and ending between midnight and 2:00 a.m. The malathion was applied at a rate of approximately 102 grams (g) of Malathion ULV® in 789 milliliters (ml) of Nu-Lure® protein bait per hectare (ha).

Malathion, introduced in 1950 by American Cyanamid Co., is a nonsystemic organophosphorous insecticide. The mode of action relies on the oxidative activation to malaoxon, a potent acetylcholinesterase inhibitor in insects; its low mammalian toxicity is due to its selective hydrolytic degradation, via mammalian carboxylesterases (Mulla et al., 1981). Numerous studies are available that report on the effect of malathion and malaoxon on mammals (O'Brien 1960; March et al. 1956), as well as, some that document the effect of degradation products and impurities present in malathion bait formulations (Brown et al., 1993). Table 1 shows the impurities present in Clean Crop Malathion ULV® (Platte Chemical Company) and their approximate percentage (Voss 1990).

Table 1. Percentage of impurities present in Clean Crop Malathion ULV® (Platte Chemical Company)

Co-products	Percent by Weight
Diethyl fumarate (DEF)	0.90%
Diethylhydroxysuccinate	0.05%
O,O-dimethyl phosphorothioite	0.05%
O,O,O-trimethyl phosphorodithioite (TMTP)	0.45%
O,O,S-trimethyl phosphorodithioate (TME)	1.20%
Ethyl nitrite	0.03%
Diethyl-bis (ethoxycarbonyl) mercaptosuccinate	0.15%
S-1,2,-ethyl-O,S-dimethyl phosphorodithioate (isomalathion)	0.20%
S-(1-methoxycarbonyl-2-ethoxycarbonyl) ethyl-O,O-dimethyl phosphorodithioate	0.60%
Bis-(O,O-dimethyl thionophosphoryl) sulfide (PSP)	0.30%
Diethyl methylthiosuccinate (DEMMS)	1.00%
S-ethyl-O,O-dimethyl phosphorodithioate	0.10%
S-1,2-bis (ethoxycarbonyl) ethyl-O,O-dimethyl phosphorodithioate (malaoxon)	0.10%
Diethyl ethylthiosuccinate	0.10%
Water	0.07%
Acidity as sulfuric acid	0.05%
Total	5.35%

## **Environmental Monitoring Program**

Staff from the Environmental Hazards Assessment Program (EHAP) conducted environmental monitoring during four aerial malathion applications to measure malathion and malaoxon (an oxidation product of malathion ) concentrations reaching the ground, in air, and in surface water. The monitoring is to assess the effectiveness of CDFA's application and to compare concentrations to previous eradication treatments to assess potential environmental or health hazards.

Extensive monitoring by EHAP during similar aerial treatments in 1981, 1989-90, and the spring of 1994 did not reveal any significant concentration of malathion on surfaces or in ambient air. Concentrations in the parts per billion (ppb) range were frequently detected in surface water. Consequently, in addition to monitoring mass deposition, air, and surface water, an expanded rain runoff study was designed to determine surface water concentrations in waterways exiting the treatment area during storm events.

## **MATERIALS AND METHODS**

### **Media and Monitoring Sites- General Information**

Sampling sites were selected based on several criteria. Mass deposition sampling sites (Fig. 1) were located at least 300 m apart and 400 m inside the perimeter of the treatment area. Sites for mass deposition samples were located so that no tree cover, building, or other obstruction could interfere with the deposition of the malathion spray. As the only waterway with a constant flow of water, Conejo Creek was monitored during the first three applications at sites located just before entering and after exiting the treatment area (Fig. 1). Sites for rain runoff sampling were selected based on drainage patterns and accessibility (Fig. 2). Air sites (Fig. 1) chosen were accessible at all hours, protected from any direct spray, e.g., by patio roofs, eaves of houses, etc., and had electrical power to run the samplers.

Figure 1. Map of the 1994/95 malathion bait aerial treatment site in Ventura County, California

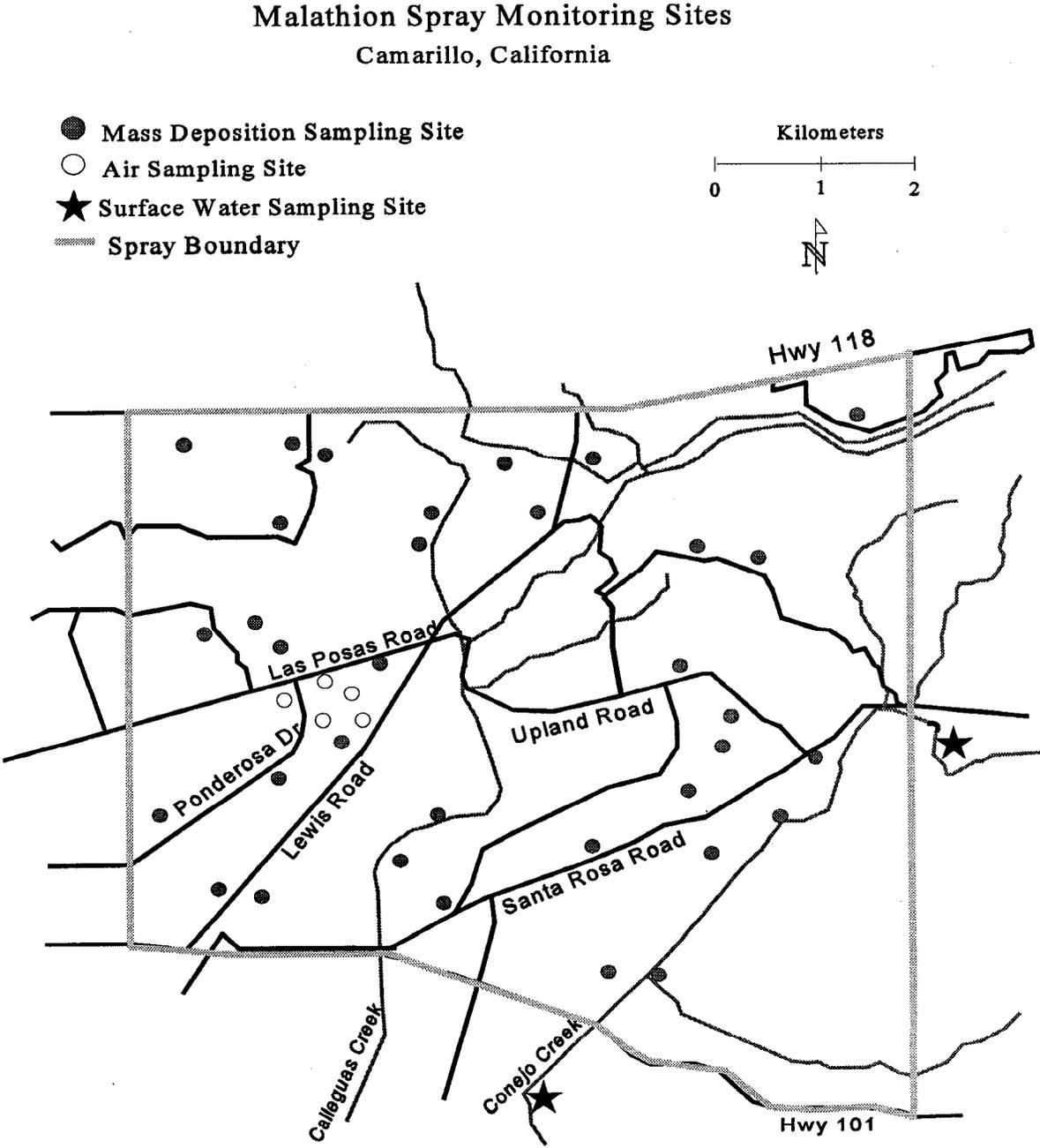
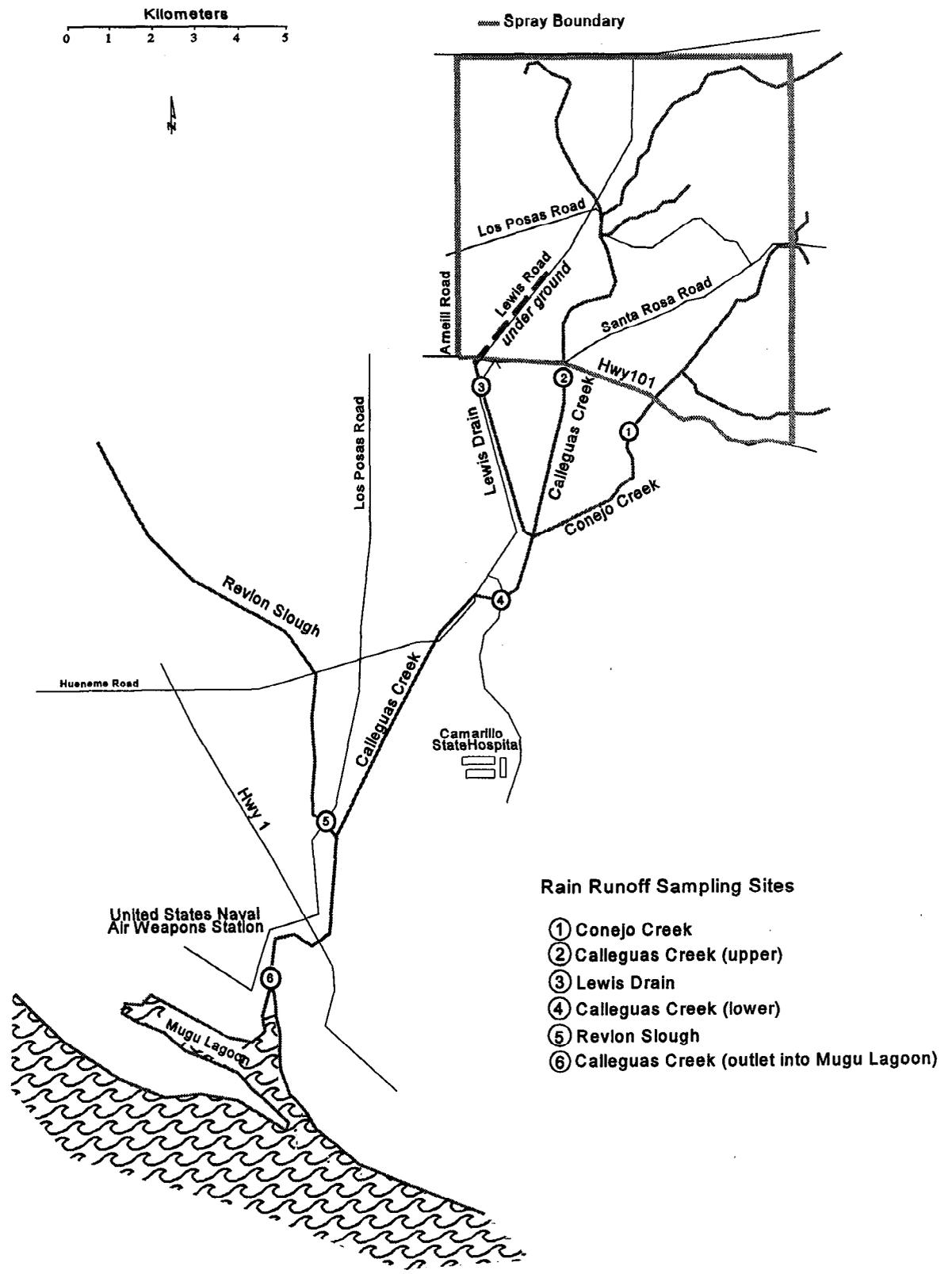


Figure 2. Map of rain runoff sampling sites in Ventura County, California



## **Mass Deposition**

Mass deposition of malathion and malaoxon reaching the ground was measured during the first three applications at 34 sites within the treatment area. At each site, one absorbent sheet with plastic backing measuring 22.86 cm x 40.64 cm (referred to as “kimbies” in previous reports) was attached with push pins to a polyethylene-covered cardboard sampling platform. The sampling platform was placed horizontally at various heights, from 20 cm to 2 m above ground level, depending on the site characteristics. The deposition sheets were set out approximately two hours before the spray and were collected approximately 30 minutes after the helicopters had sprayed the area. The absorbent sheets were folded with the plastic side out, wrapped in aluminum foil, and placed in a manilla envelope. Samples were stored on dry ice and kept frozen until extraction.

The CDFA Center for Analytical Chemistry in Sacramento, California, analyzed the sheets by extracting the pesticide residue with ethyl acetate. An aliquot of the extract was analyzed for malathion using a gas chromatograph (GC) equipped with a thermionic specific detector (TSD). Malaoxon was analyzed using a GC with a flame photometric detector (FPD) after the remainder of the extract was concentrated from each sample. The reporting limit (RL) was 0.011 mg/m<sup>2</sup> for malathion and malaoxon.

## **Ambient Air Concentrations**

To estimate levels of malathion and malaoxon in outdoor air, five sites were selected within a 0.8- km diameter region near the center of the treatment zone for the second, third, and ninth applications. The sites were clustered near the center of the treatment area in order to increase the precision of estimates for ambient air concentrations. Air samplers, equipped with resin trapping media, were placed in sheltered areas such as carports, covered patios, and eaves to avoid being sprayed directly.

At each site, one Anderson model SE-144 sampling pump was mounted with 15-ml XAD resin as a trapping medium and set at a flow rate of 15 to 21 liters per minute (L/min). Air flow

through each sampling pump was measured with a rotometer before and after each sampling interval to verify that flow rate remained constant. For each monitored application, air samples were collected for approximately 76 consecutive hours: one 24-hr background sample, one spray interval (duration of the application: 4-5 hours), one 24-hr post-spray interval immediately after application, and another consecutive 24-hr sample.

After each sampling period, sample tubes were collected and sealed with Teflon®-lined rubber stoppers. Tubes were placed in plastic bags, stored on dry ice in the field, and remained frozen until extraction. Resin samples were extracted by CDFA using acetone, concentrated, and analyzed for malathion and malaoxon using a GC with a FPD. The reporting limit was 0.1 µg per sample.

## **SURFACE WATER SAMPLES**

### **During Application**

Surface water samples were collected to determine malathion and malaoxon concentrations in the Conejo Creek during the first, second, and third applications. The creek runs across the southeastern corner of the treatment area, and flow consists of agricultural drainage and discharge from a wastewater treatment plant. Background water samples were collected one to three hours before each monitored application at an inflow site upstream of the treatment area boundary and at an outflow site immediately below the application boundary (Fig.1).

Approximately 30 minutes after the helicopters completed application in the area of the creek, a single water sample was collected from the outflow site to measure malathion and malaoxon concentrations in surface water leaving the treatment area.

Samples were collected by submersing a clean stainless steel bucket into the center channel of the creek. Prior to collecting the sample, all equipment was pre-rinsed with water from the creek. After rinsing bottles, water was poured into four 1-liter amber bottles and capped with Teflon®-lined bottle caps. The pH of each sample was recorded and adjusted to approximately 3.0 using a

3N hydrochloric acid solution to reduce malathion hydrolysis. Water samples for toxicity testing were not acidified. One field blank, consisting of deionized water, was collected during each sampling period (i.e., aerial application or rain runoff event) to determine if sample contamination had occurred during field sampling. All samples were stored on ice in the field and remained refrigerated until extraction.

Water samples were extracted by CDFR Laboratory personnel using methylene chloride. The extract was filtered, the solvent exchanged to acetone, and then the extract was analyzed for malathion and malaoxon using GC with a FPD. Results are presented in parts per billion (ppb). The RL was 0.05 ppb for malathion and malaoxon residues.

### **Rain Runoff**

In addition to the surface water samples collected during the first three applications, rain runoff samples were collected during three storms to determine malathion and malaoxon concentrations in rain runoff exiting the treatment area. Rinse blanks were collected during each monitored rain event, and consisted of deionized water used to rinse all sampling equipment. Otherwise, sampling methods and equipment were the same as those used to collect surface water from the inflow and outflow sites during application.

Rain runoff water flows into Conejo Creek, Calleguas Creek, and the Lewis Drain from the streets and fields in the area surrounding the treatment zone. On each of these waterways, one sampling site was selected immediately downstream of the treatment boundary (Fig. 2). Runoff from the agricultural portions of the treatment area drains into the Calleguas and Conejo Creeks, while the Lewis Drain contains mostly urban runoff. Sampling on the Conejo Creek began when runoff was first observed in the streets of the treatment area. Sampling at Lewis Drain and Calleguas Creek began when water flow was first observed at the sampling site.

Rain runoff samples were collected after heavy rains occurred on November 7 (12 days after the second spray), January 20 (3 days after the seventh spray), and March 21 (6 days after the tenth

spray). Sampling during the rain events on November 7 and January 20 consisted of one sample each from the three outflow sites every hour for the duration of the rain event. During the January 20 runoff sampling, a final sample was collected from Conejo Creek seven hours after flow had stopped in the Lewis Drain and Calleguas Creek to determine if malathion and malaoxon levels were similar to original levels present in the background sample. During this monitoring period no samples were collected from the Calleguas Creek for two hours because flow had stopped. Once flow was resumed, samples were collected until the rain ended, and rain runoff flow had stopped in either the Lewis Drain or Calleguas Creek.

Due to higher than expected malathion levels present in the January 20 rain runoff samples, the sampling plan was expanded to include three additional sites located downstream of the treatment area. These sites drain into the Mugu Lagoon, approximately 13-km downstream of the application boundary. To estimate malathion and malaoxon concentrations entering Mugu Lagoon, water was collected from the following sites: the Revlon Slough at the Las Posas Bridge, the Calleguas Creek prior to its convergence with the Revlon Slough Drainage, and the mouth of the Calleguas Creek in the Mugu Lagoon (Fig. 2).

Runoff water was collected during the next storm, which occurred six days after the March 14th application. Sampling on the Conejo Creek began when runoff was first observed in the streets of the application area. Sampling continued at the three sites immediately outside the spray boundary for a total of five hourly-sampling periods. Approximately one hour following the start of sampling at the upstream sites, sampling began at the lower three sites and continued for ten consecutive hours: once per hour for six hours, and at two-hour intervals for two more periods. A final sample was collected at the downstream sites 16 hours after sampling began, in order to determine if malathion and malaoxon concentrations had returned to background levels.

### **Toxicity Tests**

Additional samples were collected in 2.5-L glass jars and submitted to the California Department of Fish and Game (CDFG) for aquatic toxicity testing and water quality analysis. Four samples

were collected during the January 20 storm and six samples were collected during the March 21 storm. Cladocerans were used to test toxicity in water collected from the three upstream sites (Figure 2, sites 1-3), and from the lower Calleguas Creek near Camarillo State Hospital (site 4). Mysids were used to test toxicity at the sites nearest Mugu Lagoon (sites 5 and 6) because of the higher saltwater content. Acute (96-h) toxicity tests using undiluted samples from the March 21 storm were performed on the upstream drainage samples using *Ceriodaphnia dubia*. *Neomysis mercedis* was used to test toxicity on samples collected nearest to the Mugu Lagoon estuary. Acute toxicity tests on serial dilutions of the samples from January 20-21 were performed using cladocerans. Water quality parameters that were measured include alkalinity, hardness, electrical conductance (EC), and total ammonia. CDFG methods are described in Appendix A.

The same chemical analytical methods were used for samples collected during application and during rain events. In addition, split samples were analyzed by Agriculture Priority and Pollutants Laboratories (APPL) of Fresno, California. These samples were extracted using ethyl acetate exchanged with acetone. The extract was analyzed using a GC equipped with a nitrogen-phosphorous detector. The APPL RL for malathion and malaoxon was 0.1 ppb in most instances. A statistical comparison between the two laboratories is presented in Appendix B.

## RESULTS AND DISCUSSION

The data presented and discussed in this section, unless otherwise mentioned, refer only to those results obtained from CDFA Laboratory. When malathion or malaoxon residues were below the reporting limits, one-half the value of the reporting limit was used to calculate residue concentrations for summary statistics in all media excluding surface water. Deposition data are presented in  $\text{mg}/\text{m}^2$  units and may be converted to  $\mu\text{g}/\text{ft}^2$  by dividing the  $\text{mg}/\text{m}^2$  units by 0.01076. Field results (raw data) are shown in Appendix C.

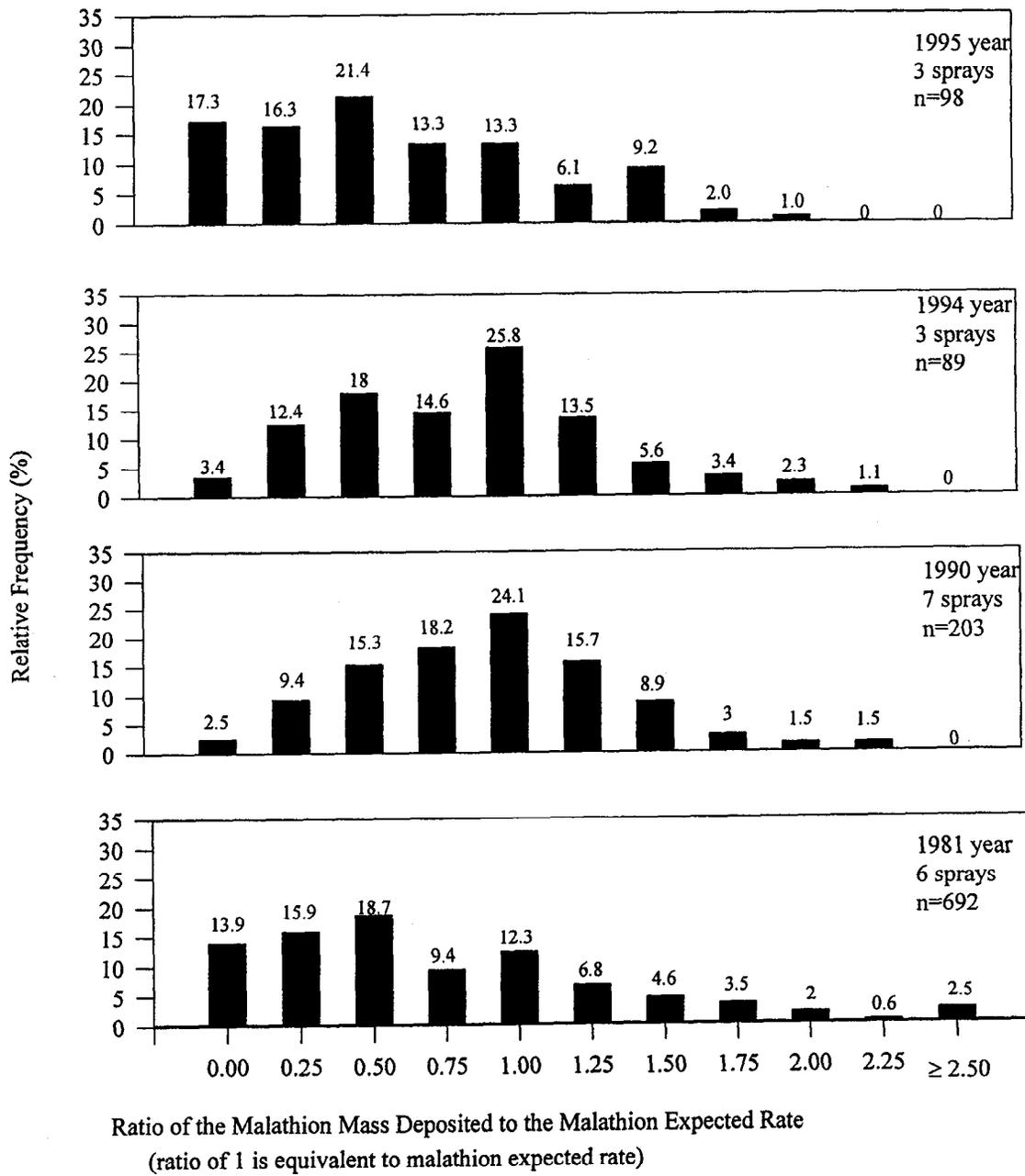


Figure 3. Distribution of the malathion mass deposition rates in the 1995, 1994, 1990, and 1981 Medfly eradication programs

Table 2. Mean, standard deviation, and 95% confidence interval for mass deposition of malathion on mass deposition sheets.<sup>a</sup>

Application Date	<u>Malathion (mg/m<sup>2</sup>)</u>		<u>95% Confidence Interval</u>	
	Mean	Standard Deviation	Lower	Upper
Spray 1 (32 samples)	6.76	4.70	5.06	8.45
Spray 2 (34 samples)	9.59	5.06	7.83	11.4
Spray 3 (32 samples)	3.23	2.85	2.20	4.26

<sup>a</sup> Malaoxon was not detected. RL= 0.011 mg/m<sup>2</sup>

Malathion deposition for the first two sprays averaged 8.21 mg/m<sup>2</sup>, which is 80% of the theoretical deposition rate of 10.19 mg/m<sup>2</sup>. Similar differences in deposition efficiency (87% of application rate in 1994, 92% in 1990, 75% in 1981) and deposition distribution (ratio of expected vs. observed deposition, see Figure 3) were found in the 1981, 1990, and 1994 eradication programs (Oshima et al., 1982, Segawa et al., 1991, and Ando et al., 1995). These lower deposition values are most likely related to normal differences in deposition efficiency and distribution associated with aerial applications (Giles, 1970), as well as to weather conditions during the treatment program.

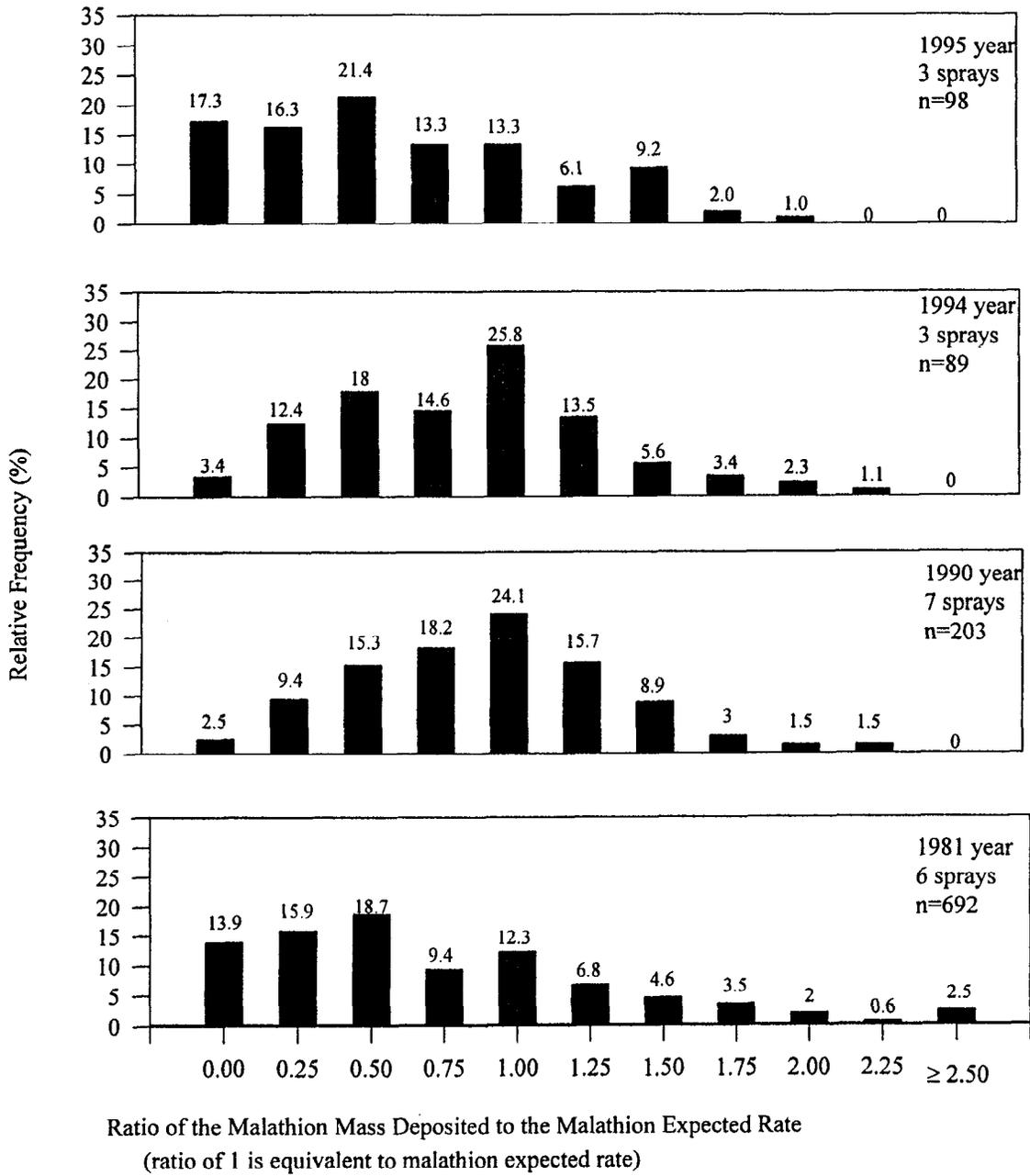


Figure 3. Distribution of the malathion mass deposition rates in the 1995, 1994, 1990, and 1981 Medfly eradication programs

The observed frequency distributions of malathion concentrations were more evenly distributed on the ground in the 1994 and 1990 study years than in the 1995 and 1981 study years. As previously reported (Ando et al. 1995), the 1994 and 1990 observed frequency distributions of malathion concentrations appeared similar. The highest observed proportion of samples were in the targeted rate. Approximately 50% of the samples were below the target rate for both years. In contrast, the 1995 distribution of malathion on the ground was similar to the 1981 distribution pattern. Nearly 68% of the 1995 samples fell below the target rate interval in comparison to 60% for 1981. As previously reported, 1981 data had some samples with unusually high deposition rates (more than two and one-half times greater than the expected deposition rate). In comparison, equivalent deposition values exceeding the ratio of 2.50 were not seen in the 1995, 1994, or 1990 study years.

Malaoxon was not detected in the majority (75%) of the deposition samples. When it was found, the amount of malaoxon deposited on the ground ranged from non-detected (ND) to 0.07 mg/m<sup>2</sup>. The small number of samples with detectable amounts of malaoxon may be partly due to the low expected deposition rate of 0.011 mg/m<sup>2</sup>, which is near the laboratory's quantification limit. In addition, tank mix samples (diluted concentrate) collected by DPR's Pesticide Enforcement staff prior to the first three sprays showed trace amounts of malaoxon before the first spray only. Of the three samples collected prior to the first spray, average malaoxon concentration was 0.10%; the minimum detection limit was 0.02%.

In the 1994 study in Corona, malaoxon was not detected in any of the deposition samples, or in the tank mix samples collected prior to sprays one and three (Ando et al. 1995). In 1990, the average mass deposition of malaoxon was 0.13 mg/m<sup>2</sup>, which was five times greater than the expected deposition rate. The malathion-bait application rate in that year was approximately two times more than the current rate. Analysis of the malathion concentrate and malathion/bait mixture showed about four times more malaoxon in the mixture than in the concentrate. Segawa et al. (1991) attributed this increase to possible oxidation of malathion to malaoxon during

storage, transport, or mixing of the malathion product. No comparisons were made for malaoxon between study years because of the lack of detections in 1994 and 1981.

### **Ambient Air Concentrations**

Malathion and malaoxon concentrations in air were measured during the second, third, and ninth sprays at five sites within a 0.8-km diameter circular area near the center of the spray area. Air samples were collected at each site for four consecutive periods: 24-hr immediately before the spray, during the spray period plus one-half hour, and for two consecutive 24-hr periods after the spray.

The highest malathion concentration measured was 13.13 ppt, and occurred during the second application. Malathion concentrations averaged 0.27 parts per trillion (ppt) during the pre-spray interval, 5.0 ppt during application, 3.7 ppt during the 24 hours immediately following application, and 3.2 ppt for the 24-48 hours after application (Table 3).

The maximum malaoxon concentration measured was 1.77 ppt and occurred during the first post spray interval. No malaoxon was detected during the pre-spray or application intervals, but concentrations averaged 0.80 ppt and 0.74 ppt during the first post-spray and second post-spray intervals, respectively.

Malathion results are different from previous aerial malathion studies, in that peak concentrations were measured during application rather than in the first 24 hours following treatment. Figure 4 shows average total malathion concentrations in air during the 1995, 1994, 1990, and 1981 eradication programs. The results are presented as average total malathion levels, which are the mean values from the sum of malathion and malaoxon. Total malathion levels are considered to be more reliable than the unsummed values (Segawa *et al.* 1991). In the 1981, 1990 and

1994 Medfly programs, results showed similar trends in air concentrations: malathion concentrations steadily decreasing during the 48 hours after spraying, and malaoxon levels reaching a peak during the 24-48 hour period after application (Brown et al. 1993; Ando et al. 1995).

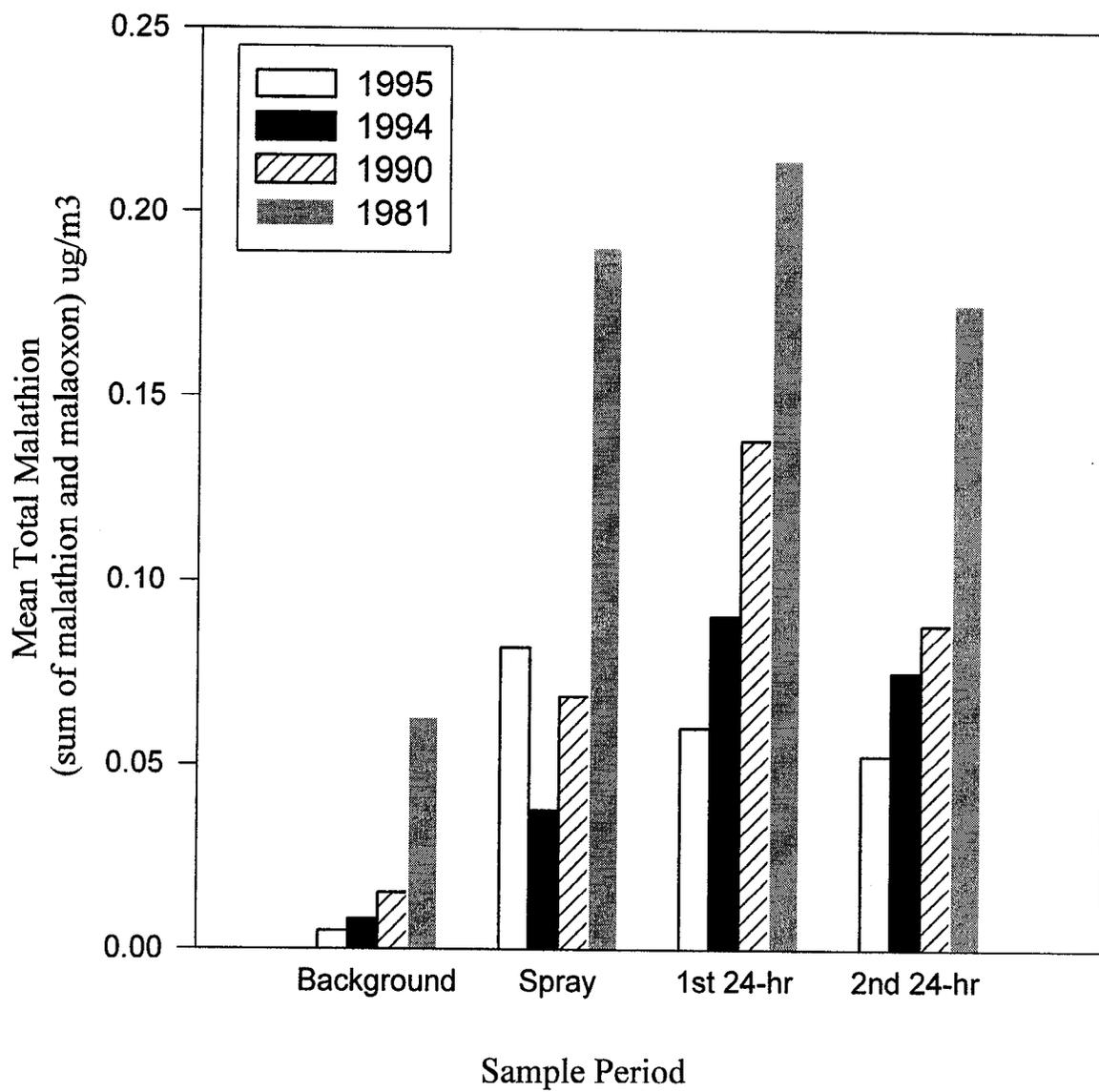
Table 3. Summary of air concentrations of malathion and malaoxon during and after the Medfly aerial applications of October 26, November 14, 1994, and March 14, 1995, in Ventura County.

		Malathion		Malaoxon	
		( $\mu\text{g}/\text{m}^3$ )	(ppt)	( $\mu\text{g}/\text{m}^3$ )	(ppt)
Pre-Spray	Average <sup>a</sup>	0.004	0.27	ND	ND
	Std. Deviation	0.003	0.24	---	---
	Minimum	ND <sup>b</sup>	ND	ND	ND
	Maximum	0.011	0.80	ND	ND
Spray	Average <sup>a</sup>	0.067	4.99	ND	ND
	Std. Deviation	0.040	2.95	---	---
	Minimum	ND	ND	ND	ND
	Maximum	0.176	13.13	ND	ND
1 <sup>st</sup> Post-Spray	Average <sup>a</sup>	0.049	3.67	0.010	0.80
	Std. Deviation	0.033	2.44	0.007	0.58
	Minimum	0.006	0.43	ND	ND
	Maximum	0.106	7.86	0.023	1.77
2 <sup>nd</sup> Post-Spray	Average <sup>a</sup>	0.042	3.16	0.010	0.74
	Std. Deviation	0.016	1.17	0.004	0.35
	Minimum	0.024	1.79	0.005	0.42
	Maximum	0.074	5.49	0.018	1.39

<sup>a</sup> Total number of samples = 15

<sup>b</sup> ND = No detectable amount, assumed to be one-half the detection limit of 0.1  $\mu\text{g}/\text{sample}$  in statistical calculations

Figure 4. Ambient air concentration results for the 1995, 1994, 1990, and 1981 Medfly eradication programs during each sampled period



In previous reports, malathion and malaoxon outdoor air concentrations between study years were not statistically compared due to differences in application rates, the number of applications made, the number of study locations monitored, and the number of samples collected. The current study had the same application rate as the 1994 study, as well as a similar sequence of three monitored sprays. In addition, the same method of sample selection and number of samples collected allowed a statistical comparison of results.

The average total malathion concentration found in 1995 and 1994 samples was compared within each sampling period. The only significant difference ( $p < 0.001$ ) was found in samples collected during the spray. The differences in average total malathion concentrations during the other sampling intervals were not significant. The atypical weather conditions during the third spray in 1995 may have contributed to this difference. A description of the statistical methods used to make these comparisons is given in Appendix C.

In the 1990 program, oxidation of malathion to malaoxon in air was rapid. At one site, malaoxon concentration in outdoor air was greater than that of malathion two days after application. Environmental factors such as ozone levels apparently influence oxidation of malathion to malaoxon (Segawa et al. 1991). Brown et al. (1993) suggest that malathion may be oxidized to malaoxon in the atmosphere via ozone or other possible oxidants such as oxides of nitrogen.

## **SURFACE WATER SAMPLES**

### **During Application**

Samples collected before the first and third sprays did not contain detectable levels of malathion or malaoxon. Prior to the second spray, water collected from the inflow site contained 0.21 ppb malathion and 0.06 ppb malaoxon. Neither chemical was detected in the background water collected from the outflow site. After application, water collected at the outflow site contained 39 ppb malathion and 0.05 ppb malaoxon. The average malathion concentration in the outflow

water after the three monitored applications was 44 ppb and ranged from 39.1 to 50.3 ppb. Malaoxon concentration averaged 0.05 ppb and ranged from none detected to 0.08 ppb (Table 4).

In general, malathion concentrations in water exiting the treatment area after application were higher than in the 1994 program, which used the same application rate. During the 1994 program, malathion concentrations from water exiting the treatment area averaged 9.15 ppb and ranged from 1.04 to 24.4 ppb (Ando et al. 1995). One reason for the lower concentrations might be that the pilots tried to avoid directly spraying Temescal Creek, the major waterway running through the Corona treatment area. In both the 1994 and 1995 programs, background water samples collected at the outflow sites before application contained no detectable residues of malathion or malaoxon.

Table 4. Summary of malathion and malaoxon concentrations in surface water during Medfly aerial applications on October 12, October 26, and November 14 in Ventura County.

		Outflow		Inflow	
		Malathion (ppb)	Malaoxon (ppb)	Malathion (ppb)	Malaoxon (ppb)
Pre-spray	Average <sup>a</sup>	ND	ND	0.09	0.04
	Std. Deviation	--	--	0.11	0.02
	Minimum	ND	ND	ND <sup>b</sup>	ND
	Maximum	ND	ND	0.21	0.06
Spray	Average <sup>a</sup>	44.2	0.05	--	--
	Std. Deviation	5.7	0.03	--	--
	Minimum	39.1	ND	--	--
	Maximum	50.3	0.08	--	--

<sup>a</sup> Total samples = 3

<sup>b</sup> ND = No detectable amount, assumed to be one-half the detection limit of 0.05 ppb in statistical calculations.

## **Rain Runoff**

Surface water was collected from Conejo Creek, Lewis Drain, and Calleguas Creek during three rain events to measure the level of malathion and malaoxon exiting the treatment area. Prior to the third event monitored, three sampling sites were added further downstream of the treatment boundary to determine malathion and malaoxon levels entering Mugu Lagoon (Fig. 2).

The maximum malathion concentration, 787.1 ppb, was found in runoff water immediately exiting the treatment area at Calleguas Creek, three days after the seventh spray (Table 5). The highest malaoxon concentration was 160.2 ppb and occurred at the same site, 12 days after the second spray.

Malathion and malaoxon concentrations in rain runoff during each monitoring period appeared to decline steadily over time (Figure 5 and 6). For the three waterways, malathion levels peaked within 1 hour after rain began, and decreased steadily for the duration of the storm.

The proportion of malaoxon to malathion increased as the number of days between application and onset of rain increased. A similar trend was seen during the 1994 program in Corona, and was attributed to the oxidation of malathion to malaoxon that may have occurred on treated surfaces (Ando et al. 1995).

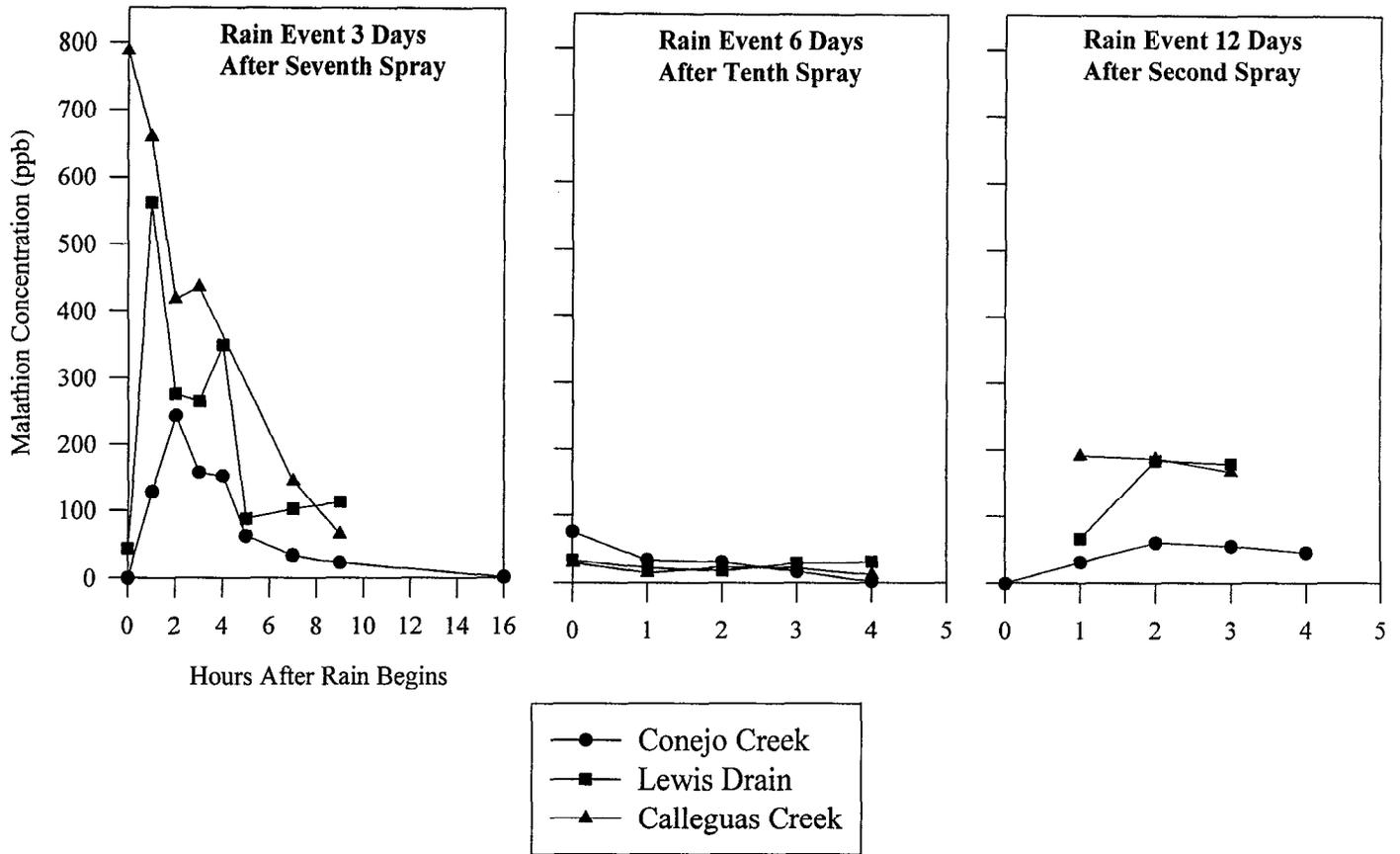
In the 1994 treatment program, results indicated that malathion became less persistent with each subsequent rain period following application (Ando et al. 1995). In that study, rain runoff samples collected 4 and 10 days following a single application showed decreased concentrations, likely due to dissipation on treated surfaces and/or increased wash-off from cumulative rainfall. Giles (1970) reported that high rainfall can result in high pesticide concentrations in surface water, although the concentration may be decreased by dilution from increased stream volume and discharge.

Table 5. Malathion and malaoxon concentrations in rain runoff samples from creeks and drains at sites outside of the application boundary.

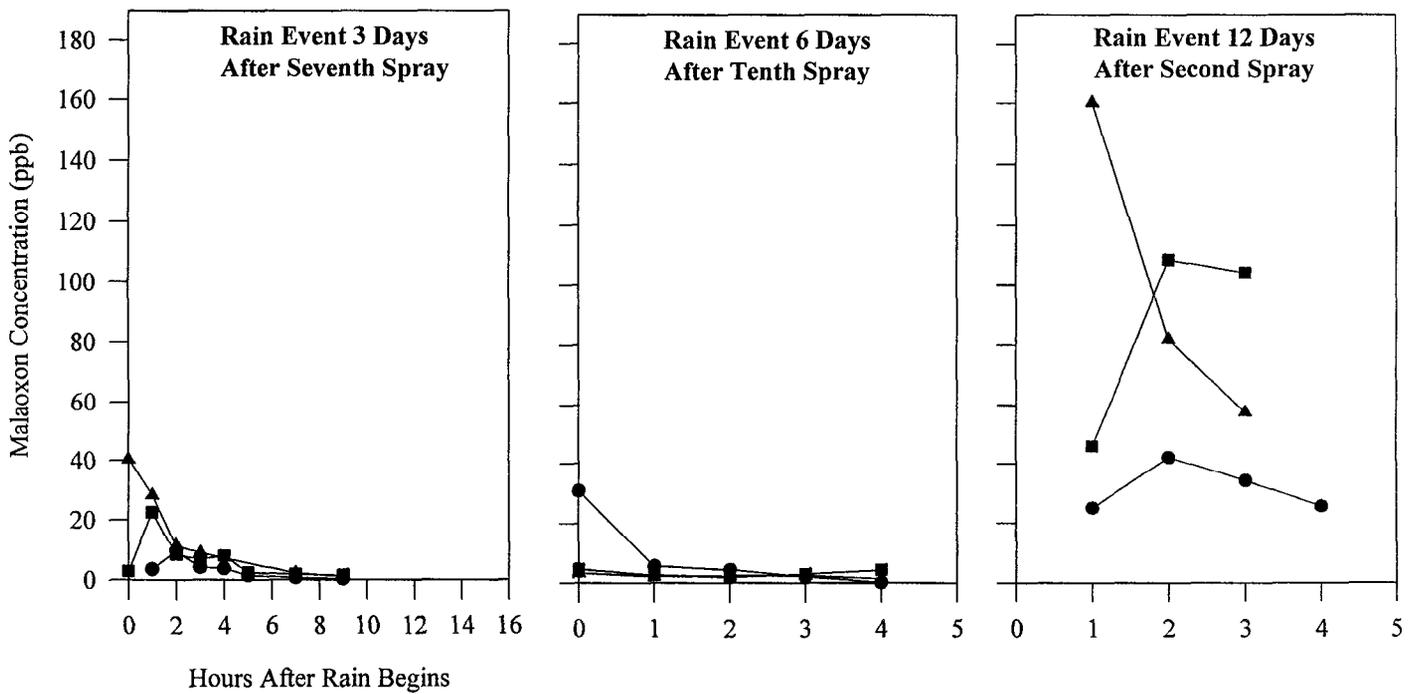
		3 days after spray 7	6 days after spray 10	12 days after spray 2	3 days after spray 7	6 days after spray 10	12 days after spray 2
	Sampling Times	Malathion (ppb)	Malathion (ppb)	Malathion (ppb)	Malaoxon (ppb)	Malaoxon (ppb)	Malaoxon (ppb)
Conejos Crk.	background			0.06			ND <sup>a</sup>
	1-hour	0.19	76.2	0.14	ND	30.8	ND
	2-hour	128.30	34.10	31.6	3.53	5.67	25.1
	3-hour	243.60	31.40	60.6	9.57	4.42	42
	4-hour	157.70	17.10	55.2	4.16	2.05	34.2
	5-hour	152.00	2.26	45.8	3.75	0.24	25.6
	6-hour	62.90			1.49		
	8-hour	34.10			0.74		
	10-hour	23.10			0.34		
	17-hour	2.07			ND		
Lewis Drain	1-hour	44.10	33.40	66.4	2.80	4.61	45.9
	2-hour	562.00	21.90	182.9	22.50	2.68	108.5
	3-hour	275.90	18.10	178.7	8.48	2.01	104.1
	4-hour	264.80	29.80		6.94	2.93	
	5-hour	349.80	31.40		8.04	4.41	
	6-hour	88.30			2.45		
	8-hour	102.80			1.84		
	10-hour	112.90			1.55		
Calleguas	1-hour	787.10	29.60	190.6	40.30	3.36	160.2
	2-hour	659.00	14.60	186.2	28.20	2.17	82
	3-hour	418.20	23.70	166.1	11.50	2.46	57.6
	4-hour	436.20	22.20		8.90	2.38	
	8-hour	144.30	12.00		2.20	1.58	
	10-hour	65.60			1.08		

<sup>a</sup>None Detected - reporting limit is 0.10 ppb

**Fig. 5. Malathion Concentration in rain runoff outside of the treatment area**



**Figure 6. Malaoxon concentration in rain runoff outside of the treatment area**



## Toxicity Tests

Cladocerans were used to test toxicity in water collected from the three upstream sites (Figure 2, sites 1-3), and from the lower Calleguas Creek near Camarillo State Hospital (site 4). Mysids were used to test toxicity at the sites nearest Mugu Lagoon (sites 5 and 6) because of the higher saltwater content. The relative sensitivity for both species is similar. The 48-h LC<sub>50</sub> value for *C. dubia* is 2.1 µg/L (Ankley et al. 1991), and for *Neomysis mercedis* the 96-h LC<sub>50</sub> value is 2.2 µg/L (Brandt et al. 1993). Additional water quality parameters measured by CDFG include alkalinity, hardness, electrical conductance (EC), and total ammonia (Fujimura, 1995) (Table 6). CDFG methods are described in Appendix A.

In general, water quality in the study area met the U.S. Environmental Protection Agency recommended quality criteria for water (US EPA, 1986). These recommendations represent the lowest observed effect level for the protection of freshwater aquatic organisms.

The results of the bioassay portion of the runoff analysis indicate that all samples were toxic to the two test organisms. Malathion concentrations found in the three samples collected January 20 (three days after the seventh spray) exceeded the 48-h LC<sub>50</sub> value for cladocerans by 100 to 200 times (Table 6). Water collected from the six sites during the March 20 storm (six days after the tenth spray) were toxic to both cladocerans and mysids. The four upstream samples killed all cladocerans within two hours of exposure, and the two estuary samples killed all mysids within 24 hours of exposure (Fujimura, 1995).

Revlon Slough (site 5) was the only site where malathion concentrations did not reach or exceed the LC<sub>50</sub> values for both species. At the other five sites, malathion concentrations were up to 16 times higher than the LC<sub>50</sub> value.

## Inter-laboratory Comparison

A comparison of the split samples analyzed by CDFA Laboratory and APPL Laboratory showed good agreement (Table B-1, Appendix B-II). Malathion was detected in eleven water samples

analyzed by CDFA and APPL Laboratories, and concentrations ranged from 0.21 ppb to 210 ppb. Regression analysis was used to investigate differences between the two sets of results. A regression of APPL concentrations on CDFA concentrations indicated that there was no evidence of systematic differences between the two sets of results. The correlation coefficient was 0.99.

Malaoxon was detected in six rain runoff samples analyzed by CDFA and APPL Laboratories (Table B-2, Appendix B-II). Malaoxon concentrations ranged from 2.27 ppb to 130 ppb. A regression of CDFA concentrations on APPL concentrations showed some evidence of systematic differences between the two sets of results. This may be indicative of a systematic error but is most likely due to the limited number of samples available for comparison. The correlation coefficient was 0.99. Details of the statistical methods used are in Appendix C.

Table 6. Toxicity test results, pesticide residues, and water quality of rain runoff samples from creeks and drains outside of the application boundary.

Site	Collection Date	Toxicity Control (% Survival)	Toxicity Sample (% Survival)	Malathion (ppb)	Malaoxon (ppb)	Alkalinity (mg/L CaCO <sub>3</sub> )	Hardness (mg/L CaCO <sub>3</sub> )	Conductivity (μS/cm)	Ammonia (mg/L N)
Lewis Drain <sup>a</sup>	1/20/95	95	< 6.2	275.9	8.5	25	35	101	0.43
	3/21/95	100	0	21.9	2.68	13	18	48	0.16
Calleguas Creek <sup>a</sup>	1/20/95	100	< 6.2	418.2	11.5	29	40	113	0.38
	3/21/95	100	0	14.6	2.17	13	16	45	0.12
Conejos Creek <sup>a</sup>	1/20/95	95	< 1.0	243.6	9.6	218	396	1146	0.24
	1/21/95	100	0	2.1	< 1.0	192	364	1020	4.5
	3/21/95	100	0	34.1	5.67	173	290	844	2.59
Lower Calleguas Creek. <sup>a</sup>	3/21/95	100	0	5.46	0.82	201	1304	985	1.93
Revlon Slough <sup>b</sup>	3/21/95	95	0	0.06	<0.10	113	554	1567	0.15
Mugu Lagoon <sup>b</sup>	3/21/95	95	0	2.25	0.98	157	1318	8790	0.34

<sup>a</sup> *Ceriodaphnia dubia* used for acute toxicity tests, malathion LC<sub>50</sub> = 2.1 ppb

<sup>b</sup> *Neomysis mercedis* used for toxicity testing on estuary samples, malathion LC<sub>50</sub> = 2.2 ppb

## CONCLUSIONS

Conclusion 1: The amount of malathion deposited on the ground during the first two sprays was 20 percent lower than the theoretical target application: 8.21 mg/m<sup>2</sup> observed versus 10.19 mg/m<sup>2</sup> expected. Values for the three monitored applications were not combined in a single average because of unusually low deposition during the third spray: 3.23 mg/m<sup>2</sup> (30% of the application rate). The cause for lower deposition values is related to variable weather conditions, and normal variability associated with collecting and analyzing environmental samples. Malaoxon levels ranged from none detected to 0.7 mg/m<sup>2</sup>. The small amount of malaoxon detected is likely due to the low expected deposition rate, which is near the laboratory's reporting limit.

Conclusion 2: The total malathion level measured in air was highest during the application period. These results differ from three previous studies that were done during an urban application of aerially applied malathion bait. In these studies, malathion concentrations were highest in the 24-48 hr. period following application.

Conclusion 3: After application of malathion bait, levels of malathion that were potentially toxic to aquatic life were measured in surface and rain runoff water samples collected in and downstream of the spray area from tributaries to Mugu Lagoon, and from Mugu Lagoon. These were the highest levels of malathion and malaoxon detected in water in any of the four study years.

Conclusion 4: Rain runoff water collected downstream of the treatment area was acutely toxic to test organisms. Malathion concentrations found in samples collected three days after treatment were 100 to 200 times the 48-hr LC<sub>50</sub> value for cladocerans. These concentrations may pose a significant hazard to aquatic biota both within and downstream of the treatment area.

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**APPENDIX A - California Department of Fish and Game Results**



Table. Acute toxicity (96-h LC<sub>50</sub> in v/v) values, pesticide residues, and water quality of rain runoff samples from Camarillo, Ventura County to cladocerans *Ceriodaphnia dubia*. Pesticide residue data (in µg/L) provided by Department of Pesticide Regulation (Sanders 1995).

Collection Date	Site	Toxicity Results		Pesticide Residues		Water Quality <sup>a</sup>			
		Control Survival	Acute Value	Malathion	Malaoxon	Alkalinity	Hardness	Cond	NH4
1/20/95	Lewis Drain (DPR # 4001)	95 %	< 6.2 %	275.9	8.5	25	35	101	0.43
1/20/95	Calleguas Creek (DPR # 4002)	100 %	< 6.2 %	418.2	11.5	29	40	113	0.38
1/20/95	Conejos Creek (DPR # 4004)	95 %	< 1.0 %	243.6	9.6	218	396	1146	0.24
1/21/95	Conejos Creek (DPR # 4003)	100 %	10.0 %	2.1 <sup>b</sup>	< 0.1	192	364	1020	4.50

<sup>a</sup> Total alkalinity and total hardness reported in mg/L CaCO<sub>3</sub>; specific conductivity reported in µS/cm; and total ammonia reported in mg/L N.

<sup>b</sup> About 0.68 µg/L of diazinon was also found in this sample (Pam Waldford, DPR, personal communication); the 96-h LC<sub>50</sub> value is 0.5 µg/L diazinon (unpublished data).

\* also a test. dilute down to 1%.

STATE OF CALIFORNIA  
DEPARTMENT OF FISH AND GAME

AQUATIC TOXICOLOGY LABORATORY REPORT

9300 Elk Grove-Florin Road  
Elk Grove, California 95624

Lab No. P-1725

Date Received March 23, 1995  
Sample Rain runoff

E.P. No. \_\_\_\_\_

To : Mr. Brian Finlayson, Chief

Report Date April 24, 1995

ADDRESS: Pesticide Investigations Unit  
1701 Nimbus Road, Suite F  
Rancho Cordova, CA 95624

Remarks

Rain runoff samples were collected after a rainfall event from an area treated with malathion for the eradication of Mediterranean fruit flies. Total of six sites were sampled from Camarillo, California on March 21, 1995 within the drainage area including Mugu Lagoon. Acute (96-h) toxicity tests using undiluted samples were performed using the cladoceran *Ceriodaphnia dubia* and the mysid *Neomysis mercedis*. Cladocerans were used to test the upstream drainage samples and mysids were used to test samples nearest the estuary. The samples were analyzed for residues of malathion by DPR. The samples were analyzed by ATL staff for total alkalinity, total hardness, total ammonia, and specific conductivity.

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RESULTS OF EXAMINATION

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All six samples were found to be toxic to either cladocerans or mysids (Table 1). The four upstream runoff samples killed all cladocerans within 2 hours of exposure. The two estuary samples killed all mysids within 24 hours of exposure. The malathion concentrations found at five locations met or exceeded the LC<sub>50</sub> values for both species by up to 16 times (Table 2, Sanders 1995). An exception was the sample from Revlon Slough which contained a trace concentration of malathion. The relative sensitivity of mysids and cladocerans to malathion are similar. The 48-h LC<sub>50</sub> value is 2.1 µg/L for *C. dubia* (Ankley et al. 1991), and the 96-h LC<sub>50</sub> is 2.2 µg/L for *Neomysis mercedis* (Brandt et al. 1993). Therefore, we conclude the malathion concentrations could explain the acute toxicity found with five of the six rain runoff samples.

\_\_\_\_\_

PESTICIDE INVESTIGATIONS UNIT  
ENVIRONMENTAL SERVICES DIVISION

Original signed by  
B. Fujimura

By \_\_\_\_\_

Robert Fujimura  
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P-1725  
April 24, 1995  
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Sacramento, California

Table 1. Acute toxicity of undiluted sample and water quality of rain runoff from Camarillo, Ventura County to cladocerans *Ceriodaphnia dubia* (C) and mysids *Neomysis mercedis* (N) after a malathion application.

Sample Number	Collection Site	Test Organism	Percent Survival		Water Quality <sup>a</sup>			
			Control <sup>b</sup> Water	Undiluted Sample	Alkalinity	Hardness	Conductivity	Ammonia
S032195-1	Conejos Creek (P-1725)	C	100	0 <sup>c</sup>	173	290	844	2.59
S032195-2	Lewis Creek	C	100	0 <sup>c</sup>	13	18	48	0.16
S032195-3	Calleguas Creek	C	100	0 <sup>c</sup>	13	16	45	0.12
S032195-4	Lower Calleguas Creek	C	100	0 <sup>c</sup>	201	1304	985	1.93
S032195-5	Revlon Slough	N	95	0 <sup>d</sup>	113	554	1567	0.15
S032195-6	Mugu Lagoon	N	95 (100)	0 <sup>d</sup>	157	1318	8790	0.34

<sup>a</sup> Total alkalinity and total hardness reported in mg/L CaCO<sub>3</sub>; specific conductivity reported in  $\mu$ S/cm; and total ammonia reported in mg/L N.

<sup>b</sup> High salinity control water group survival reported in parentheses.

<sup>c</sup> All neonates dead within first 2 hours.

<sup>d</sup> All neonates dead within first 24 hours.

Table 2. Malathion and malaoxon concentration in rain runoff from Camarillo, Ventura County after a malathion application. Data from Department of Pesticide Regulation (Sanders 1995).

<u>Collection Site</u>	<u>Collection Date</u>	<u>Collection Time</u>	<u>Malathion (ug/L)</u>	<u>Malaoxon (ug/L)</u>
1 Conejos Creek	3/21/95	4:40	34.1	5.67
3 Lewis Drain	3/21/95	5:00	21.9	2.68
2 Calleguas Creek	3/21/95	5:15	14.6	2.17
4 Lower Calleguas Creek	3/21/95	6:00	5.46	0.82
5 Revlon Slough	3/21/95	6:40	0.06 <sup>a</sup>	<0.10 <sup>a</sup>
6 Mugu Lagoon	3/21/95	10:10 <sup>c</sup>	2.25 <sup>b</sup>	0.98 <sup>b</sup>

<sup>a</sup> Concentration of a water sample collected at 6:30.  
<sup>b</sup> Concentration of a water sample collected at 10:00.  
<sup>c</sup> Pam Walford, DPR, personal communication.

**APPENDIX B- Laboratory Quality Control Data**

**I. Continuing Quality Control Data**

Table 1. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.

Study No.: 132  
 MDL: 1.0 ug/sample  
 Date of Report: 7/11/95

Matrix: Kimbie  
 Chemical: Malathion  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ug/sample)	Amount Recovered (ug/sample)	Recovery (%)	$\bar{X}$	SD	CV (%)
1003, 1066, 1106, 1109, 1110, 1201, 1202, 1203, 1205, 1209, 1217, 1218	1000	948.5	95			
1106, 1107, 1108, 1212, 1213, 1214, 1215, 1216, 1217, 1218, 1219, 1220	1000	1007	101			
1211-1216	1000	1005	100			
1220, 1221, 1222, 1223, 1257, 1258, 1259, 1261, 1269, 1270, 1271, 1272	1000	992.3	99			
1221, 1222, 1223, 1224, 1226, 1227, 1228, 1229, 1230, 1231, 1262, 1263	1000	1060	106			
1273, 1274, 1275, 1286, 1287, 1288, 1289, 1300, 3178, 3281, 8693, 8694	1000	1034.5	103			
1290-1299, 1209B, 1210	1000	1001	100			
3009, 3021, 3031, 3000-3011	1000	970.2	97			
3012-3024	1000	967	97			
3025-3037	1000	957.2	96			
3038-3049	1000	964.6	96			
3050-3065	1000	973.6	97			
3007, 3008, 3020, 3022, 3030	1000	1002.7	100			
9001-9005	1000	1017	102			
3074-3078	1000	1033	103			

Overall: 99 3.2 3.2

Table 2. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.

Study No.: 132  
 MDL: 1.0 ug/sample  
 Date of Report: 7/11/95

Matrix: Kimbie  
 Chemical: Malaoxon  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ug/sample)	Amount Recovered (ug/sample)	Recovery (%)	$\bar{X}$	SD	CV (%)
1003, 1066, 1106, 1109, 1110, 1201, 1202, 1203, 1205, 1209, 1217, 1218	1000	1038	104			
1106, 1107, 1108, 1212, 1213, 1214, 1215, 1216, 1217, 1218, 1219, 1220	1.0	0.92	92			
1211-1216	1.0	1.20	120			
1220, 1221, 1222, 1223, 1257, 1258, 1259, 1261, 1269, 1270, 1271, 1272	1000	1064	106			
1221, 1222, 1223, 1224, 1226, 1227, 1228, 1229, 1230, 1231, 1262, 1263	1.0	1.25	125			
1273, 1274, 1275, 1286, 1287, 1288, 1289, 1300, 3178, 3281, 8693, 8694	1000	1054	105			
1290-1299, 1209B, 1210B	1.0	0.78	78			
3009, 3021, 3031, 3000-3011	1.0	1.01	101			
3012-3024	1.0	0.99	99			
3025-3037	1.0	1.17	117			
3038-3049	1.0	0.93	93			
3050-3065	1.0	0.89	89			
3007, 1008, 3020, 3022, 3030	1.0	1.09	109			
9001-9005	1.0	1.01	101			
3074-3078	1.0	1.19	119			
			Overall:	104	12.9	12.4

Table 3. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.

Study No.: 132  
 MDL: 0.1 ug/sample  
 Date of Report: 7/11/95

Matrix: XAD-2 Resin  
 Chemical: Malathion  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ug/sample)	Amount Recovered (ug/sample)	Recovery (%)	$\bar{X}$	SD	CV (%)
56, 58, 59, 60, 62, 63, 66, 67, 73, 78	1.0	0.97	97			
64, 65, 68, 69, 70, 71, 72, 74, 75, 77	1.0	0.90	90			
76, 80, 271, 277, 278, 279, 280, 281, 283, 294	1.0	0.87	87			
268, 282, 284, 285, 286, 288, 289, 290, 291, 293	1.0	1.00	100			
265-267, 269, 270, 272-276	1.0	1.06	106			
320-324, 329-333	1.0	1.05	105			
			Overall:	98	7.8	8.0

**Table 4. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.**

Study No.: 132  
 MDL: 0.1 ug/sample  
 Date of Report: 7/11/95

Matrix: XAD-2 Resin  
 Chemical: Malaoxon  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ug/sample)	Amount Recovered (ug/sample)	Recovery (%)	$\bar{X}$	SD	CV (%)
56, 58, 59, 60, 62, 63, 66, 67, 73, 78	1.0	0.85	85			
64, 65, 68, 69, 70, 71, 72, 74, 75, 77	1.0	0.93	93			
76, 80, 271, 277, 278, 279, 280, 281, 283, 294	1.0	1.10	110			
268, 282, 284, 285, 286, 288, 289, 290, 291, 293	1.0	1.15	115			
265-267,269,270,272-276	1.0	1.14	114			
320-324,329-333	1.0	1.01	101			
			Overall:	103	12.2	11.8

**Table 5. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.**

Study No.: 132  
 MDL: 0.1 ug/sample  
 Date of Report: 7/11/95

Matrix: XAD-2 Resin  
 Chemical: Diazinon  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ug/sample)	Amount Recovered (ug/sample)	Recovery (%)	$\bar{X}$	SD	CV (%)
265-267,269,270,272-276	1.0	1.01	101			
320-324,329-333	1.0	1.01	101			
76, 80, 271, 277, 278, 279, 280, 281, 283, 294	1.0	0.89	89			
268, 282, 284, 285, 286, 288, 289, 290, 291, 293	1.0	0.95	95			
			Overall:	96	5.7	6.0

**Table 6. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.**

Study No.: 132  
 MDL: 0.1 ug/sample  
 Date of Report: 7/11/95

Matrix: XAD-2 Resin  
 Chemical: Diazoxon  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ug/sample)	Amount Recovered (ug/sample)	Recovery (%)	$\bar{X}$	SD	CV (%)
265-267,269,270,272-276	1.0	1.03	103			
320-324,329-333	1.0	0.97	97			
76, 80, 271, 277, 278, 279, 280, 281, 283, 294	1.0	1.03	103			
268, 282, 284, 285, 286, 288, 289, 290, 291, 293	1.0	0.98	98			
			Overall:	100	3.20	3.19

Table 7. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.

Study No.: 132  
 MDL: 0.1 ug/sample  
 Date of Report: 7/11/95

Matrix: XAD-2 Resin  
 Chemical: Chlorpyrifos  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ug/sample)	Amount Recovered (ug/sample)	Recovery (%)	$\bar{X}$	SD	CV (%)
265-267,269,270,272-276	1.0	1.03	103			
320-324,329-333	1.0	1.03	103			
76, 80, 271, 277, 278, 279, 280, 281, 283, 294	1.0	0.89	89			
268, 282, 284, 285, 286, 288, 289, 290, 291, 293	1.0	0.97	97			
			Overall:	98	6.6	6.8

**Table 8. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.**

Study No.: 132  
 MDL: 0.1 ug/sample  
 Date of Report: 7/11/95

Matrix: XAD-2 Resin  
 Chemical: Chlorpyrifos OA  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ug/sample)	Amount Recovered (ug/sample)	Recovery (%)	$\bar{X}$	SD	CV (%)
265-267,269,270,272-276	1.0	1.15	115			
320-324,329-333	1.0	1.01	101			
76, 80, 271, 277, 278, 279, 280, 281, 283, 294	1.0	1.12	112			
268, 282, 284, 285, 286, 288, 289, 290, 291, 293	1.0	1.04	104			
			Overall:	108	6.58	6.10

Table 9. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.

Study No.: 132  
 MDL: 0.05 ppb  
 Date of Report: 7/11/95

Matrix: Surface Water  
 Chemical: Malathion  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ppb)	Amount Recovered (ppb)	Recovery (%)	$\bar{X}$	SD	CV (%)
001, 004, 007, 010, 045, 046	1.0	1.07	107			
0013, 0016, 0019, 0022	1.0	0.95	95			
0025, 0026, 0028, 0029	1.0	1.06	106			
017, 148, 151, 154	1.0	1.09	109			
31, 33, 34, 35, 38, 40, 41, 121, 122, 124	1.0	0.89	89			
126, 127, 129, 130, 132, 145, 147, 241, 243, 244	1.0	1.04	104			
246, 247, 249, 250, 252	1.0	0.89	89			
96,99,103,106,157,160,163, 166,181,184,187,193, 196	1.0	0.89	89			
199,202,217,218,229,232, 235,238,253,256,259, 262	1.0	0.88	88			
109,219,221,225	1.0	1.18	118			
84,86,88,90,92,94,133, 135,137,139	1.0	1.12	112			
141,169,171,173,175,177, 179,205,207,209	1.0	1.24	124			
295,297,299,301,303,305, 334,336,346,348	1.0	0.97	97			
350,352,354,356,358,360, 362,364,366,368	1.0	1.03	103			

OVERALL: 102 11.5 11.2

Table 10. Continuing Quality Control Data ( % recoveries ) for the 1994 Medfly Study.

Study No.: 132  
 MDL: 0.05 ppb  
 Date of Report: 7/11/95

Matrix: Surface Water  
 Chemical: Malaoxon  
 Lab: CDFA  
 Chemist: P. Lee

Extraction Set No's.	Amount Spiked (ppb)	Amount Recovered (ppb)	Recovery (%)	$\bar{X}$	SD	CV (%)
001, 004, 007, 010, 045, 046	1.0	0.89	89			
0013, 0016, 0019, 0022	1.0	0.94	94			
0025, 0026, 0028, 0029	1.0	1.11	111			
017, 148, 151, 154	1.0	1.07	107			
31, 33, 34, 35, 38, 40, 41, 121, 122, 124	1.0	0.97	97			
126, 127, 129, 130, 132, 145, 147, 241, 243, 244	1.0	0.96	96			
246, 247, 249, 250, 252	1.0	1.02	102			
96,99,103,106,157,160,163, 166,181,184,187,193, 196	1.0	0.88	88			
199,202,217,218,229,232, 235,238,253,256,259, 262	1.0	0.92	92			
109,219,221,225	1.0	1.0	100			
84,86,88,90,92,94,133, 135,137,139	1.0	0.99	99			
141,169,171,173,175,177, 179,205,207,209	1.0	1.04	104			
295,297,299,301,303,305, 334,336,346,348	1.0	0.90	90			
350,352,354,356,358,360, 362,364,366,368	1.0	0.90	90			
Overall:				97	7.1	7.3

Table 11. Continuing Quality Control Data (% recoveries) for the 1994 Medfly Study.

Study No.: 132  
 MDL: 0.1 ppb  
 Date of Report: 7/11/95

Matrix: Surface Water  
 Chemical: Malathion  
 Lab: APPL  
 Chemist: S. Tallman

Extraction Set No's.	Amount Spiked (ppb)	Amount Recovered (ppb)	Recovery (%)	$\bar{X}$	SD	CV (%)
003, 004	100	93.5 82.6	94 83	88	7.8	8.8
002, 005, 008, 47, 48	100	80.7 84.9	81 85	83	2.8	3.4
014, 020, 023	100	92.7 86.1	93 86	90	4.9	5.5
110, 220, 222, 226	100	101.0 93.5	101 94	98	4.9	5.1
298,337,347,349	100	97.0 101.0	97 101	99	2.8	2.9
			Overall:	92	7.3	8.0

Table 12. Continuing Quality Control Data (% recoveries) for the 1994 Medfly Study.

Study No.: 132  
 MDL: 0.1 ppb  
 Date of Report: 7/11/95

Matrix: Surface Water  
 Chemical: Malaoxon  
 Lab: APPL  
 Chemist: S. Tallman

Extraction Set No's.	Amount Spiked (ppb)	Amount Recovered (ppb)	Recovery (%)	$\bar{X}$	SD	CV (%)
003, 004	100	96.7 103.0	97 103	100	4.2	4.2
002, 005, 008, 47, 48	100	89.2 91.8	89 92	90	2.1	2.3
014, 020, 023	100	96.8 90.3	97 90	94	4.9	5.3
110, 220, 222, 226	100	112.0 105.0	112 105	108	4.95	4.56
298,337,347,349	100	103.0 106.0	103 106	104	2.12	2.03
			Overall:	99	7.6	7.7

## APPENDIX B- Laboratory Quality Control Data

### II. Inter-Laboratory Comparison

The CDFA and APPL Laboratories analyzed split water samples for an interlaboratory comparison. Samples included background samples collected before the spray, samples collected the day of the spray, and samples collected during periods of precipitation.

A comparison of the samples split between CDFA Laboratory and APPL Laboratory showed good agreement (Table B-1). Of the 19 surface water samples split between CDFA and APPL Laboratories, two samples were in disagreement for malathion residues only. One sample was reported positive by CDFA Laboratory and non-positive by APPL Laboratory. The second sample was reported positive by APPL Laboratory and non-positive by CDFA Laboratory.

Table B-1. Inter-Laboratory Distribution of Split Water Samples

Variable	Malathion	Malaoxon
Number of Positive Split Samples in Agreement <sup>a</sup>	11	6
Number of Non-positive Split Samples in Agreement <sup>b</sup>	6	13
Number of Split Samples in Disagreement	2	0
Total Number of Split Samples	19	19

<sup>a</sup> Residue detected in split samples analyzed by both laboratories

<sup>b</sup> Residue not detected in split samples analyzed by both laboratories

Malathion was detected in eleven water samples analyzed by CDFA and APPL Laboratories (Table B-2). Malathion concentrations ranged from 0.21 ppb to 210 ppb. Regression analysis was used to investigate differences between the two sets of results. A regression of APPL concentrations on CDFA concentrations indicated that the calculated slope did not differ significantly from one, and the calculated intercept did not differ significantly from zero at the 5% level of significance. The correlation coefficient was 0.99. The result (CDFA=50 ppb,

APPL= 75 ppb) was flagged as an observation having a large standardized residual in comparison to other results. On further investigation, nothing unusual about this observation was determined. The regression analysis, with or without this observation, indicated there was no evidence of systematic differences between the two sets of results for concentration of malathion in water samples.

Malaoxon was detected in six rain runoff samples analyzed by CDFA and APPL Laboratories (Table B-2). Concentrations ranged from 2.7 ppb to 130 ppb. A regression of CDFA concentrations on APPL concentrations indicated that the calculated slope was significantly different from one at the 5% level of significance. This may be indicative of a systematic error, but could also be attributed to the limited number of samples available for comparison. The calculated intercept was not significantly different from zero at the 5% level of significance. The correlation coefficient was 0.99.

Table B-2. Interlaboratory Comparison of Malathion and Malaoxon Results in Surface Water <sup>a</sup>

<u>Malathion (ppb)</u>		<u>Malaoxon (ppb)</u>	
<u>CDEA</u>	<u>APPL</u>	<u>CDEA</u>	<u>APPL</u>
43.1	34	108.5	130
39.1	43	82.1	100
182.9	190	42	58
186.2	210	2.62	2.7
60.6	73	30.8	26
50.3	75	4.61	2.8
0.21	0.2		
0.37	0.34		
11.1	10.7		
76.2	67		
33.4	29		

<sup>a</sup> Malathion and malaoxon results reported crosswise from each other are not necessarily cross-linked residue levels.

Only positive detections reported by both laboratories are presented.

## **Appendix C- Statistical Analysis**

## APPENDIX C- Statistical Analysis

### Mass Deposition on Kimbie Material

The hypothesis of normality was rejected for samples collected during spray 1 ( $p < 0.02$ ) and spray 3 ( $p < 0.01$ ) using the Ryan-Joiner procedure. The hypothesis of normality was not rejected for spray 2 samples at the 5% level of significance. The hypothesis of homogeneity of variances between the three sprays was rejected ( $p < 0.05$ ) using Levine's test. As previously reported (Ando et al, 1995), the form of the underlying within spray distribution and yearly deposition distribution varies. Given that the underlying distribution is uncertain, non-parametric estimation techniques for data analysis are also provided.

Median values and median deviations are presented for each spray (Table C-1) with corresponding 95% confidence intervals. The H test of Kruskal and Wallis was used to compare the 1995 spray medians. The null hypothesis that the three samples came from a common population was rejected ( $p < 0.001$ ). As Table C-1 shows, there is a difference in location (median) but not in shape (median deviation). The median for sprays 1 and 2 combined was 7.62  $\text{mg}/\text{m}^2$ . The overall median for the three sprays combined was 5.71  $\text{mg}/\text{m}^2$ .

Table C-1. Median and the 95% confidence interval for mass deposition of malathion on Kimbie Material <sup>a</sup>.

Application Date	Median	<u>Malathion (<math>\text{mg}/\text{m}^2</math>)</u>	
		Lower	Upper
Spray 1 (32) <sup>b</sup>	5.64	4.03	7.68
Spray 2 (30)	9.63	7.40	11
Spray 3 (32)	2.17	0.848	4.51
Combined Sprays (98)	5.71	4.41	6.76

<sup>a</sup> Malaaxon was not included due to the low number of positive detection. RL of 0.011  $\text{mg}/\text{m}^3$

<sup>b</sup> Spray day followed by number of samples in parenthesis.

In Figure C-1, the whiskers are the vertical lines that extend from the top and the bottom of the transparent box to the values which are the lowest and highest observation which are not considered outliers. Outliers are individual observations falling outside limits based on the interquartile range of the distribution and are plotted with asterisks. For the 1995 data there were no samples flagged as outliers (Fig C-1).

The within spray data sets differ in location and spread. The distributions for spray 1 and 3 are skewed to the left. The boxplot of deposition data from the four study years is shown in Figure C-2. Outliers occur in all years except the 1995 study year. The distributions for the two study years 1981 and 1995 are skewed to the left. The 1995 data is similar in location to 1981 data but dissimilar to 1990 and 1994 data. The 1995 data is more variable in comparison to the 1981, 1994, and 1990 data.

For each study year, the distribution was partitioned into three categories: the percentage of samples within  $\pm 25\%$  of the expected application rate, the percentage of samples more than 25% below the expected application rate, and the percentage of samples more than 25% above the expected application rate (Table C-2). As previously reported, (Ando et al, 1995), comparison of results showed similar deposition patterns in 1994 and 1990 study years. Table C-2 shows that approximately 40% of the samples were within 25% of the target rate for both years.

Figure C-1. Distribution of malathion mass deposition for each spray in the 1995 medfly eradication program, shown as a box-and-whisker plot

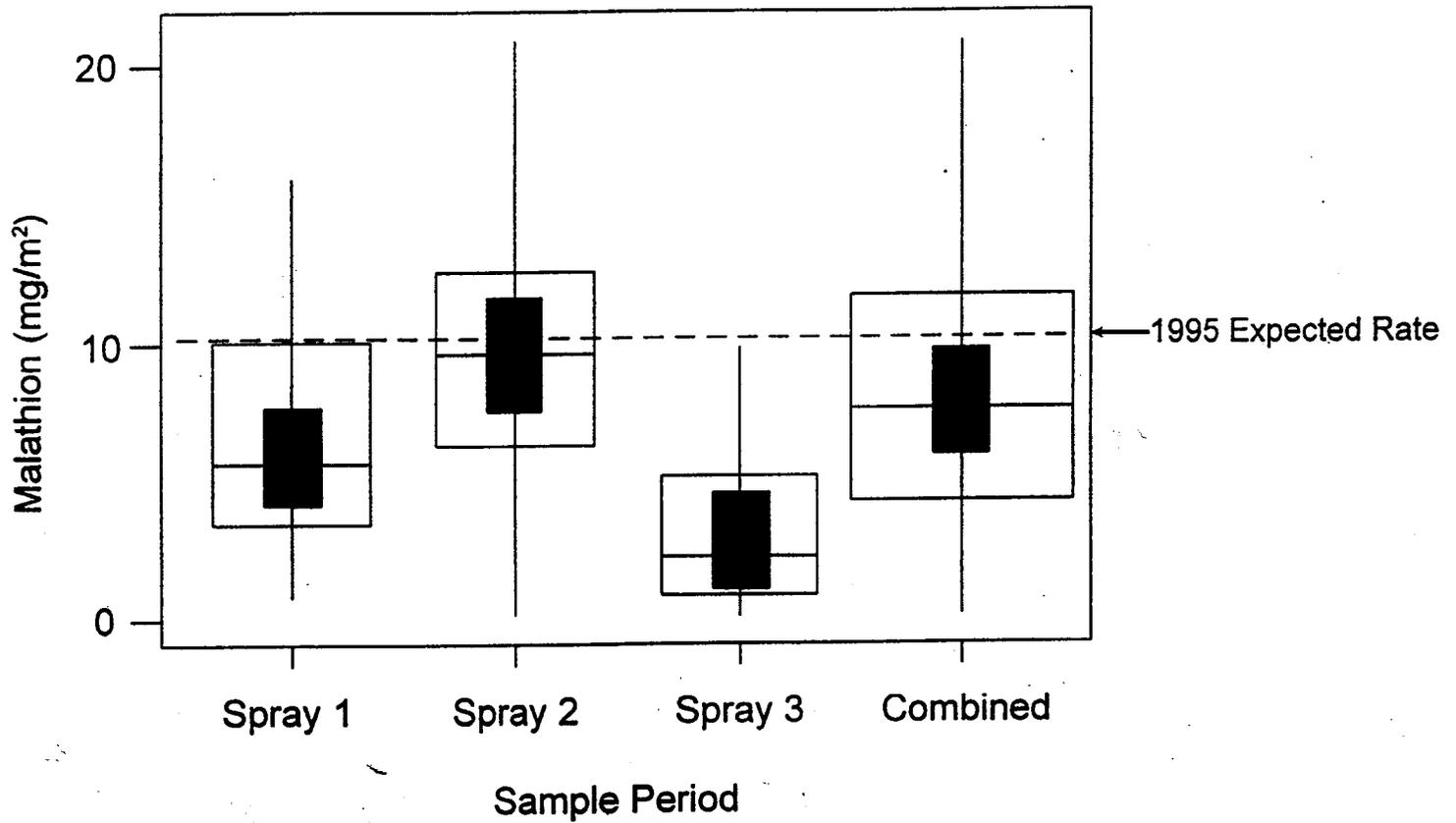


Figure C-2. Malathion mass deposition data for the 1995, 1994, 1990, and 1981 medfly eradication programs. Box-and-whisker plot of data expressed as a fraction of the expected rate (ratio of one is equivalent to malathion expected rate)

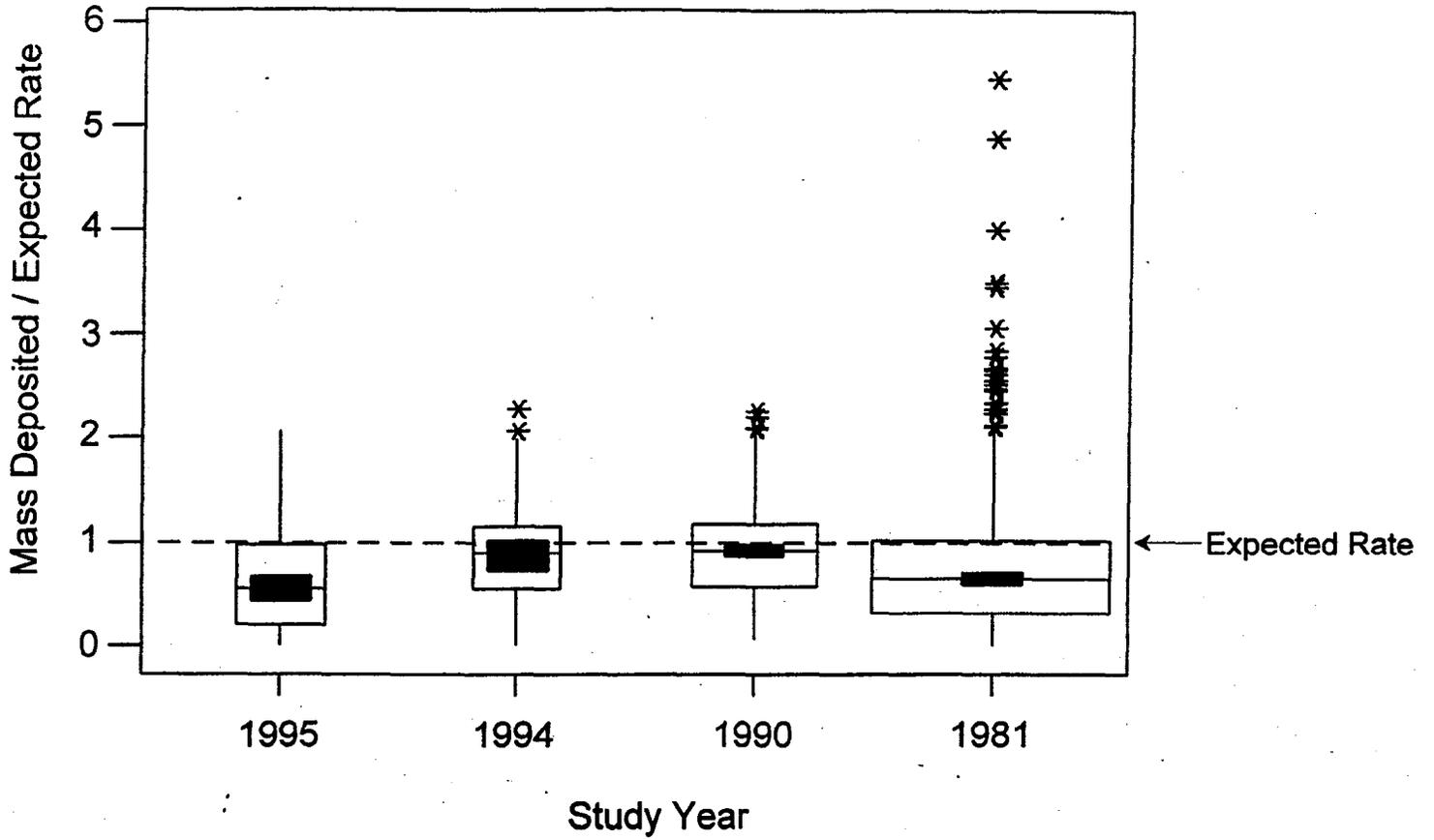


Table C-2. Relative frequency of malathion samples within 25% of expected application rate for the 1995, 1994, 1990, and 1981 Medfly eradication programs.

Year	Expected Malathion Application Rate (mg/m <sup>2</sup> ) <sup>a</sup>	Percent of Samples		
		<ar <sup>a</sup> - Δ <sup>b</sup>	ar ± Δ	>ar + Δ
1995	10.19	61.2	17.4	21.4
1994	10.19	40.5	40.5	19.1
1990	23.78	35	46.3	18.7
1981	19.76	58.9	24.5	16.6

<sup>a</sup> Expected application rate

<sup>b</sup> Δ = 0.25 x ar.

In contrast, the 1995 and 1981 results had a much lower percentage of samples falling near the expected application rate. For 1995, approximately 17% of samples fell near the target rate compared with 25% for the 1981 study results. The percentages in the remaining two categories were very similar for 1981 and 1995 data. As previously reported (Oshima et al, 1981), malathion appeared to be under-applied to the vast majority of 1981 samples. Under application occurred during each of the three sprays monitored during the 1995 program. The low deposition values observed during the third spray were attributed to weather conditions.

A statistical comparison of the four independent distributions of frequency data for the four study years was made using a X<sup>2</sup> test. The chi-square test of whether the 1995, 1994, 1990, and 1981 target distributions could have come from the same population was rejected at the p<0.01 level of significance. As previously reported (Ando et al, 1995), the observed pattern of deposition in 1994 was similar to 1990 whereas the observed pattern of deposition for 1981 was dissimilar to 1994 and 1990.

The chi-square test of whether the 1995 data could have come from a population having similar percentages to the 1994 target distribution was rejected at the p<0.05 level of significance. The

chi-square test of whether the 1995 data could have come from a population having similar percentages to the 1990 target distribution was rejected at the  $p < 0.01$  level of significance. However, the chi-square test of whether the 1995 data could have come from a population having similar percentages to the 1981 target distribution was not rejected at the 5% level of significance. All critical bounds for comparisons were determined from a Bonferroni  $X^2$  table.

### **Ambient Air Concentrations**

A comparison was made between the average total malathion concentration found in 1995 samples and 1994 samples within each sampling period. Samples reported as ND were assigned the value of one-half the reporting limit in order to complete the analysis. An unpaired student's t-test assuming unequal variances was used to test for differences within each sampling period for the two study years. There was no difference between years in the average total malathion concentration measured in background samples collected before the spray at the 5% level of significance. There was no difference between years in the average total malathion concentration measured during each of the two consecutive 24-hour periods after the spray at the 5% level of significance. However, there was a significant difference between the average total malathion concentration found in samples collected during the spray period for the 1994 study year in comparison to the 1995 study year ( $p < 0.001$ ). The atypical weather conditions during the third spray in the 1995 study year may have contributed to this difference.

## **APPENDIX D- Field Results**

Field Results: Malathion Concentrations in Air

site	Period	10/26/94	11/14/94	3/14/95	10/26/94	11/14/94	3/14/95
		malathion			malathion		
		ug/m3	ug/m3	ug/m3	ppt	ppt	ppt
41	bg	0.0077	ND	ND	0.57	ND	ND
42	bg	0.0051	ND	ND	0.38	ND	ND
43	bg	0.0107	ND	ND	0.80	ND	ND
44	bg	0.0069	ND	ND	0.51	ND	ND
45	bg	0.0080	ND	ND	0.60	ND	ND
41	1	0.0864	0.0959	0.089	6.44	7.14	6.652
42	1	0.0535	0.0670	0.046	3.99	4.99	3.433
43	1	0.1762	0.0305	0.073	13.13	2.27	5.458
44	1	0.0613	ND	0.019	4.57	ND	1.433
45	1	0.0920	0.0540	0.045	6.85	4.02	3.326
41	2	0.0716	0.0073	0.059	5.34	0.54	4.392
42	2	0.0603	0.0057	0.063	4.49	0.43	4.725
43	2	0.0772	0.0063	0.106	5.76	0.47	7.865
44	2	0.0758	0.0097	0.061	5.65	0.72	4.555
45	2	0.0511	0.0091	0.075	3.81	0.68	5.573
41	3	0.0615	0.0253	0.045	4.58	1.88	3.375
42	3	0.0457	0.0240	0.030	3.41	1.79	2.245
43	3	0.0737	0.0252	0.048	5.49	1.88	3.554
44	3	0.0578	0.0290	0.045	4.30	2.16	3.342
45	3	0.0612	0.0282	0.037	4.56	2.10	2.758

Field Results: Malaoxon Concentrations in Air

10/26/94	11/14/94	3/14/95	10/26/94	11/14/94	3/14/95
malaoxon			malaoxon		
ug/m3	ug/m3	ug/m3	ppt	ppt	ppt
ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND
0.023	ND	0.0083	1.77	ND	0.651
0.020	ND	0.0099	1.57	ND	0.773
0.016	ND	0.0141	1.24	ND	1.100
0.019	ND	0.0076	1.53	ND	0.595
0.014	ND	0.0114	1.11	ND	0.892
0.015	0.0056	0.007	1.19	0.44	0.44
0.013	0.0066	0.006	1.04	0.52	0.52
0.016	0.0063	0.010	1.27	0.49	0.49
0.013	0.0054	0.007	1.01	0.42	0.42
0.018	0.0095	0.007	1.39	0.75	0.75

Rain Runoff 3 days after aerial application

Conejos Creek:

Sample #	Time	Date	Interval	(MDL = 0.1 ppb) Malathion (ppb)	(MDL = 0.1 ppb) Malaoxon (ppb)
157	1515	1/20/95	1	0.19	ND
158					
166	1615	1/20/95	2	128.3	3.53
167					
199	1715	1/20/95	3	243.6	9.57
200					
256	1815	1/20/95	4	157.7	4.16
257					
96	1915	1/20/95	5	152.0	3.75
97					
103	2010	1/20/95	6	62.9	1.49
104					
229	2215	1/20/95	7	34.1	0.74
230					
238	0015	1/21/95	8	23.1	0.34
239					
187	0715	1/21/95	9	2.07	ND
188					

Lewis Drain:

160	1530	1/20/95	1	44.1	2.80
161					
193	1625	1/20/95	2	562.0	22.5
194					
202	1730	1/20/95	3	275.9	8.48
203					
259	1830	1/20/95	4	264.8	6.94
260					
99	1930	1/20/95	5	349.8	8.04
100					
106	2030	1/20/95	6	88.3	2.45
107					
232	2230	1/20/95	7	102.8	1.84
233					
181	0030	1/21/95	8	112.9	1.55
182					

Calleguas Creek:

163	1545	1/20/95	1	787.1	40.3
164					
196	1640	1/20/95	2	659.0	28.2
197					
253	1745	1/20/95	3	418.2	11.5
254					
262	1845	1/20/95	4	436.2	8.9
263					
235	2245	1/20/95	7	144.3	2.2
236					
184	0045	1/21/95	8	65.6	1.08
185					

Field Blanks:

1	217	1655	1/20/95	3	ND	ND
2	218	0030	1/21/95	8	ND	ND

Rain Runoff 6 days after aerial application

Sample #	Time	Date	Interval	(MDL = 0.05 ppb)	(MDL = 0.1 ppb)
				Malathion (ppb)	Malaoxon (ppb)
<b>Conejos Creek:</b>					
346	340	3/21/95	1	76.2	30.8
352	440	3/21/95	2	34.10	5.67
358	540	3/21/95	3	31.40	4.42
364	640	3/21/95	4	17.10	2.05
205	745	3/21/95	5	2.26	0.24
<b>Lewis Drain</b>					
348	356	3/21/95	1	33.40	4.61
354	500	3/21/95	2	21.90	2.68
360	600	3/21/95	3	18.10	2.01
366	700	3/21/95	4	29.80	2.93
207	800	3/21/95	5	31.40	4.41
<b>Calleguas (upper)</b>					
350	410	3/21/95	1	29.60	3.36
356	515	3/21/95	2	14.60	2.17
362	610	3/21/95	3	23.70	2.46
368	0710	3/21/95	4	22.20	2.38
209	0810	3/21/95	5	12.00	1.58
<b>Calleguas Creek (at state hospital):</b>					
295	0450	3/21/95	1	17.70	9.21
299	0600	3/21/95	2	5.46	0.82
303	0720	3/21/95	3	23.4	7.21
171	900	3/21/95	4	14.10	3.56
177	1015	3/21/95	5	3.03	0.32
84	1200	3/21/95	6	1.55	0.13
88	1440	3/21/95	7	0.89	ND
94	1640	3/21/95	8	0.66	ND
137	2250	3/21/95	9	0.33	ND
<b>Reylon Slough:</b>					
297	525	3/21/95	1	ND	ND
301	630	3/21/95	2	0.06	ND
305	745	3/21/95	3	3.24	1.34
173	935	3/21/95	4	2.62	0.53
179	1100	3/21/95	5	1.83	0.20
86	1230	3/21/95	6	1.74	0.12
90	1505	3/21/95	7	1.36	0.10
133	1710	3/21/95	8	1.44	0.10
139	2325	3/21/95	9	0.87	ND
<b>Mugu Lagoon:</b>					
169	830	3/21/95	3	ND	ND
175	1000	3/21/95	4	2.25	0.98
334	1115	3/21/95	5	0.97	0.29
336	1300	3/21/95	6	11.10	2.62
92	1545	3/21/95	7	1.76	0.16
135	1730	3/21/95	8	1.03	ND
141	2340	3/21/95	9	0.16	ND

Rain runoff: 12 days after application

Conejos Creek				Malathion	Malaoxon
	sample #	Date	Time	ppb	ppb
Background	241	11/7/94	2215	0.06	ND
	244	11/8/94	0001	0.14	ND
	31		0105	31.6	25.1
	121		0215	60.6	42.0
	130		0315	55.2	34.2
	145		0350	45.8	25.6
Field Blank	34		0115	ND	ND
	41		0320	ND	ND
Calleguas	260	11/8/94	0045	190.6	160.2
	38		0145	186.2	82.1
	127		0255	166.1	57.6
Lewis Drain	247	11/8/94	0025	66.4	45.9
	35		0125	182.9	108.5
	124		0235	178.1	104.1

Malathion, malaoxon and Diazinon MDL = 0.05  
 Chlorpyriphos MDL = 0.1