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MEMORANDUM

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SUBJECT: PRELIMINARY METHYL PARATHION AIR CONCENTRATIONS MEASURED ADJACENT TO TWO WALNUT ORCHARD APPLICATIONS

SUMMARY

Background
The Department of Pesticide Regulation (DPR) is responsible for evaluating pesticide compounds to determine whether certain active ingredients pose a potential threat to public health as toxic air contaminants. In 1986, at the request of DPR, Air Resources Board staff measured methyl parathion air concentrations in the residential areas of Sutter and Colusa counties in California. Results from collected air samples indicated that persons residing near agricultural applications were potentially exposed to methyl parathion via the inhalation route when flooded rice fields were aerially treated during peak use months of May and June (ARB, 1989). Based on review of the Air Resources Board study, in addition to review of other published methyl parathion studies, DPR determined that methyl parathion poses a present or potential hazard to human health and designated it a toxic air contaminant in 2000.

In 1999, a methyl parathion reference concentration (RfC) of 40 $\mu g/m^3$ was calculated by DPR staff using an estimated No-Observed-Effect Level concentration (DPR, 1999). More recent submission of toxicological data resulted in the recalculation of the RfC value to 0.42 $\mu g/m^3$ to reflect a lower default breathing rate for children (Koshlukova and Reed, 2003). This maximum 24-hour (hr) air concentration level, if not exceeded, would provide generally adequate acute inhalation exposure protection with a 100 times margin of exposure from non-oncogenic effects of methyl parathion.

Methyl parathion is a restricted use organophosphate pesticide with insecticidal and acaricidal activity. It is a nonsystemic compound that controls sucking and biting pests by contact, stomach, and respiratory action. Currently, Penncap-M® is the only methyl parathion product available. It is a flowable formulation consisting of polymeric microcapsules designed for slow release of methyl parathion. In 2000, there were two additional methyl parathion products available in California. However, registration for these two emulsifiable concentrate formulations are no longer active.

In January 2000, the U.S. Environmental Protection Agency cancelled methyl parathion use in all fruit and some vegetable crops, citing that the pesticide posed an unacceptable dietary risk to the young (U.S. EPA, 1999). Pesticide usage was also cancelled for nonfood crops such as ornamentals, grasses grown for seed, mosquito use, and nursery stock.

Because of these new restrictions, methyl parathion use within several California counties was halted in the year 2000, as many of the prior applications were directed to tree or other cancelled food crops. Use on walnuts, however, was unaffected in 2000 and data indicate that methyl parathion use on walnuts accounted for over 90 percent of the methyl parathion used during that year.

Use on walnuts is through a special local need (SLN) registration originally granted for Penncap-M® in 1997 due to the limited number of alternative registered pesticides to control codling moth, the major walnut insect pest. Two pounds active ingredient (ai)/acre is the maximum application rate to walnuts on the current SLN label with a minimum spray interval of 21 days between applications (DPR, 2000).

To determine if control measures are needed to reduce public exposure to methyl parathion, the Environmental Monitoring Branch of DPR monitored the application of methyl parathion to two walnut orchards. This memorandum reports the preliminary results from both applications.

FIELD AND APPLICATION DESCRIPTIONS

General

Two San Joaquin Valley walnut orchards were selected for monitoring by DPR staff: one orchard in the south-central valley and the other orchard in the northern valley. Methyl parathion was applied at a rate of two pounds ai/acre to both orchards during the summer months when overall usage of the pesticide (pound/season) is typically highest for walnuts. Additional pesticides were also applied with methyl parathion at both sites and following completion of applications, flood irrigation of the orchards was observed throughout the air monitoring study.

Application Site 1

Air monitoring was conducted around a mature 38-acre walnut orchard block (Figure 1) located at the corner of a county intersection in Tulare County. The trees were approximately 25 feet (ft) tall with full canopies. Agricultural crops surrounded the orchard on all sides with the exception of the south side, where rural homes, a horse corral, and canal were located. A walnut orchard to the east and cornfield to the southeast of the study block were approximately 25 and 6 ft tall, respectively. All other crops surrounding the field were less than two ft in height. Permission to place air sampling equipment was obtained from property owners on all sides of the study orchard, with the exception of the orchard's east side where permission was not granted.

Consequently, equipment placement for the study was altered from the design described in the study protocol (June, 2002).

Methyl parathion, avermectin (a miticide), and spray oil were mixed with water and applied on June 18, 2002, at respective rates of 2 pound ai, 0.01 pound ai, and 1.5 gallons per acre. Three specially engineered airblast sprayers, each pulled and powered by tractors, were used to deliver the spray material. During application, spray fans were elevated above their base positions to deliver tank material higher into the tree canopy.

Spraying commenced at approximately 7:30 a.m. with one sprayer beginning in the orchard's center row and working outwards. The remaining two sprayers began treatment at the orchard's outside east and west row, respectively, working inwards. After completion of the internal orchard rows, the orchard perimeter was treated with the spray fan adjusted to 90° from the full 180° coverage. Application finished at approximately 10:40 a.m. Flood irrigation of the orchard started the following day and extended through the monitoring period.

Pesticide use records indicated that methyl parathion was not used within a one-mile radius of the study orchard during the monitoring period of June 17 to 22, 2002.

Application Site 2

Air monitoring was conducted around a mature 100-acre walnut orchard block (Figure 2) located in San Joaquin County. Trees were approximately 25 ft tall with full canopies. A forty-acre extension on the north end of the 100-acre monitored orchard block consisted of a different walnut variety that did not receive methyl parathion treatment and, therefore, was not monitored in this study. Agricultural crops surrounded the orchard study block on all sides with the exception of the northeast side. A walnut and apple orchard to the west were approximately seven to ten ft tall and a cornfield to the east and grape vineyard to the south of the study block were five to six ft tall.

Methyl parathion, propargite (a miticide), and dibrom (an insecticide) were mixed with water and an adjuvant and applied on July 17, 2003, at respective rates of two pound ai, 2.4 pound ai, and 16 ounces per acre. Two traditional airblast sprayers, each pulled and powered by tractors, were used to deliver the spray material.

Spraying commenced at approximately 10:00 p.m. with two sprayers, each starting at the north and south ends of the orchard, respectively, and working inwards. After completion of the internal orchard rows, the orchard perimeter was also treated. Application finished at approximately 7:15 a.m. Flood irrigation of the walnut orchard started the following day and extended through the monitoring period.

STUDY DESIGN AND SAMPLING METHODS

General

Prior to methyl parathion application, meteorological data was collected near the study orchards using a Met-One/Campbell Scientific weather station (Met One Instrument sensors/Campbell Scientific CR-21XL data logger). Wind direction, wind speed, air temperature, and relative humidity were recorded for 24 hr prior to pesticide application and for the duration of the monitoring period. Average values for these variables were recorded at one-minute intervals. The weather stations were located in open areas, approximately 450 to 640 feet meters away from the first and second orchard, respectively.

Clear glass air sampling tubes containing XAD-4 resin were elevated to a breathing height of four to five ft and used to trap methyl parathion and methyl paraoxon residues using a low volume SKC air sampler adjusted to run at a flow rate of 2 L/min for each sampling interval. Tubes were covered with foil to prevent photodegradation and were collected during background, application, and post-application periods.

Air samplers were not placed at the canopy edge during the application period due to concerns over contamination. However, once application was completed, sites were set up at the edge. Following the application period, one sample was collected from each sampling location for one six-hr and seven 12-hr sampling periods (four days) for Application Site 1 and additional nine 12-hr sampling periods (five days) for Application Site 2 (Table 1). Post-application sample run time was set at 7 a.m. to 7 p.m. for both studies. Flow rates were measured with a flowmeter and recorded at the beginning and end of most sampling intervals. All collected samples were immediately capped and placed on dry ice with samples remaining frozen until extracted in the laboratory.

The California Department of Food and Agriculture Center for Analytical Chemistry performed the chemical analyses. The reporting limits for methyl parathion and methyl paraoxon in XAD-4 resin are 0.1 and 0.2 microgram/sample (µg/sample), respectively.

Application 1

Seventeen air monitoring stations were positioned around the Tulare County orchard (Figure 1). At the canopy's edge, samplers were placed at the mid-distance length of each orchard side. Samplers were also placed up to 80 ft away from the orchard edge at each orchard corner and at the mid-distance length of each orchard side (excluding the east side where permission was not granted). Samplers were also placed up to 153 ft from the orchard edge on each orchard side excluding the east side where permission to place equipment was not obtained.

Application 2
Twenty air monitoring stations were positioned around the San Joaquin County orchard. Samplers were located at the edge of the orchard canopy and approximately 30 ft from the edge, with three samplers at further distances of 54, 71 and 171 ft in the downwind direction (Figure 2). No samplers were placed on the north end of the treatment area due to resource considerations.

DATA ANALYSES

Data were compiled and presented as 24-hr time weighted averages (TWA) with the exception of sampling intervals representing shorter sampling (indicated in tables). The averages from Applications 1 and 2 are presented in Tables 2 and 3, respectively and can be compared with the acute RfC value of 0.42 $\mu g/m^3$. The 24-hr TWAs were calculated for each combination of sequential intervals that comprised a possible 24-hr periods so the peak 24-hr periods could be determined. When calculating average concentrations, samples with no detectable residue of methyl parathion were assumed to have a concentration of one-half the detection limit. There were no detections of the breakdown product methyl paraoxon during Application 1. During Application 2, eight samples contained measurable amounts of methyl paraoxon. The 21 to 24-hr TWA of methyl paraoxon are presented in Table 3 in parenthesis next to the methyl parathion concentration detected in the samples. When calculating average concentrations for methyl paraoxon, samples with no detectable residue were assumed to have a concentration of one-half the detection limit

PRELIMINARY RESULTS

During a study in 1985, a peak 24-hr concentration of 0.49 $\mu g/m^3$ methyl parathion was measured 50 feet from the edge of a rice field (DPR 1999). The highest 24-hr TWA measured during the 1989 ARB study was 0.22 $\mu g/m^3$ methyl parathion at a location 60 feet from the edge of the rice field (DPR 1999). Both studies were conducted on a different formulation of methyl parathion product which is no longer registered. The application rates are unknown.

Methyl parathion concentrations measured at Application sites 1 and 2 exceeded the 24-hr acute RfC value of 0.42 $\mu g/m^3$ during several periods. The 24-hr TWA concentrations at Application Site 1 exceeded the acute RfC value at the orchard's edge from the time of application through the third day of monitoring and at 93 ft (location 10) until the morning of the third day. The highest 24-hr concentration (1.75 $\mu g/m^3$) occurred during the second day post-application (intervals 3 and 4) next to the orchard (location 17).

The acute RfC at Application Site 2 was exceeded through the fourth day after the application at the orchard's edge and through the third day approximately 30 ft from the orchard. Due to shorter sampling durations during intervals 1 and 2 (Table 1) only a 21-hr TWA can be calculated for the first day of monitoring. The highest concentration (4.38 $\mu g/m^3$) occurred during that 21-hr period consisting of the application night and the following day at a distance of 29 feet from orchard edge (location 17). The 24-hr TWA concentrations measured during the sampling intervals with the highest average over all locations are presented in Figures 1 and 2. The 24-hr TWA from intervals 3 and 4 from Table 2 were used in Figure 1 and intervals 1 and 2 from Table 3 were used in Figure 2.

The background samples collected before application contained no detectable amount of methyl parathion or methyl paraoxon during both application studies. Continuing quality control recoveries for methyl parathion during the studies ranged from 84 to 101 percent and 69 to 125 percent in 2002 and 2003, respectively. The continuing quality control recoveries for methyl paraoxon ranged from 60 to103 percent and 75 to 141 percent in 2002 and 2003, respectively.

The general wind direction for both applications was from the northwest towards the southeast. Higher concentrations were measured at the downwind monitoring stations.

Attachments

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ARB.1989. Pesticide Monitoring Report – Methyl parathion monitoring in Sutter County. Engineering Evaluation Branch, Monitoring and Laboratory Division, California Air Resources Board, Test Report #C89-024.

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Koshlukova, S. and N. Reed. 2003. Memoradum Subject: Exposure Criteria for Methyl Parathion. Memorandum to Randy Segawa dated June 16, 2003. Department of Pesticide Regulation. 1001 I Street. P.O. Box 4015. Sacramento, CA 95812.

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Table 1. Approximate starting dates and times for sampling intervals for each study.

	Tulare Co. site			San Joaquin Co. site		
Interval	Start Date	Start time	Duration (hours)	Start Date	Start time	Duration (hours)
1*	6/18/2002	7:30	6.5	7/17/2003	22:00	11
2	6/18/2002	14:00	6	7/18/2003	9:00	10
3	6/18/2002	20:00	12	7/18/2003	19:00	12
4	6/19/2002	7:00	12	7/19/2003	7:00	12
5	6/19/2002	20:00	12	7/19/2003	19:00	12
6	6/20/2002	7:00	12	7/20/2003	7:00	12
7	6/20/2002	19:00	12	7/20/2003	19:00	12
8	6/21/2002	7:00	12	7/21/2003	7:00	12
9	6/21/2002	19:00	12	7/21/2003	19:00	12
10				7/22/2003	7:00	12

*Application took place during this period.

Table 2. Running 24-hour time-weighted averages for 2002 monitoring study. All concentrations are ug/m^3.

		Interval						
	Distance	1, 2 & 3	3 & 4	4 & 5	5 & 6	6 & 7	7 & 8	8 & 9
Location	(ft)	24-hr TWA	24-hr TWA	24-hr TWA	24-hr TWA	24-hr TWA	24-hr TWA	24-hr TWA
1	37	0.11	0.10	0.09	0.11	0.05	ND	0.06
2	153	0.17	0.15	0.19	0.22	0.11	0.09	0.07
3	33	0.27	0.26	0.30	0.39	0.25	0.16	0.08
4	147	0.15	0.14	0.23	0.27	0.13	N/A	N/A
5	37	0.08	0.07	0.15	0.15	0.10	0.10	ND
6	147	0.09	0.07	0.22	0.26	0.14	0.10	ND
7	30	0.45	0.13	0.34	0.48	0.25	0.12	0.08
8	150	0.10	0.09	0.19	0.22	0.11	0.08	ND
9	25	0.20	0.09	0.23	0.31	0.14	0.05	0.06
10	93	0.95	0.78	0.74	0.68	0.20	0.12	0.13
11	63	1.59	0.93	0.72	0.73	0.26	0.18	0.19
12	147	0.75	0.52	0.36	0.34	0.14	0.09	0.08
13	80	0.73	0.51	0.21	0.13	0.07	0.07	0.09
14	0	*	1.41	0.69	0.51	0.24	0.18	0.23
15	0	*	0.32	0.42	0.58	0.29	0.14	0.11
16	0	*	0.13	0.44	0.63	0.34	0.21	0.13
17	0	*	1.75	1.14	1.06	0.56	0.34	0.33

*sample were not collected during the application interval (1).

NA – one of the sample results used in the calculation was unavailable due to mechanical failure.

Table 3. Running 24-hour time-weighted averages for 2003 monitoring study. Averages for methyl paraoxon are presented in parenthesis. All concentrations are ug/m^3.

Location	Distance	Interval 1 & 2	2 & 3	3 & 4	4 & 5	5 & 6	6 & 7	7 & 8	8 & 9	9 & 10
	(ft)	21-hr TWA[1]	22-hr TWA[1]	24-hr TWA	24-hr TWA	24-hr TWA	24-hr TWA	24-hr TWA	24-hr TWA	24-hr TWA
1	0	*	1.24	0.79	0.23	0.21	0.14	0.11	0.08	0.09
2	36	3.72 (0.29)	1.47 (0.27)	1.09	NA	NA	0.19	0.14	0.07	0.07
3	0	*	1.48 (0.18)	0.87	0.54	0.38	0.38	0.23	0.11	0.13
4	39	3.36 (0.18)	1.34 (0.17)	1.28 (0.19)	0.64 (0.19)	0.39	NA	NA	0.09	0.09
5	9	*	0.72	NA	NA	0.14	0.10	0.10	ND	ND
6	22	3.03	0.73	0.68	0.27	0.18	0.09	0.09	ND	ND
7	7	*	0.73	0.68	0.15	0.13	0.23	0.24	0.07	0.07
8	29	0.78	0.47	0.43	0.11	0.11	0.22	0.22	ND	ND
9	0	*	0.41	0.38	0.17	0.13	0.29	0.29	0.08	0.08
10	30	1.51	0.64	0.63	0.17	0.12	0.14	0.14	0.07	0.07
11	24	*	0.31	0.32	0.10	0.07	ND	ND	ND	ND
12	0	*	0.26	NA	NA	0.05	0.06	0.06	ND	ND
13	28	1.68	0.97	0.63	0.39	0.48	0.34	0.23	0.09	0.05
14	0	*	1.56	0.87	0.68	0.88	0.60	0.46	0.26	0.14
15	33	1.57	0.91	0.67	0.29	0.33	0.35	0.28	0.09	0.06
16	0	*	2.34 (0.16)	1.13	0.83	0.79	0.54	0.49	0.21	0.06
17	29	4.38	1.50	0.96	0.62	0.52	0.18	NA	0.12	0.07
18	71	2.87 (0.21)	1.22 (0.20)	0.84	0.45	0.37	0.14	0.10	ND	ND
19	171	1.25 (0.13)	0.69 (0.12)	0.42	0.13	0.13	0.06	0.07	ND	NA
20	54	2.86 (0.18)	1.11 (0.18)	0.72	0.40	0.33	0.13	0.10	ND	ND

*samples were not collected during the application interval (1).

NA – one of the sample results used in the calculation was unavailable due to mechanical failure.

[1]Interval 1 had a sampling time of 11 hours and interval 2 had a sampling time of 10 hours, therefore concentrations are not a full 24-hr TWA.

Figure 1. Walnut orchard monitored in Tulare County in 2002. 24-hour TWA concentrations are from intervals 3 and 4, which had the highest average overall locations.

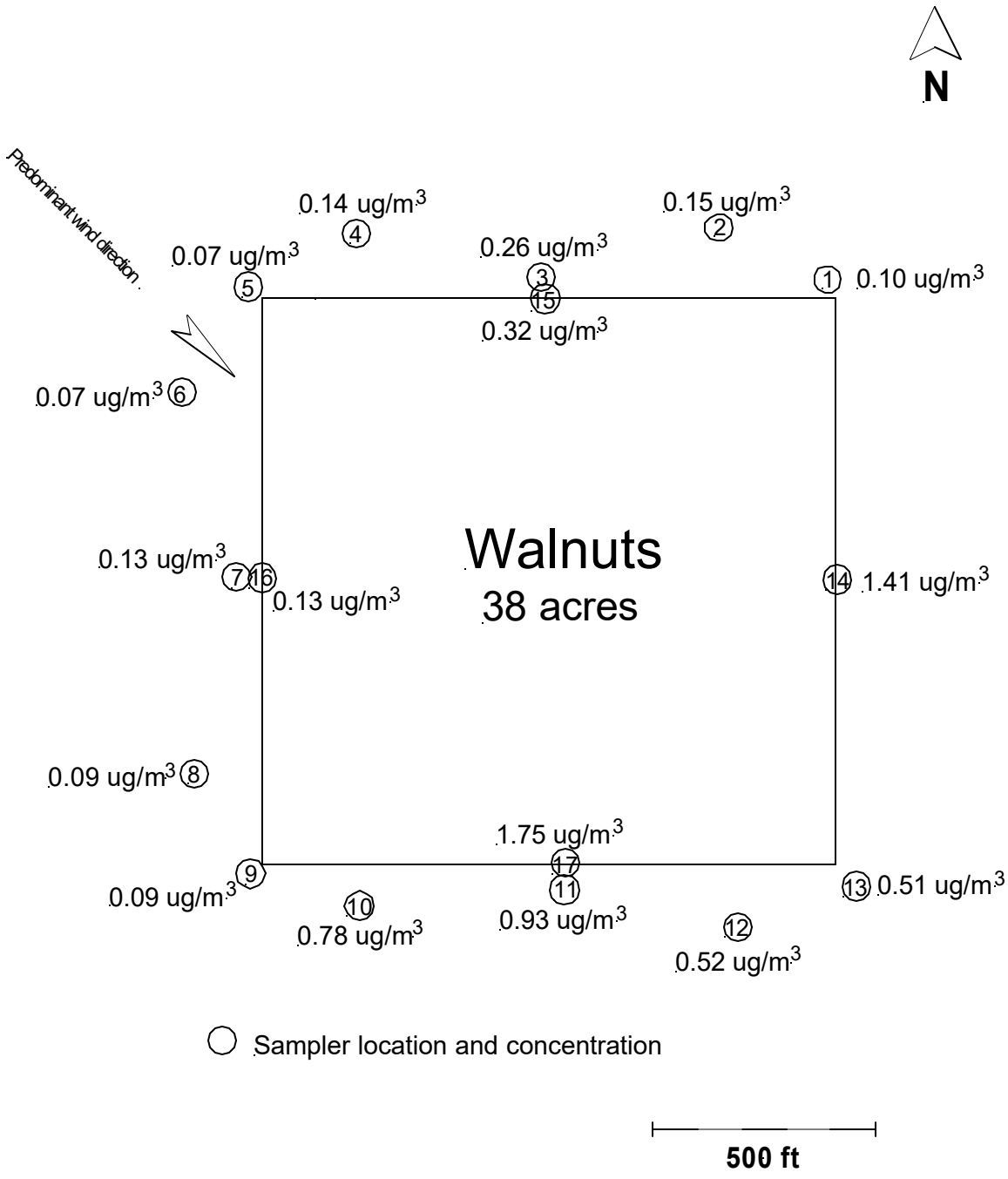

Figure 2. Walnut orchard monitored in San Joaquin County in 2003. 24-hour TWA concentrations are from intervals 1 and 2, which had the highest average overall locations.