APPENDIX H

METHYL BROMIDE AIR MONITORING STUDIES AND BUFFER ZONES

Beginning in 1992, DPR, methyl bromide registrants, and academic researchers began more comprehensive monitoring of field and commodity fumigations.

Appenix H.1. Field Fumigation

Methyl bromide flux was measured in several studies. The flux of methyl bromide from tarped field ranged from 22% in 5 days (Majewski *et al.*, 1995), 34% in 7 days (Yagi *et al.*, 1995), to 61% after 5.6 days (Yates *et al.*, 1996a and b) depending on the experimental conditions. The loss of applied methyl bromide in a tarped field was 4 times less than that from a nontarped field (Majewski *et al.*, 1995). The highest rate of loss was during the day when the temperature was high and the atmosphere was unstable. The remainder of the applied methyl bromide was adsorbed to the soil or degraded.

DPR used the initial studies to develop mitigation measures (permit conditions, including buffer zones), and later studies to check the effectiveness of the mitigation measures. Several different field fumigation methods were monitored (Table H1). In these studies, air monitoring was conducted using personal air sampling pumps equipped with activated charcoal tubes. The samplers were set up around the field at a distance of 30 feet from the edge of field and at the permit condition buffer zone determined for the application. Sampling was initiated at the start of the application and continued for one to seven days, with each sampling interval 6 - 12 hours. The air flow rate for all samplers was calibrated to approximately 15 mL/min. Wind speed, wind direction, air temperature, and relative humidity were recorded every five minutes with a Met-1® meteorological station.

A summary of the monitoring results from 39 field fumigations is shown in Table H1. Initial monitoring in 1992 showed air concentrations as high as 1.8 ppm (24-hour time-weighted average). The highest concentrations were detected at downwind locations closest to the treated area and declined with distance. Initial monitoring data indicated that methyl bromide air concentrations varied with application rate, acreage treated, and method of application. DPR used the Industrial Source Complex-Short Term computer model to assist in the data evaluation. This model was used to normalize for field-to-field differences such as application rate, acreage treated, field dimensions, and weather. After accounting for field-to-field differences, the monitoring data indicated that tarpaulin applications had lower air concentrations than nontarpaulin applications. Deep injections (20 inches or more) showed lower air concentrations than shallow injections (12 inches or less). However, deep injections continued to off-gas for a longer period of time. Based on the initial monitoring data, DPR recommended buffer zones so that air concentrations are not likely to exceed a target level at the specified distance. The target level currently used for the buffer zones is 0.21 ppm (24-hour time-weighted average), identified in the Preliminary Risk Assessment (Appendix A). Buffer zones varied in size with application rate, acreage, and application method.

Table H1. Maximum methyl bromide air concentration from different application methods at buffer zones specified by Department of Pesticide Regulation permit conditions.

Application Monitored and Study ID	Permit Condition Application Method	Date Applied	County	Applic Rate (lb/ac)	Acres	24-hr Max Conc @ Buffer (ppm)[a]	Perm Cond Buffer (ft)[b]
1: Hicks, 1992b	1-nontarp shallow	8/19/92	Monterey	186	19	0.042@300ft	390
2: Hicks, 1992b	1-nontarp shallow	9/24/92	Monterey	180	15	0.26@300ft	330
3: Hicks, 1992b/Ross, 1996	1-nontarp shallow	10/27/92	Monterey	180	15	0.55@50ft	330
4: Wofford and Segawa, 1998e	1.1-nontarp shallow (wing chisel)	3/12/98	Merced	150	7.5	0.15	200
5: Hicks, 1992a	2-nontarp deep	7/28/92	Kern	350	17	0.70@600ft	1060
6: Hicks, 1992a	2-nontarp deep	10/21/92	Kern	396	15	0.61@600ft	1170
7: Wofford and Segawa, 1998a	2-nontarp deep	1/22/98	Madera	348	33	0.11	510
8: Hicks, 1993a	3-nontarp deep (implements)	3/8/93	Fresno	396	40	0.56@200ft	2010
9: Hicks, 1993b	3-nontarp deep (implements)	3/13/93	Madera	400	20	0.34@200ft	940
10: Hicks, 1996	3-nontarp deep (implements)	10/31/95	San Joaquin	450	7	0.11@80ft	780
11: Siemer, 1992	4/5-tarp shallow	6/30/92	Kern	396	20	0.07@600ft	590
12: Ross, 1996	4/5-tarp shallow	10/26/92	Monterey	235	10	0.15@30ft	90
13: Sanders, 1997a	4/5-tarp shallow	2/13/97	SLO	200	10	0.082	30
14: Gosselin, 1997 a & b	4/5-tarp shallow	8/21/97	Ventura	180	9	0.069	30
15: Wofford and Segawa, 1998b	4/5-tarp shallow	11/1/97	Monterey	205	12	0.13	70

Table H1. (continued)

Application Monitored and Study ID	Permit Condition Application Method	Date Applied	County	Applic Rate (lb/ac)	Acres	24-hr Max Conc @ Buffer (ppm)[a]	Perm Cond Buffer (ft)[b]
	4/5-tarp shallow						
16: Kim and Segawa, 1998b	normal	6/5/98	Orange	231	1	0.069@30ft	100
17: “	edge panels	“	“	234	“	0.060@30ft	“
18: “	normal	6/7/98	“	231	“	0.053@30ft	“
19: “	edge panels	“	“	226	“	0.046@30ft	“
20: Gillis, 1998a	4/5-tarp shallow	7/25/98	Monterey	216	5	0.043	100
21: Gillis, 1998b	4/5-tarp shallow	8/7/98	Ventura	206	4	0.029	100
22: Gillis and Becker, 1993	8.1-tarp shallow Very High Barrier	10/19/93	Monterey	392	7	0.13	30
23: Sanders, 1997a	8.1-tarp shallow Very High Barrier	2/6/97	Madera	350	19	0.99	30
24: Sanders, 1997b	8.1-tarp shallow Very High Barrier	7/28/97	Monterey	240	12	0.23@25ft	200/30
25: “		8/1/97			10	0.44@60ft	200/30
26: Segawa and Sanders, 1997	8.1-tarp shallow Very High Barrier	9/25/97	Santa Cruz	210	10	0.054	60
“	tarp removal	10/25/97	“	“	8	0.042@30ft	50
27: Hicks, 1993c	9-tarp bed	7/13/93	SLO	256	9	0.092@30ft	110
28: Wofford and Segawa, 1998c	9.1-tarp bed (Colby)	9/8/97	Orange	160	4	0.17@20ft	30
29: Sanders, 1997a	10-tarp bed (Kenco)	12/12/96	Riverside	200	20	0.57	470
30: Wofford and Segawa, 1998d	10-tarp bed (Kenco)	12/17/97	Riverside	196	16	0.59@625ft	420

Table H1. (continued)

Application Monitored and Study ID	Permit Condition Application Method	Date Applied	County	Applic Rate (lb/ac)	Acres	24-hr Max Conc @ Buffer (ppm)[a]	Perm Cond Buffer (ft)[b]
31: Gillis, 1992	11-tarp deep	11/9/92	Merced	405	7	0.06@300ft	300
32: Sanders, 1997a	12-tarp bed (hot gas)	12/11/96	Riverside	200	25	1.7@330ft	550
33: Sanders, 1997a	12-tarp bed (hot gas)	1/20/97	Kern	200	14	0.16	360
34: Sanders, 1997a	12-tarp bed (hot gas)	1/27/97	Imperial	200	14	0.55	360
35: Kim and Segawa, 1998a	Virtually Impermeable-method 5	5/2/98	Orange	235	11	0.16@60ft	200
	Virtually Impermeable-method 5						
36: Kim and Segawa, 1998b	edge panels	6/5/98	Orange	234	1	0.066@30ft	100
37: "	normal	"	"	233	"	0.072@30ft	"
38: "	edge panels	6/7/98	"	220	"	0.065@30ft	"
39: "	normal	"	"	238	"	0.042@30ft	"

a/ Highest measured concentration at the buffer zone distance (some samplers not at buffer distance, as noted). Values as reported from the laboratory; S and TC studies are adjusted for lab recovery, EH studies are not adjusted for recovery.

b/ Buffer zone size required by permit conditions at the time of the monitoring. Some buffer zones were subsequently revised.

Additional monitoring conducted since 1996 indicated that air concentrations may also vary with other factors. However, there were insufficient data to show clear correlations. Of the 39 applications monitored, seven exceeded the 0.21 ppm target level at the buffer zone distance (Table H1, applications 23, 24, 25, 29, 30, 32, 34).[a] Tarpaulin-bedded applications and applications using “very high barrier” tarpaulins appeared to have higher air concentrations than originally assumed in the permit conditions. Of the seven tarpaulin-bedded applications monitored, four exceeded the 0.21 ppm target level at the original buffer zone distance. Of the five very high barrier tarpaulin applications monitored, three exceeded the target level at the original buffer zone distance. None of the other application methods exceeded the target level at the buffer zone distance. Applications monitored in inland areas of California exceeded the target level at the original buffer zone distance more frequently (5 of 15 applications), compared to coastal areas (2 of 24 applications). Applications monitored during winter months exceeded the target level more frequently (5 of 8 applications), compared to other seasons (2 of 31 applications). It is unclear if method of application, geographic area, or season exerts the greater influence on air concentrations.

The monitoring data indicated that while tarped applications had lower air concentrations than untarped applications, tarpaulin permeability (as measured in the laboratory) had little influence on air concentrations detected in the field. Five applications were monitored using “very high barrier” tarpaulins, with methyl bromide permeability approximately one-half the standard tarpaulin. Three of these exceeded the target concentration at the buffer zone distance (Table H1, applications 23 to 25). In addition, a series of field tests with a “virtually impermeable film” showed no difference in air concentrations between the virtually impermeable film and a standard tarpaulin (Table H1, applications 16 to19, 35 to 39). Other factors measured during the monitoring such as soil texture, soil moisture content, and air temperature did not show any correlations with air concentrations, or the correlations are masked by other factors.

Appendix H.2. Commodity Fumigation

DPR and commodity groups have also conducted air monitoring for post-harvest commodity fumigations. These types of fumigations are very different from field fumigations (see section **II.D. USAGE**) and methods of application vary widely, both in the types of enclosures used to contain the methyl bromide and in the methods of aerating the enclosures. Examples of enclosures used for fumigation include dedicated fumigation chambers, large food processing plants, wood bins covered with tarpaulins, and transportation containers. Examples of aeration methods include forced air exhaust stacks, opening doors, and removing tarpaulins. The amount of methyl bromide used for a single fumigation ranges from one pound to several thousand pounds. Air concentrations vary widely because of the variation in the methods of application and amounts of methyl bromide. Most of the monitoring was conducted for fumigations using larger amounts of methyl bromide (Table H2).

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[a] DPR revised the buffer zones in 1997 and 1998 to provide a higher margin of safety. Under the revised buffer zones, none of the 39 fields monitored exceed 0.21 ppm at the buffer zone distance.

The most complete off-site air concentration data came from chamber fumigations which are forcibly exhausted through stacks (Table H2). Off-site concentrations of methyl bromide during commodity fumigations depended on various conditions of the treatment and aeration. Off-site concentrations during a treatment in a sealed chamber were usually low, although at one site a 2-hour concentration of 1.8 ppm was detected 2 meters from a chamber (Radian Corp., 1992), indicating a leaky seal. Another study measured a maximum 12-hour concentration of 0.228 ppm 12 meters from a chamber during treatment. The highest concentrations were usually found during aeration, and is dependent on stack height, fan velocity and meteorological conditions during exhaust. During aeration, downwind concentrations were detected up to 250 meters away and a concentration of 6.8 ppm was measured 116 meters away in a 5 minute sample (Segawa *et al.*, 1992). Downwind concentrations from commodity fumigations seemed to decrease rapidly over time and crosswind distance. Concentrations away from the downwind plume decreased rapidly, but with a direct wind the plume could extend for several hundred meters.

Appendix H.3. Warehouse (Building) Fumigation

Very large warehouses and processing plants are fumigated using thousands of pounds of methyl bromide during each treatment (Segawa *et al.*, 1994a, Segawa *et al.*, 1994b and Segawa *et al.*, 1995). Several types of buildings were monitored, such as large cement-wall food processing plants, warehouses, mills, and corrugated metal buildings (Table H2). The construction of the building being fumigated made a large difference in the ability to contain the methyl bromide. As much as 70% of the applied methyl bromide leaked out of one metal building monitored during the first 24 hour of fumigation (Segawa *et al.*, 1994c) where a 20-hour concentration of 0.131 ppm was measured 152 meters from the building. Measurements of air concentration in a cement-wall warehouse indicated that at least 59% of the applied methyl bromide was retained during a 23-hour treatment period (Segawa *et al.*, 1994b). Increased retention during treatment normally caused higher concentrations of methyl bromide during aeration. Concentrations as high as 6.44 ppm were measured during the first hour of aeration 9.1 meters from one building. During aeration, concentrations exceeding the 0.21 ppm exposure level were detected as far as 262 meters from another warehouse.

Appendix H.4. Other Commodity Fumigations

Tarpaulin-covered commodities retained approximately 77% of the injected methyl bromide before aeration (Air Toxics Limited, 1993). Stacks attached to the tarped commodities assist in aeration, which showed a 64% loss over the first 2 hours. Measurable concentrations of methyl bromide were detected 1248 meters downwind from the application area. Containers used to ship products by truck, ship, or railroad are also used for methyl bromide fumigation. The transportation containers are usually aerated passively by opening the doors. During both applications monitored, measurable concentrations were still detected 15 meters downwind from the containers an hour after the doors were open (Radian Corp., 1992).

Table H2. Maximum methyl bromide air concentration from various commodity fumigations.

Type	Study ID	Date	Volume (ft^3)	Aeration method	Total MeBr (lbs)	Max conc. and distance from source (ppm)[a]	Furthest measured conc. (ppm)
Chamber	Segawa et al, 1992	5/21/92	21,280	Stack	64	0.235 for 30 min at 108m	same
Chamber	Segawa et al, 1992	6/1/92	16,000	Stack	50	1.005 for 5 min at 75m	0.031 for 5 min at 125m
Chamber	Segawa et al, 1992	6/5/92	14,000	Stack	30	0.786 for 5 min at 52m	0.11 for 5 min at 250m
Chamber	Segawa et al, 1992	6/23/92	16,000	Stack	50	0.012 for 5 min at 152m	same
Chamber	Segawa et al, 1992	6/25/92	18,000	Stack	45	6.79 for 5 min at 116m	0.375 for 5 min at 152m
Chamber	Radian Corp., 1992	8/11/92 8/17/92	15,000	Stack	12	1.8 for 120 min at 2m (fumigation)	0.10 for 15 min 50m
Chamber (2)	Wofford and Segawa, 1997	10/23/96	11,000 11,970	Stack	22 32	0.228 for 12 hr at 12m (fumigation)	0.009 for 12 hr at 22m (fumigation)
Warehouse	Wofford and Bennett, 1993	4/6/93	144,000	Doors	108	0.30 for 24 hr at 9.1m	same
Warehouse	Segawa et al, 1994a	10/15/93	6,800,000	Doors w/floor fans	7,350	5.522 for 2.3 hr at 104m	0.889 for 2.3 hr at 284m
Warehouse	Segawa et al, 1994a	10/20/93	3,100,000	Doors w/4 roof vents	2,975	3.17 for 2 hr at 100m	0.528 for 2 hr at 314m
Processing plant	Segawa et al, 1994b	4/8/93	1,450,000	Doors w/3 roof vents	2,175	14.98 for 15 min at 9.1m	12.93 for 15 min at 30m
Processing plant	Segawa et al, 1994c	5/28/93	320,000	Doors	700	1.041 for 7 hrs at 9.1m (fumigation)	0.301 for 7 hrs at 152m fumigation)

Table H2. Maximum methyl bromide air concentration from various commodity fumigations (cont.).

Type	Study ID	Date	Volume (ft^3)	Aeration method	Total MeBr (lbs)	Max conc. and distance from source (ppm)[a]	Furthest measured conc. (ppm)
Processing plant	Segawa et al, 1995	6/5/93	2,600,000	Roof fans	5,325	0.575 for 2.7 hr at 9.1m	0.107 for 2.7 hr at 116m
Processing plant	Segawa et al, 1995	6/12/93	2,160,000	Roof fans	4,320	1.403 for 12 hr at 9.1m (fumigation)	0.008 for 9 hrs at 52m (fumigation)
Tarped commodity	Air Toxics Limited, 1993	4/13/93	5(53,975) 1(46,750)	Stack	1,262	5.4 for 30 min at 15m	0.0015 for 2 hr at 1248m
Transport containers	Radian Corp., 1992	8/6/92	2,200	Doors	5	1.2 for 2 min at 15m	same
Transport containers	Radian Corp., 1992	10/1/92	2,200	Doors	6	0.84 for 16 min at 18m	same

a/ All concentrations measured during aeration period unless otherwise noted.