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MEMORANDUM

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DATE: April 29, 2010

SUBJECT: METHYL IODIDE (IODOMETHANE) MITIGATION EVALUATION AND OPTIONS

Summary

The Department of Pesticide Regulation's (DPR's) risk assessment for methyl iodide describes several exposure scenarios of concern, including exposure to bystanders. DPR's Environmental Monitoring Branch (EMB) staff evaluated several alternatives to reduce methyl iodide bystander exposure to acceptable levels. The evaluation included an assessment of fumigations using virtually impermeable film (VIF) to suppress emissions. EMB staff found that three methyl iodide studies using VIF likely underestimate the air concentrations and flux, and use poor methodology, as indicated by the quality control results. In addition, the studies did not include measurements during tarp cutting or removal. Despite the study problems, changing from standard tarps to VIF likely reduces methyl iodide flux 30–40 percent (%). The registrant (Arysta LifeScience North American Corporation; Arysta) estimates a 68% reduction due to VIF based on the studies. EMB staff estimated buffer zones for various application methods. Restrictions to mitigate potential groundwater contamination by iodide breakdown product may be needed.

Background

Methyl iodide is a soil fumigant pesticide used prior to planting agricultural fields for controlling a variety of pests including weeds, nematodes, insects, and diseases. DPR is considering four products for registration: Midas EC Gold (33% methyl iodide, 62% chloropicrin); Midas 33:67 (33%methyl iodide, 67% chloropicrin); Midas 50:50 (50% methyl iodide, 50% chloropicrin); and Midas 98:2 (98% methyl iodide, 2% chloropicrin). This evaluation does not address mitigation of chloropicrin. DPR's risk assessment for methyl iodide describes several exposure scenarios of concern, including exposure to bystanders. EMB staff evaluated various options to reduce bystander exposure to methyl iodide. Due to its volatility, the main route of exposure is inhalation. Similar to mitigation for other fumigants, the primary measures to reduce bystander exposure is to modify application methods and/or implement buffer zones. Both mitigation measures are normally based on air monitoring data, specifically studies that determine the flux or emission rate from treated fields. Flux estimates are used in conjunction with weather data and computer modeling to estimate downwind air concentrations for various scenarios. For methyl iodide, Arysta conducted several studies that include VIF to reduce flux. As potential mitigation measures, the VIF studies were not previously reviewed or included in the risk assessment.

Virtually Impermeable Film Study Reviews

Arysta conducted three studies that included direct and indirect flux measurements for methyl iodide applications that use VIF. Methyl iodide was applied with a Symmetry tractor using a bed-shank method, and three different VIF tarps. Studies were done in Dover, Florida, January 2007; Bainbridge, Georgia, March 2007; and Hart, Michigan, May 2007. While out of state, the study conditions were similar to California. Arysta determined that these three studies had an average peak 24-hour flux of 11 ug/m^2-sec normalized to a 100 lbs/acre application rate (8.5% of the amount applied). In comparison, three other Arysta studies of a standard tractor rig and standard tarp had an average peak 24-hour flux of 74 ug/m^2-sec normalized to a 100 lbs/ac application rate (57% of the amount applied). Arysta believes these studies demonstrate that Symmetry and VIF combined reduce methyl iodide flux by 85 percent (difference between 74 and 11 ug/m^2-sec) and that 80% of the reduction is due to VIF. Arysta estimates that VIF reduces flux by 68% compared to standard tarps.

Environmental Monitoring Branch's Staff Review of the Three Methyl Iodide Virtually Impermeable Film Studies Indicates Several Major Issues

Breakthrough–There appears to be significant breakthrough from the front sampling bed to the back sampling bed. Not all back sections were analyzed. Arysta believes this is due to contamination of the back sections during storage. Arysta provided additional information for this explanation, but the data are not conclusive. Specifically, some of the front and back sections were stored together and analyzed at the same time. It is unlikely that the back sections were contaminated, but the front sections were not. No field blanks were collected that would provide conclusive evidence of contamination.

Spikes and recovery adjustment–The lab spikes were prepared in an unusual manner and do not indicate method performance. Trapping efficiency and field spikes were variable, ranging from 64% to 86% recovery. The trapping efficiency tests may overestimate recoveries because they were run for 6 hours. Most field samples were run for 12 hours. Field sample results were not adjusted for trapping efficiency or field spike recoveries.

Storage stability - Storage stability results were variable, with recoveries ranging from 47% to 76% after one week. Sample extracts of back sections were held much longer than the storage stability test duration.

Field results–Some results were atypical. Highest concentrations for methyl iodide and chloropicrin sometimes occurred at different locations. The unusual results may be due to poor sampler placement. Some of the chloropicrin results were very unusual and cannot be used to determine the flux. The tarps were not cut or removed during the studies. The flux calculations were not checked.

EMB staff found that the studies likely underestimate the air concentrations and flux, and used poor methodology.

Virtually Impermeable Film Flux Estimation

Despite the problems with the studies, it is possible to use them to estimate the maximum possible flux for VIF applications. EMB staff have not verified the flux calculations, but even if there are some errors, they would have little or no impact on the relative adjustments described below. Table 1 shows the fluxes estimated by Arysta.

Table 1. Methyl iodide flux estimated by Arysta for Symmetry bed-shank VIF method, assuming 100 lbs/acre application rate (Exponent memo dated 2/1/10).

Study	**24-hr peak flux for 100 lbs/ac app rate**			**Total flux (lbs/ac and % of applied)**
	ug/m^2-sec	**lbs/ac-day**	**% of applied**	
FL	15.6	12	12	29
GA	10.9	8.4	8.4	23
MI	6.5	5.0	5.0	33
Average	11.0	8.5	8.5	28
Max possible flux estimated by DPR*	38.9	30	30	100

*Max possible flux estimated by adjusting the average measured flux by 3.57x, increasing the total flux from 28 to 100% of the amount applied and increasing the 24-hour peak flux from 8.5 to 30% of the amount applied.

A reliable adjustment to account for breakthrough, spike recoveries, and storage stability cannot be determined. A maximum worst-case flux can be estimated by assuming that the total flux is 100% of the amount applied. For example, if the application rate is 100 lbs/acre, the total flux is 100 lbs/acre over the entire 6-day study period. This is 3.57x higher than the 28 lbs/acre total flux estimated by Arysta as the average for the three VIF flux studies. Applying the same 3.57x adjustment factor increases the average 24-hour peak flux value from 11.0 ug/m^2-day (8.5 lbs/acre or 8.5% of the amount applied) to 38.9 ug/m^2-day (30 lbs/ac-day or 30% of the amount applied). The maximum worst-case 24-hour peak flux for methyl iodide applied with the bed-shank method using a Symmetry rig and VIF is 30 percent of the amount applied. For comparison, Table 2 shows the fluxes estimated by Arysta (and verified by EMB staff) for the other studies.

Table 2. Methyl iodide flux estimated by Arysta (and verified by EM, except as noted) for all studies.

Location	**Fumigation Method**	**Peak 24-hr Flux (% of applied)**	**Total Flux (% of applied)**
Manteca, CA	Broadcast-shank, std tarp	51	93
Watsonville, CA	Broadcast-shank, std tarp	35	57
Guadalupe, CA	Bed-shank, std tarp	60	96
Oxnard, CA	Bed-shank, std tarp	54	102
Plant City, FL*	Bed-shank, std tarp	56	71
Camarillo, CA	Drip, std tarp	50	83
La Selva Beach, CA	Drip, std tarp	42	62
Guadalupe, CA	Drip, std tarp	71	100
Average	Broadcast-shank, std tarp	43	75
Average	Bed-shank, std tarp	56	98
Average	Drip, std tarp	54	82
Average (estimated by Arysta)	Bed-shank, Symmetry, VIF	8.5	28
Average (estimated by EM)	Bed-shank, Symmetry, VIF	30	100

* Plant City flux not included in the average due to rainfall and other problems with the study. However, this makes little or no difference in the average flux estimate.

The average 24-hour peak flux from two bed-shank studies (Guadalupe and Oxnard) that used standard tractor rigs and standard tarps was 56% of the amount applied (74 ug/m^2-sec for a 100 lbs/ac application rate). Therefore, the combined effect of the Symmetry rig and VIF reduced the 24-hour peak flux from 56% of the amount applied to no more than 30% of the amount applied (74 ug/m^2-sec to 39 ug/m^2-sec). The difference between the two values is a 47% reduction in flux. The relative contribution of the Symmetry rig and VIF to flux reduction cannot be determined with the available data, but the majority of the reduction is likely due to

VIF. Changing from standard tarps to VIF (without Symmetry rig) may reduce methyl iodide flux between 30 and 40%.

All of these estimates are consistent with the variation in the apparent VIF reduction for other fumigants. Arysta provided a list of VIF studies for other fumigants, but most of these studies used chambers or other unacceptable methods to measure flux (Arysta note dated February 24, 2010). Similarly, tarp permeability data provided by Arysta cannot be used to estimate flux under field conditions. Lab permeability measurements indicate that VIF flux should be several orders of magnitude lower than standard tarps. Field studies show less than 10x reduction. Table 4 summarizes the flux reduction measured for other field studies that likely used acceptable flux measurement methods. Complete reports are not yet available, so none of these studies have been reviewed or accepted.

Table 4. Approximate flux reduction from other VIF field studies. Reduction based on difference between two nearby simultaneous plots, one with standard tarp and one with VIF.

Location/Year	**Fumigant**	**Fumigation Method**	**VIF Reduction of Peak Flux (%)**
Santa Maria 2006	Chloropicrin	Drip VIF	68
Salinas 2007	Chloropicrin	Drip VIF	88
Oxnard 2007	1,3-D	Drip VIF	44
Oxnard 2007	Chloropicrin	Drip VIF	70
Salinas 2008	Methyl bromide	Drip TIF*	37
Salinas 2008	Chloropicrin	Drip TIF*	33
Wasco 2009	Methyl bromide	Broadcast shallow shank TIF*	66
Wasco 2009	Chloropicrin	Broadcast shallow shank TIF*	19
Ventura 2009	1,3-D	Broadcast shallow shank TIF*	25
Ventura 2009	Chloropicrin	Broadcast shallow shank TIF*	44

* TIF – totally impermeable film

Flux estimates for all fumigation methods

EMB previously reviewed and verified Arysta’s flux estimates for the standard fumigation methods. EMB’s review of the VIF studies are described above. Table 5 summarizes the flux estimates, including various assumptions of the reduction due to VIF.

Table 5. Estimates of flux for each fumigation method and various assumptions of reduction due to VIF.

Fumigation Method	Flux with Standard Tarp (% of applied)	Flux with 30% VIF Reduction (% of applied)	Flux with 40% VIF Reduction (% of applied)	Flux with 50% VIF Reduction (% of applied)
Broadcast-shallow shank	43	30	26	22
Bed-shallow shank	56	39	34	28
Drip	54	38	32	27
Auger probe	Not determined	Not determined	Not determined	Not determined

Buffer zones

EMB staff calculated approximate buffer zones for several application methods, with standard tarps and with VIF. Buffer zones were calculated with the PERFUM model. The PERFUM model buffer zones are the 95th percentile maximum direction buffer zones calculated using mean flux profiles and 5 years of Ventura weather data. Flux profiles developed by Arysta for each of the seven accepted studies were used (Table 2). The mean flux profiles were developed for each application method as follows: (1) each flux profile used was aligned with 0800 hours and (2) the flux for each hour was averaged. The average flux profile was input into PERFUM and the 95th percentile maximum direction buffer zone for desired application rates of each application method were determined. The buffer zone distances using PERFUM for a 24-hour target concentration of 32 parts per billion (ppb) (C. Andrews, personal communication) are shown in Attachment 1.

Buffer zones for auger probe applications (tree and vine replacement) cannot be determined due to lack of monitoring data. It is likely that the flux is approximately the same as a standard shallow shank injection method. Auger probe applications are deeper than shallow shank (12 inches versus. 18-24 inches), but without a tarp. The label does not clearly state the number of applications allowed. It appears that the maximum number is 53 sites and 106 pounds per acre (2 pounds per injection site, and injection site every 100 square feet). Determining the appropriate buffer zone is more difficult than the other application methods due to the uneven number of sites treated across a field. There are at least three buffer zone alternatives for auger probe applications. (1) Use the same buffer zones as broadcast-shallow shank or bed-shallow shank applications, (2) Limit the number of auger probe applications, and (3) Establish the same buffer zone around each individual injection site.

The monitoring data indicates that peak concentrations occur within the first two days of fumigation, and flux is minimal on later days, including the day standard tarps are cut. Air concentrations at the edge of treated areas should be less than the 32 ppb target concentration two days after fumigation. The 48-hour buffer zone duration specified on labels should be sufficient, assuming the flux is minimal when VIFs are cut (see next section).

DPR's methyl bromide regulations specify that two nearby fumigations should be combined to determine the buffer zone, if the fumigations are separated by less than 1320 feet (1/4 mile) or 36 hours. EMB staff determined this separation distance based on consistency of wind direction and the probability of the plumes from two 40-acre fields would overlap a significant period of time. Air concentrations should be less than the 32 ppb target concentration with the same separation requirements, assuming the treated field size is no more than 40 acres. The proposed label requirement to prohibit overlapping buffer zones would likely provide adequate separation if the minimum buffer zone is large enough and the field size is less than 40 acres.

Virtually Impermeable Film Tarp Cutting and Removal

The other main shortcoming with the VIF studies is the lack of measurements during tarp cutting and removal, for both flux and worker exposure. Several of the VIF studies listed above show a secondary peak of emissions when tarps are cut. Buffer zones or worker protection measures may be needed when tarps are cut. Arysta provided air concentration measurements under VIF from a separate study (Arysta memorandum dated March 14, 2010). These data have minimal value due to small plot size, unusual methods to measure air concentrations, and lack of quality control data. Air concentrations under the tarps reached no detectable levels ten days after application for each of the seven types of VIF measured. Two studies monitored both soil concentrations and air concentrations following applications using standard tarps. Emission rates were also estimated. Those results are discussed in a separate memoranda by Barry dated April, 29, 2010 and indicate that after 14 days for a standard tarp application that both soil concentrations and emissions are minimal. It is possible that the half-life of MeI in the soil will be longer for applications using VIF tarps. A longer soil half-life may lead to higher emission rates when the tarp is cut and/or removed.

Groundwater

As described in the risk assessment, EMB's evaluation indicates virtually no possibility of groundwater contamination by methyl iodide. The groundwater contamination by the iodide anion breakdown product is uncertain due to the lack of adequate field dissipation data, but potentially high based on a conservative mass-balance calculation. Use of VIF could increase the retention of methyl iodide and amount of iodide in the soil, causing higher groundwater concentrations than estimated in the risk assessment. Any groundwater contamination would take years to occur. An adequate field dissipation study would provide data to better estimate groundwater concentrations, followed by mitigation measures if needed. Alternatively, mitigation measures could be implemented immediately. Mitigation measures should include buffer zones around wellheads, and irrigation restrictions in ground water protection areas.

Attachment 1–Estimated Buffer Zone Distances

Methyl iodide buffer zone distances (feet) for **32 ppb**, 24-hour exposure.
Buffers calculated using PERFUM model and Ventura weather data.
Buffers longer than 4723 feet (1440 meters) estimated by extrapolation.
Distances represent the 95th percentile in the maximum direction.
Broadcast-shallow shank fumigation method.
Flux is average of Manteca and Watsonville studies (43% of applied amount for peak 24 hrs).

Table 1-1. Broadcast-shallow shank method with standard tarp

Broadcast app rate (lbs MeI/acre)	Buffer Zone (feet) for Various Field Sizes					
	1 acre	5 acres	10 acres	20 acres	30 acres	40 acres
51	67	296	480	793	1,034	1,269
75	162	532	841	1,318	1,665	2,055
100	236	734	1,154	1,788	2,241	2,770
125	319	937	1,464	2,239	2,782	3,443
176	462	1,306	2,031	3,075	3,795	4,704

Table 1-2. Broadcast-shallow shank with VIF (30% flux reduction)

Broadcast app rate (lbs MeI/acre)	Buffer Zone (feet) for Various Field Sizes					
	1 acre	5 acres	10 acres	20 acres	30 acres	40 acres
50	14	162	274	489	666	811
75	92	360	578	937	1,207	1,485
100	166	546	863	1,352	1,707	2,107
125	227	705	1,108	1,717	2,151	2,659
175	343	1,009	1,577	2,411	2,995	3,708

Table 1-3. Broadcast-shallow shank with VIF (40% flux reduction)

Broadcast app rate (lbs MeI/acre)	Buffer Zone (feet) for Various Field Sizes					
	1 acre	5 acres	10 acres	20 acres	30 acres	40 acres
50	13	150	255	455	619	754
75	70	310	503	830	1,082	1,328
100	129	470	750	1,201	1,535	1,891
125	211	656	1,031	1,597	2,001	2,473
175	319	937	1,464	2,239	2,782	3,443

Table 1-4. Broadcast-shallow shank with VIF (50% flux reduction)

Broadcast app rate (lbs MeI/acre)	Buffer Zone (feet) for Various Field Sizes					
	1 acre	5 acres	10 acres	20 acres	30 acres	40 acres
50	12	93	170	340	489	590
75	65	289	469	774	1,009	1,239
100	121	439	700	1,120	1,433	1,765
125	180	591	934	1,465	1,849	2,283
175	289	870	1,363	2,095	2,612	3,232

Methyl iodide buffer zone distances (feet) for **32 ppb**, 24-hour exposure.
Buffers calculated using PERFUM model and Ventura weather data.
Buffers longer than 4723 feet (1440 meters) estimated by extrapolation.
Distances represent the 95th percentile in the maximum direction.
Bed-shallow shank fumigation method.
Flux is average of Guadalupe and Oxnard studies (57% of applied amount for peak 24 hrs).

Table 1-5. Bed-shallow shank method with standard tarp

Broadcast app rate (lbs MeI/acre)	**Buffer Zone (feet) for Various Field Sizes**					
	1 acre	**5 acres**	**10 acres**	**20 acres**	**30 acres**	**40 acres**
50	157	588	965	1,507	2,273	2,418
75	300	951	1,502	2,198	3,315	3,527
100	417	1,275	1,993	2,865	4,321	4,597
125	538	1,575	2,432	3,422	5,160	5,489
176	754	2,140	3,274	4,528	6,827	7,262

Table 1-6. Bed-shallow shank with VIF (30% flux reduction)

Broadcast app rate (lbs MeI/acre)	**Buffer Zone (feet) for Various Field Sizes**					
	1 acre	**5 acres**	**10 acres**	**20 acres**	**30 acres**	**40 acres**
50	81	397	684	1,145	1,728	1,839
75	198	698	1,132	1,731	2,611	2,778
100	308	976	1,541	2,254	3,400	3,617
125	401	1,224	1,913	2,751	4,148	4,413
175	579	1,696	2,619	3,685	5,557	5,911

Table 1-7. Bed-shallow shank with VIF (40% flux reduction)

Broadcast app rate (lbs MeI/acre)	**Buffer Zone (feet) for Various Field Sizes**					
	1 acre	**5 acres**	**10 acres**	**20 acres**	**30 acres**	**40 acres**
50	76	369	636	1,065	1,607	1,710
75	168	630	1,034	1,614	2,435	2,591
100	261	884	1,419	2,134	3,219	3,425
125	357	1,133	1,788	2,617	3,946	4,198
175	538	1,575	2,432	3,422	5,160	5,489

Table 1-8. Bed-shallow shank with VIF (50% flux reduction)

Broadcast app rate (lbs MeI/acre)	**Buffer Zone (feet) for Various Field Sizes**					
	1 acre	**5 acres**	**10 acres**	**20 acres**	**30 acres**	**40 acres**
50	41	299	543	971	1,466	1,560
75	157	588	965	1,507	2,273	2,418
100	244	825	1,324	1,992	3,005	3,197
125	333	1,057	1,669	2,442	3,683	3,919
175	497	1,482	2,301	3,267	4,926	5,240

Methyl iodide buffer zone distances (feet) for **32 ppb**, 24-hour exposure.
Buffers calculated using PERFUM model and Ventura weather data.
Buffers longer than 4723 feet (1440 meters) estimated by extrapolation.
Distances represent the 95th percentile in the maximum direction.
Drip fumigation method.
Flux is average of Camarillo, La Selva, Guadalupe studies (54% of applied amount for 24 hrs).

Table 1-9. Drip with standard tarp

Broadcast app rate (lbs MeI/acre)	Buffer Zone (feet) for Various Field Sizes					
	1 acre	5 acres	10 acres	20 acres	30 acres	40 acres
51	47	175	340	530	707	878
75	116	346	588	911	1,173	1,451
100	170	486	805	1,245	1,591	1,966
125	230	634	1,018	1,572	1,991	2,457
176	334	896	1,409	2,174	2,734	3,371

Table 1-10. Drip with VIF (30% flux reduction)

Broadcast app rate (lbs MeI/acre)	Buffer Zone (feet) for Various Field Sizes					
	1 acre	5 acres	10 acres	20 acres	30 acres	40 acres
50	9	79	198	311	437	546
75	65	221	408	634	834	1,035
100	119	355	603	934	1,203	1,488
125	163	467	773	1,195	1,527	1,887
175	248	682	1,097	1,693	2,144	2,646

Table 1-11. Drip with VIF (40% flux reduction)

Broadcast app rate (lbs MeI/acre)	Buffer Zone (feet) for Various Field Sizes					
	1 acre	5 acres	10 acres	20 acres	30 acres	40 acres
50	8	74	184	289	406	508
75	49	184	356	555	740	919
100	92	295	528	819	1,069	1,325
125	152	434	719	1,112	1,420	1,755
175	230	634	1,018	1,572	1,991	2,457

Table 1-12. Drip with VIF (50% flux reduction)

Broadcast app rate (lbs MeI/acre)	Buffer Zone (feet) for Various Field Sizes					
	1 acre	5 acres	10 acres	20 acres	30 acres	40 acres
50	7	29	127	202	305	384
75	46	171	332	518	690	858
100	86	276	492	764	998	1,236
125	129	384	654	1,012	1,304	1,612
175	192	538	875	1,351	1,717	2,120