Staff Report

Use Information and Air Monitoring Recommendation for the Pesticide Active Ingredients 1,3-Dichloropropene and Methyl Bromide

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USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR THE PESTICIDE ACTIVE INGREDIENTS 1,3-DICHLOROPROPENE AND METHYL BROMIDE

A. BACKGROUND

This recommendation contains general information regarding the physical-chemical properties and the historical uses of 1,3-dichloropropene and methyl bromide. The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

1,3-Dichloropropene

Table 1 describes some of the physical-chemical properties of 1,3-dichloropropene.

Table 1. Some Physical-Chemical Properties of 1,3-dichloropropene.

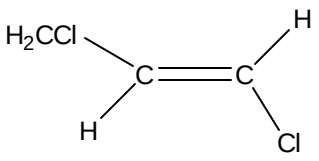
Chemical name	(*EZ*)-1-3-dichloropropene
Common name	1,3-dichloropropene
Some tradenames[†]	Telone II, Tri-Form
CAS number	542-75-6
Molecular formula	$C_3H_4Cl_2$
Molecular weight	111.0
Form	Colorless-to-amber liquid with sweet penetrating odor (Tomlin, 1997)
Solubility	Water: 2 g/L at 20°C (Tomlin, 1997)
Vapor pressure	3.43×10^{1} mmHg at 25°C (Kollman and Segawa, 1995)
Henry's Law Constant (KH)	2.29×10^{-3} atm-m^3/ mole at 25°C (Kollman and Segawa, 1995)
Soil adsorption Coefficient (Kd)	3.91×10^{-1} g/cm^3 (Kollman and Segawa, 1995)
Aerobic soil metabolism half-life	11.5 to 53.9 days (Kollman and Segawa, 1995)
Anaerobic soil metabolism half-life	2.5 days at 25°C (Tomlin, 1997)

The technical product is a mixture of approximately equal quantities of (*E*)- and (*Z*)- isomers (figures 1a and 1b), of which the (*Z*) isomer is more nematicidally active (Tomlin, 1997). In soil, 1,3-dichloropropene undergoes hydrolysis to the respective 3-chloroallyl alcohols and is considered non

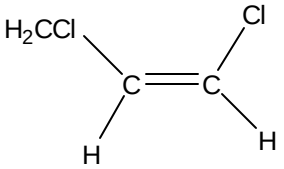
[†] Disclaimer: The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

persistent. The chemical is phytotoxic to plants and is rapidly metabolized to normal plant constituents (Tomlin, 1997).

Figure 1. The chemical structures of the 1,3-dichloropropene isomers.



(a) E-1-3-dichloropropene



(b) Z-1-3-dichloropropene

1,3- Dichloropropene is reported to hydrolyze to 3-chloro-2-propen-1-ol, which may be biologically oxidized to 3-chloropropenoic acid (Montgomery, 1997). Breakdown of this chemical eventually yields carbon dioxide (Connors *et al*., 1990). Chloroacetaldehyde, formyl chloride, and chloroacetic acid are formed from the ozoneation of 1,3-dichloropropene at 25°C and 730 mmHg (Tuazon et al., 1984).

1,3-Dichloropropene has an LC_{50} (96 hour) of 3.9 mg/L for rainbow trout and 7.1 mg/L bluegill sunfish. It is nontoxic to bees, with an oral and contact LD_{50} (90 hour) of 6.6 µg/bee (Tomlin, 1994).

Methyl Bromide

Table 2 describes some of the physical-chemical properties of methyl bromide.

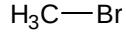
Table 2 Some Physical-Chemical Properties of methyl bromide.

Chemical name	Bromomethane
Common name	Methyl bromide
Some tradenames	Metabrom, Terr-O-Gas 75
CAS number	74-83-9
Molecular formula	CH_3Br
Molecular weight	94.9
Form	Non-flammable, colorless, odorless gas at room temperature (Tomlin, 1997).
Solubility	Water: 17.5 g/L at 20°C (Tomlin, 1997)
Vapor pressure	190 kPa at 20°C (Tomlin, 1997).
Henry's Law Constant (KH)	1.61 x 10^3 atm-m^3/ mole at 25°C (USDA, 1995).
Soil adsorption Coefficient (Kd)	3.45- 9.4 g/cm^3 (Kollman and Segawa, 1995).
Aerobic soil metabolism half-life	.15- 17 days (Kollman and Segawa, 1995).

Anaerobic soil metabolism half-life	1.63- 6.0 days (Kollman and Segawa, 1995).

Methyl bromide (figure 2) readily evaporates at temperatures normally encountered during fumigation, but some of the chemical may become entrapped in soil microspores following application (EXTOXNET, 1996). Transformation of methyl bromide to bromide increases as the amount of organic matter in the soil increases. Methyl bromide hydrolyzes in water forming methane and hydrobromic acid with an estimated hydrolysis half-life of 20 days at water temperature of 25°C and pH 7 (Montgomery, 1997).

Figure 2. The chemical structure of methyl bromide.



methyl bromide

Methyl bromide is moderately toxic to fish with an LC_{50} (96 hour) of 3.9 mg/L. It is nontoxic to bees when used as recommended.

B. CHEMICAL USES

1,3-Dichloropropene

As of May 2000, eleven products containing 1,3-dichloropropene were registered for use in California. 1,3-Dichloropropene is a multi-purpose liquid fumigant used to control nematodes, wireworms, and certain soil borne diseases in cropland. It is used for pre-planting control of most species of nematode in deciduous fruit and nuts, citrus fruit, berry fruit, vines, strawberries, hops, field crops, vegetables, tobacco, beet, pineapples, peanuts, ornamental and flower crops, tree nurseries, etc. It also has secondary insecticidal and fungicidal activity (Tomlin, 1994).

In California's agricultural setting, growers primarily use 1,3-dichloropropene on carrots, sweet potatoes, wine grapes, and for preplant soil preparation. 1,3-Dichloropropene recommended label use rates range from 9 to 55 gallons per acre depending on soil type or texture for a broadcast application and 26 to 162 fluid ounces per 1000 feet of row per outlet depending on soil type or texture.

The 1,3-dichloropropene product label offers methods for application, including: broadcast (using chisel, offset swing shank, Nobel plow or plow-sole application equipment) and row application. Immediately after application, the soil must be "sealed" to prevent fumigant loss and to ensure that an effective concentration of fumigant is maintained within the soil for a period of several days. 1,3-Dichloropropene is available as a liquid fumigant, is a restricted use pesticide due to its high acute inhalation toxicity and carcinogenity, and includes the Signal Word "Warning" on the label.

Methyl bromide

As of May 2000, fifty-four products containing methyl bromide were registered for use in California. Methyl bromide is a multi purpose fumigant used for insecticideal, acaricidal, and rodenticidal control in mills, warehouses, grain elevators, ships, etc., stored products, soil fumigations, greenhouses, and mushroom houses. In field fumigations it is used to treat a wide range of insects, nematodes, soil-borne diseases, and seed weeds.

In California's agricultural setting, growers primarily use methyl bromide on strawberries, almonds, and sweet potatoes. Methyl bromide recommended label use rates range from 1 to 20 pounds per 1000 cubic feet for non-food products, 0.2-9 pounds per 1000 cubic feet for structures associated with raw or processed commodities, 1 to 2 pounds per 1000 cubic feet for processed foods, and 1.5 to 9 pounds per 1000 cubic feet for raw agricultural commodities. The methyl bromide product label recommends use rates of 1.5 to 3 pounds active ingredient per 100 cubic feet for almonds and strawberries and 2 to 4 pounds 100 cubic feet for sweet potatoes (where fumigations below 70°F may result in damage). The label for methyl bromide also lists tolerances (ppm) and exposure times for raw agricultural commodities and processed foods. For structures and non-food products exposure times are listed. For field pre-plant applications of methyl bromide, the label suggests using 240-320 pounds per acre and waiting two weeks after the exposure period before introducing transplants or vegetative plant parts and waiting 96 hours before planting crop seeds. Methyl bromide is odorless, except at high concentrations, and is generally used with a warning agent such as chloropicrin.

The methyl bromide product label offers several methods for application, including: chamber and vault fumigation, vacuum chamber fumigation, tarpaulin fumigation, warehouse, grain elevator, food processing plant, restaurant and other structures containing commodities, and shipboard fumigations. Methyl bromide is available as a gas fumigant, is a restricted use pesticide due to its acute toxicity, and includes the Signal Word "Danger" on the label.

With DPR's implementation of full pesticide use reporting in 1990, all users must report the agricultural use of any pesticide to their county agricultural commissioner, who subsequently forwards this information to DPR. DPR compiles and publishes the use information in the annual Pesticide Use Report (PUR). Because of California's broad definition for agricultural use, DPR includes data from pesticide applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way, postharvest applications of pesticides to agricultural commodities, and all pesticides used in poultry and fish production, and some livestock applications in the PUR. DPR does not collect use information for home and garden use, or for most industrial and institutional uses. The information included in this monitoring recommendation reflects widespread cropland applications of 1,3-dichloropropene and methyl bromide. Use rates were calculated by dividing the total pounds of each chemical used (where the chemical was applied to acreage) by the total number of acres treated.

According to the PUR, the total amount of 1,3-dichloropropene and methyl bromide used in California from 1996 to 1998 has ranged annually between slightly over 16,500,000 to over 17,500,000 pounds (Table 3). The majority of California's total use of these chemicals occurred in five counties—Monterey, Kern, Ventura, Merced, and Santa Cruz. On average the total use for the highest 15 counties in California made up 85% of the total use in California.

In California, growers use 1,3-dichloropropene primarily to control nematodes in carrots, sweet potatoes, preplant soil application and potatoes (Table 4). Table 6 displays the use of 1,3-dichloropropene by month in Monterey, Kern, Ventura, Merced, and Santa Cruz Counties. Methyl bromide is used primarily on strawberries, preplant soil applications, and outdoor container/ field grown plants (Table 5). Table 7 displays the use of methyl bromide by month in Monterey, Kern, Ventura, Merced, and Santa Cruz Counties. Use of these chemicals is difficult to predict as disease and nematode pressure is somewhat dependent on weather and other factors, such as cultural practices. However, assuming that no significant changes in weather occur, use is not expected to change.

Table 3. Annual Cropland Use of 1,3-Dichloropropene and Methyl Bromide by County (Pounds of Active Ingredient)

County	1996		1997		1998		Total
	1,3-dichloropropene	Methyl bromide	1,3-dichloropropene	Methyl bromide	1,3-dichloropropene	Methyl bromide	
MONTEREY	242,779	3,278,991	273,347	3,332,526	367,613	3,267,556	10,762,812
KERN	602,527	1,520,245	730,507	1,344,482	684,146	1,038,477	5,920,384
VENTURA	22,025	1,676,398	89,756	1,618,110	46,091	2,111,545	5,563,925
MERCED	144,223	1,381,889	85,805	1,255,093	288,513	999,915	4,155,438
SANTA CRUZ	62,129	1,053,817	50,155	1,100,498	67,448	1,109,563	3,443,610
FRESNO	270,836	853,518	228,256	1,049,669	192,733	707,337	3,302,349
SANTA BARBARA	5,458	905,182	19,651	983,246	58,379	1,025,058	2,996,974
SAN JOAQUIN	34,259	879,029	196,877	695,664	118,995	587,093	2,511,917
STANISLAUS	44,061	807,070	156,282	705,315	206,514	551,292	2,470,534
TULARE	79,782	716,703	90,718	947,699	198,622	374,598	2,408,122
RIVERSIDE	0	753,075	723	598,894	20,265	664,934	2,037,891
ORANGE	248	624,879	1,267	576,888	0	581,282	1,784,564
SAN DIEGO	5	587,681	23	554,463	3,415	439,391	1,584,978
IMPERIAL	259,682	165,954	265,340	189,949	364,962	233,510	1,479,397
LOS ANGELES	17	515,803	0	444,072	646	363,481	1,324,019
Total for Top 15 Counties	*1,768,031*	*15,720,234*	*2,188,707*	*15,396,568*	*2,618,342*	*14,055,032*	*51,746,914*
Percent of CA Total	*91*	*84*	*89*	*84*	*88*	*86*	*85*
Total Statewide Use	*1,950,684*	*18,727,175*	*2,457,881*	*18,294,606*	*2,980,930*	*16,362,548*	*60,773,824*

Table 4. Annual Cropland Use of 1,3- Dichloropropene by Commodity (Pounds of Active Ingredient)

Crop	1996	1997	1998	Total
CARROTS, GENERAL	730,564	929,297	923,379	2,583,240
SWEET POTATO	73,194	75,080	279,827	428,101
SOIL APPLICATION, PREPLANT-OUTDOOR (SEEDBED)	296,937	144,061	273,525	714,523
POTATO (WHITE, IRISH, RED, RUSSET)	93,724	264,134	169,057	526,915
GRAPES, WINE	24,036	99,350	150,468	273,854
CANTALOUPE	35,918	15,759	129,331	181,008
ALMOND	108,408	56,052	109,414	273,874
BRUSSELS SPROUTS	70,784	72,516	94,870	238,170
TOMATOES, FOR PROCESSING/CANNING	14,175	42,176	88,090	144,441
WALNUT (ENGLISH WALNUT, PERSIAN WALNUT)	15,257	26,291	62,276	103,824
OUTDOOR GROWN CUT FLOWERS OR GREENS	199	414	61,125	61,738
BROCCOLI	24,646	56,417	60,923	141,986
Total	*1,489,838*	*1,783,544*	*2,404,283*	*5,677,665*

Table 5. Annual Cropland Use of Methyl Bromide by Commodity (Pounds of Active Ingredient)

Crop	1996	1997	1998	Total
STRAWBERRY (ALL OR UNSPEC)	4,374,955	4,041,796	4,251,831	12,668,582
SOIL APPLICATION, PREPLANT-OUTDOOR (SEEDBED)	1,403,438	2,148,825	1,522,671	5,074,934
OUTDOOR CONTAINER/FIELD GROWN PLANTS	1,122,379	922,653	1,064,688	3,109,720
OUTDOOR GROWN TRANSPLANT	515,562	509,527	547,145	1,572,234
SWEET POTATO	611,586	766,042	541,923	1,919,551
ALMOND	613,743	881,792	502,949	1,998,484
GRAPES, WINE	1,480,701	897,380	478,272	2,856,353
OUTDOOR GROWN CUT FLOWERS OR GREENS	426,511	545,718	444,971	1,417,200
PEPPERS (FRUITING VEGETABLE), (BELL, CHILI, ETC.)	344,828	295,151	403,080	1,043,059
TOMATO	336,194	263,210	304,411	903,815
PEACH	248,082	287,120	280,028	815,230
GRAPES	299,627	569,054	273,836	1,142,517
Total	*11,779,602*	*12,130,265*	*10,617,803*	*34,521,679*

Table 6. Monthly Use of 1,3-Dichloropropene for 1996-1998 in Monterey, Kern, Ventura, Merced, and Santa Cruz Counties (Pounds of Active Ingredient)

Month	Monterey	Kern	Ventura	Merced	Santa Cruz	Total
January	1,911	33,168	1,591	1,816	0	38,486
February	38,750	240,842	9,902	11,207	1,082	301,783
March	62,785	107,009	40,623	149,818	4,720	364,955
April	77,376	36,105	27,974	86,803	22,980	251,238
May	169,759	24,765	24,259	61,943	99,926	380,652
June	111,724	90,681	2,006	0	26,641	231,052
July	30,717	589,512	1,636	0	2,656	624,521
August	20,041	271,511	35,660	185	5,829	333,226
September	38,431	17,248	2,015	0	7,049	64,743
October	79,253	189,594	1,106	19,847	3,590	293,390
November	187,546	274,863	11,094	123,190	4,753	601,446
December	65,447	141,882	6	63,733	507	271,575
Total	*883,740*	*2,017,180*	*157,872*	*518,542*	*179,733*	*3,757,067*

Table 7. Monthly Use of Methyl Bromide for 1996-1998 in Monterey, Kern, Ventura, Merced, and Santa Cruz Counties (Pounds of Active Ingredient)

Month	Monterey	Kern	Ventura	Merced	Santa Cruz	Total
January	63,440	379,271	15,556	463,855	4,602	926,724
February	52,240	249,662	32,160	638,968	9,857	982,887
March	142,934	309,359	125,890	557,505	27,244	1,162,932
April	92,483	134,745	218,149	413,841	62,018	921,236
May	204,725	45,906	212,633	139,518	57,281	660,063
June	475,446	98,449	575,527	29,885	52,534	1,231,841
July	684,920	370,021	694,969	69,678	133,677	1,953,265
August	1,473,668	629,830	1,975,388	91,752	476,961	4,647,599
September	2,729,203	566,764	1,357,077	127,428	1,190,349	5,970,821
October	2,894,964	237,378	118,854	155,292	1,067,609	4,474,097
November	1,037,011	501,930	58,124	277,586	176,728	2,051,379
December	28,014	379,888	21,725	671,588	5,020	1,106,235
Total	*9,879,048*	*3,903,203*	*5,406,052*	*3,636,896*	*3,263,880*	*26,089,079*

RECOMMENDATIONS

1. Ambient Air Monitoring

The historical trends in 1,3-dichlorpropene and methyl bromide use suggest that monitoring should occur over a two-month period during July and August in Kern County and September and October in Monterey or Santa Cruz County. Figures 5(a-b) display 1,3-dichlorpropene and methyl bromide use in Kern County during the period from July 1 through September 15 for 1996, 1997, and 1998. Figures 6(a-b) and Figures 7(a-b) display 1,3-dichlorpropene and methyl bromide use respectively in Monterey and Santa Cruz Counties during the period from September 1 through November 15 for 1996, 1997, and 1998. Attachments A and B display methyl bromide and 1,3-dichloropropene use by section in the Central Coast during 1997 and 1998. Attachments C and D display methyl bromide and 1,3-dichloropropene use by section in the Central Valley during 1997 and 1998. Six sampling sites should be selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). Monitoring for both chemicals should be simultaneous. Samples should be collected and analyzed for 1,3-dichloropropene and methyl bromide. At each site, 4 samples per week should be collected during the sampling period. Background samples should be collected in an area as distant as practical to applications of 1,3-dichloropropene and methyl bromide. Four replicate (collocated) samples are needed for each week of monitoring. The replicate samples may be collected at a single site over four days, or multiple sites for fewer days each week. Target 24-hour quantitation limits of at least 0.01 $\mu g/m^3$ for 1,3-dichloropropene and 0.4 $\mu g/m^3$ for methyl bromide are recommended.

Figure 3(a) 1,3-Dichloropropene Applications in Kern County

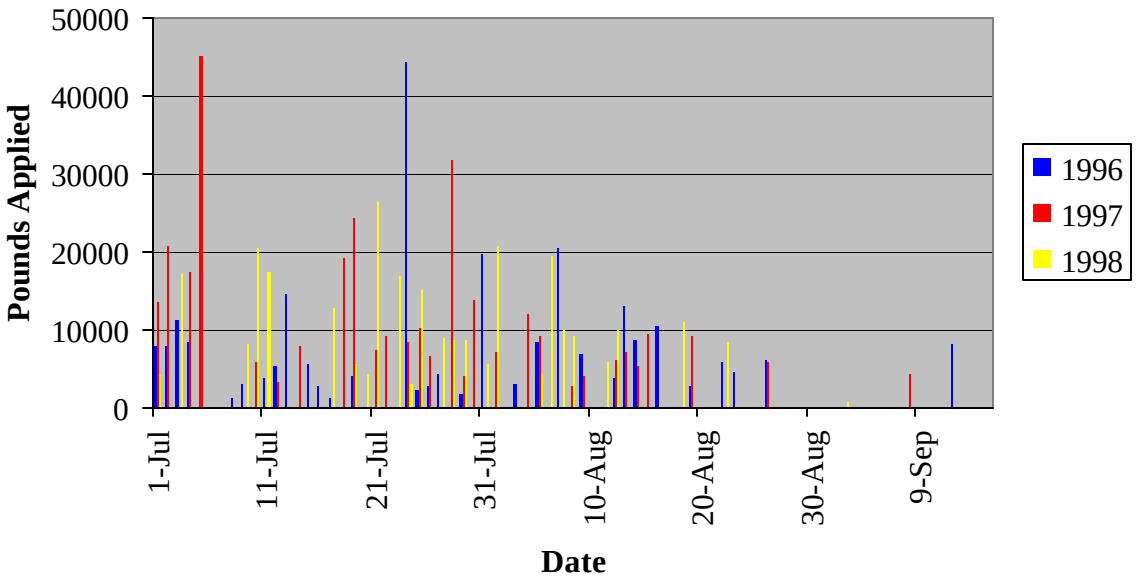
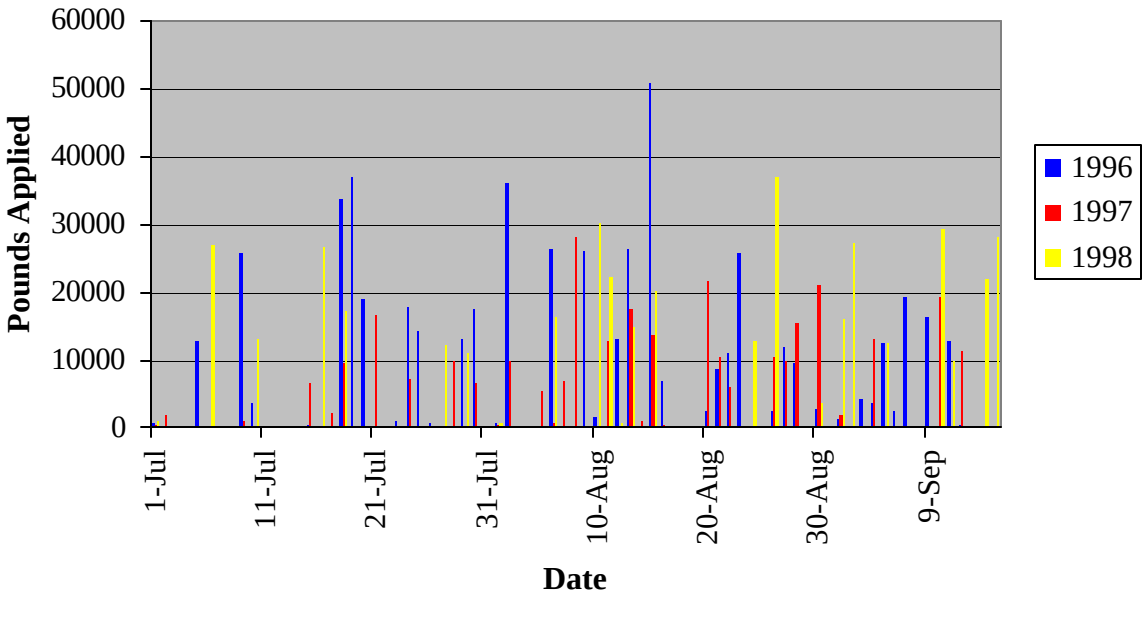


Figure 3(b) Methyl Bromide Applications in Kern County



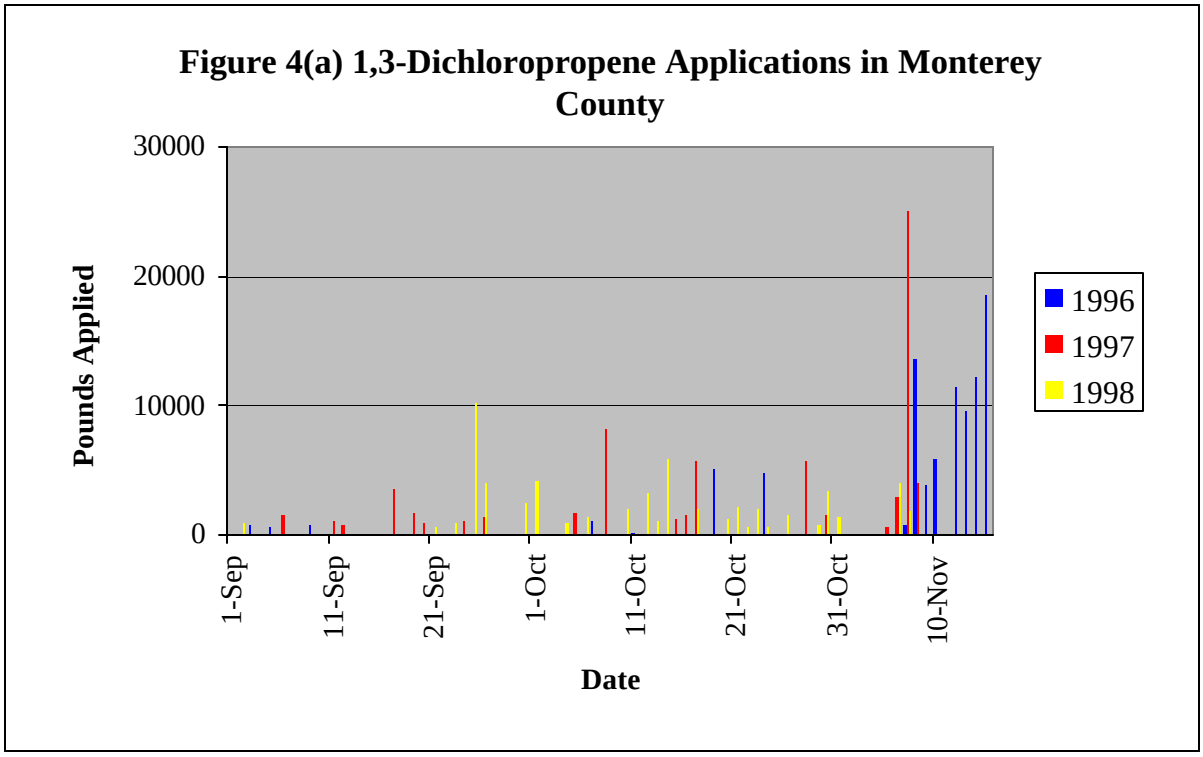


Figure 4(a) 1,3-Dichloropropene Applications in Monterey County
Pounds Applied
30000
20000
10000
0
1-Sep
11-Sep
21-Sep
1-Oct
11-Oct
21-Oct
31-Oct
10-Nov
Date
1996
1997
1998

Figure 4(b) Methyl Bromide Applications in Monterey County

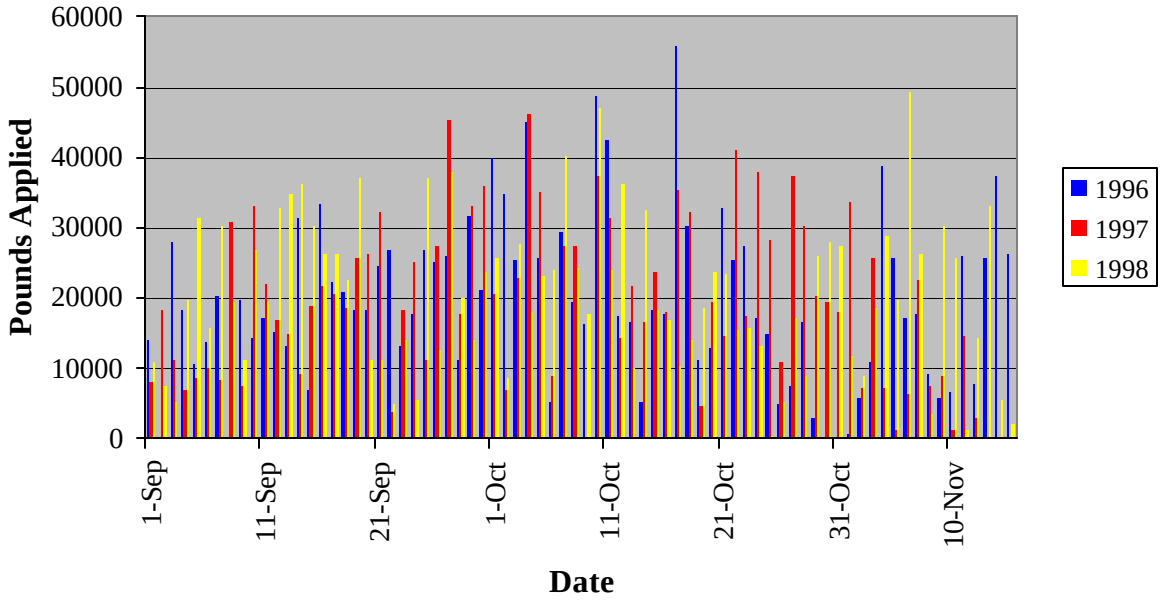


Figure 5(a) 1,3-Dichloropropene Applications in Santa Cruz County

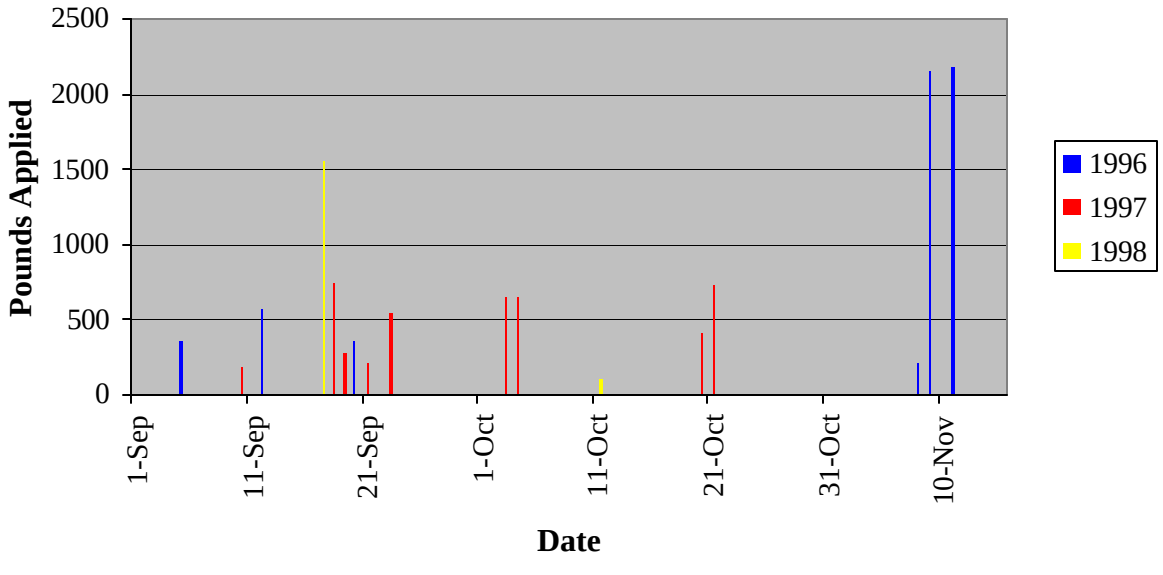
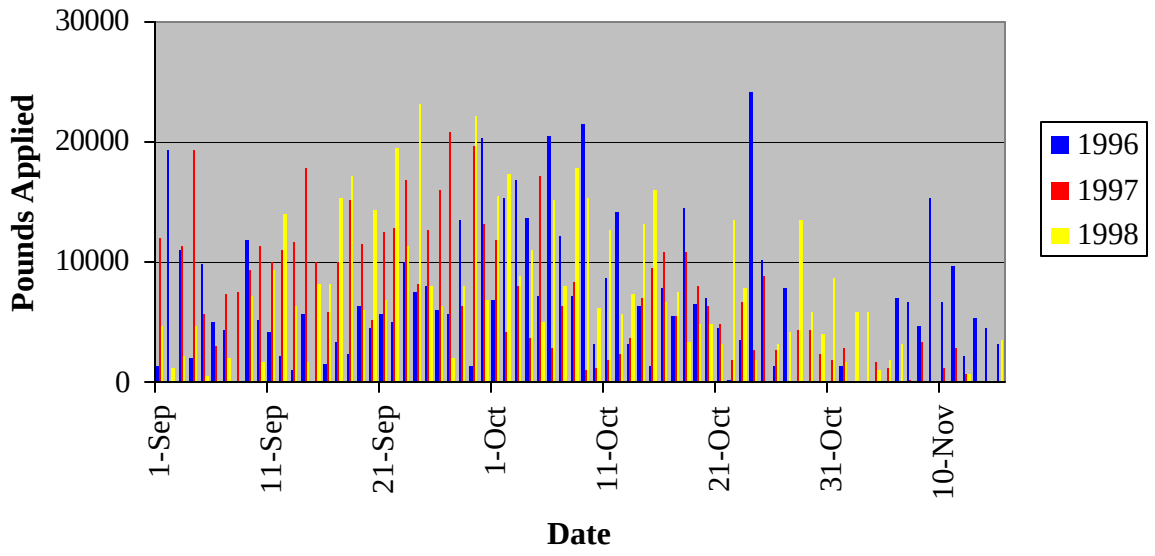


Figure 5(b) Methyl Bromide Applications in Santa Cruz County



DPR recommends close coordination with the county agricultural commissioner to select the best sampling sites and periods. Field spike samples should be collected at the same environmental conditions (e.g., temperature, humidity, exposure to sunlight) and experimental conditions (e.g., air flow rates) as those occurring at the time of ambient sampling. Additionally, we request that you provide in the ambient monitoring report: 1) the proximity of the sampler to treated or potentially treated fields, including the distance and direction, and 2) the distance the sampler is located above the ground.

2. Application-Site Air Monitoring

DPR has several studies that included application-site monitoring. No application-site monitoring is required for these chemicals.

D. SAFETY RECOMMENDATIONS

1,3-Dichloropropene

The 1,3-dichloropropene product label warns that 1,3-dichloropropene may cause substantial, but temporary eyes injury if the product gets into the eyes. The product may cause skin irritation, skin burns, allergic skin reaction and be fatal if absorbed through the skin. The vapor may be fatal if inhaled and may cause lung, liver, and kidney damage and respiratory system irritation upon prolonged contact.

Monitoring personnel should use proper protective equipment to prevent exposure to the dust, vapors or spray mist. According to the product labels, proper protective equipment for applicators making direct contact or for applicators outside an enclosed cab includes coveralls, chemical-resistant gloves and footwear plus socks, face sealing goggles, chemical resistant headgear (for overhead exposure) and apron, and a respirator with an organic-vapor removing cartridge. Monitoring personnel should refer to the label of the actual product used for further precautions.

Methyl bromide

According to the product label for methyl bromide, it is an extremely hazardous liquid and vapor under pressure. Inhalation may be fatal or cause serious acute illness or delayed lung or nervous system injury. Liquid or vapor may cause skin or eye injury. Methyl bromide vapor is odorless and non-irritating to skin and eyes during exposure and toxic levels may occur without warning or detection.

The acceptable air concentration for persons exposed to methyl bromide is 5 ppm, except for those in residential or commercial structures. A respirator is required if air concentrations exceed 5 ppm at any time. According to the label, proper protective equipment for applicators include loose fitting or well ventilated long-sleeved shirt and long pants, shoes and socks, full-face shield or safety glasses with brow and temple shields. Monitoring personnel should refer to the label of the actual product used for further precautions.

E. ANALYTICAL METHODS

There are several analytical methods for both 1,3-dichloropropene and methyl bromide. DPR is familiar with three of these methods: sorbent tube/solvent extraction, sorbent tube/headspace analysis, and canisters. There is some question regarding the performance of these methods, particularly for methyl bromide (Biermann and Barry, 1999). Assuming that the desired detection limits can be achieved, DPR prefers methods using canisters. The canisters offer several advantages over sorbent tubes. For example, canisters do not have any breakthrough problems. Quality control tests involve air spikes and more closely resemble actual conditions than the liquid spikes used for sorbent tubes. Methyl bromide and 1,3-dichloropropene can also be determined simultaneously with canisters. This is unlikely for sorbent tubes. In the long-term, DPR would like ARB to develop a method that will also sample for these two chemicals in addition to methyl isothiocyanate, methyl isocyanate, and chloropicrin simultaneously. This is also unlikely for sorbent tubes.

DPR would also like to take this opportunity to compare the different sampling and analytical methods. If ARB can collect these samples, DPR will oversee this part of the monitoring and arrange for cooperators to conduct analyses that ARB cannot conduct. DPR estimates that this will add 10 to 20 samples for each of the other methods. The scheduling and location of this comparison is flexible.

F. REFERENCES

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