CALIFORNIA STRAWBERRY COMMISSION
A HEALTHY INDULGENCE

June 20, 2007

Chairman Robert Sawyer, Ph.D. and Members of the Board
California Air Resources Board
1001 I Street
Sacramento, CA 95812

RE: Comments on the 2007 SIP – Appendix H

Dear Chairman Sawyer and Members of the Board:

The California Strawberry Commission would like to express our support for amendment of the 1994 SIP for Ventura in Appendix H of your June 22, 2007, agenda item considering a statewide strategy for the 2007 California SIP. The California Strawberry Commission (CSC) represents all the 600+ growers, shippers, and processors of strawberries in California. California produces 88% of the fresh and frozen strawberry fruit in the USA with a current value of $1.6 billion.

We would like to bring the following to your attention:

- Ventura achieved the 1-Hour Ozone Standard in 2002;
- Ventura County agriculture has significantly reduced emissions and adopted the best available control technology;
- the economic and environmental impacts if appendix H is not approved;
- amending the 1994 SIP is good for the economy and the environment;
- the 1994 SIP has been amended for Ventura in the past.

If Appendix H is not approved to transfer 1.9 tpd to the pesticide element of the 1994 SIP, DPR has reported that 10,000 acres will have to stop current production practices. According to the Ventura County Agricultural Commissioner's most current Annual Crop Report (2005), this would have an economic impact of $286 million and we believe a loss of as many as 20,000 jobs. Moreover, the resulting pressure to develop these lands would likely lead to more emissions.

Ventura achieved the 1-Hour Ozone Standard in 2002

As you know, Ventura satisfied the 1994 SIP and achieved compliance with the federal 1-Hour Ozone Standard in 2002. "Best Air on Record…" reads a December 10, 2004 press release by the Ventura County Air Pollution Control District, noting, "There were NO exceedances of the federal one-hour ozone standard and NO health advisories" The release further states, "With no exceedances during 2004, two exceedances in 2003, and one exceedance in 2002, Ventura County has effectively attained the federal one-hour ozone standard."

Ventura County agriculture has reduced emissions and adopted BACT

When the 1994 SIP was approved, the most common fumigation technology resulted in 74% emissions.[1] In 1996, the United States Department of Agriculture, Agriculture Research Service formed a partnership with the California Strawberry Commission to evaluate fumigant alternatives. For the next several years, the partnership conducted over 25 on-farm, large scale demonstration projects. These projects showed that drip technology could both reduce the amount of fumigant needed to be used, and that the drip technology also reduced the emissions from 74% down to 22%[1]. In other words, compared to the standard technology used in 1994, the new drip technology is at least 80% cleaner.

Beginning in 1999 and continuing for several years, the Commission published multiple papers on drip technology and recommended its adoption. Over the next 8 years the strawberry industry overwhelming adopted this new method and over 95% of the strawberry acreage in Ventura now use the lowest emission methods identified by DPR for each fumigant applied.

Flawed science leads to a flawed judicial order

Despite the fact that Ventura has achieved the federal 1-hour ozone standard, and that Ventura agriculture has adopted BACT, there is a remnant in the 1994 SIP that will cause an economic hardship if Appendix H is not approved and will directly lead to changes in land use that will likely result in significant increases in VOC emissions compared to the current agricultural uses.

In *El Comite para el Bienestar de Earlmart v. Helliker*, the Judge ordered DPR to implement a regulation using 1991 as a base year. Because the Judge only considered information that was used to develop the 1994 SIP, the court did not receive information about the numerous scientific flaws in the 1990/91 base years. For example, in 2003, EPA sent a letter to ARB stating that Methyl Bromide is not a VOC[2]. Simply subtracting Methyl Bromide from the Ventura inventory reduces total pesticide emission by nearly 50%, resulting in total pesticide emissions constituting less than 3.5% of Ventura's total ROG emissions.

The Economic Impact

Because the judge got it wrong, the DPR regulation will be about satisfying an obsolete process and have a minimal effect on improving air quality. More specifically, because the order is based on obsolete scientific findings, DPR has reported that the new regulation would cause 10,000 acres[3] to stop production, kill 20,000 jobs and result in an economic loss of up to $286 million[4]; all to accomplish a 2% reduction in total VOC emissions in Ventura, for an air district that has already achieved the federal 1-hour ozone standard.

The Environmental Impact

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[1] DPR VOC Emission Adjustment Memo, April 6, 2007
[2] EPA Asst. Administrator Holmstead, November 13, 2003
[3] DPR Press release, May 18, 2007
[4] Ventura County Ag Commissioner Crop Report

DPR Director, Mary Ann Wamerdam recently stated, "Is California agriculture part of our air-quality problem or is it part of the solution? The shift to higher-value crops and more fumigant use, for example, is one side effect of a statewide real-estate boom. Farmers who lease their fields have a hard time competing with land speculators. And farmers who own land have good reason to cash out before the next commodity price downturn, drought, or flood pulls them into debt for years to come. With so much riding on every year's crop, it's little wonder that lenders and landowners require growers to fumigate their fields — whether they want to or not — to ensure profitability. We must recognize that every segment of our society has some value in the overall scheme of things. Grow crops or suburbs? It's a false choice for the environment to swap one source of smog for another that could be worse."[5]

As published in the DPR Statement of Reasons for their proposed VOC regulation, if Appendix H is not approved 10,000 acres will be impacted. The loss of fumigation will mean that yield will drop by half[6] and growers will face financial hardship for no good reason. Without profitable agricultural use, this land will ultimately be developed into uses that will undoubtedly result in increased VOC emissions.

Not a Precedent

The 1994 SIP was a plan. New data becomes available and plans change. Since 1994, we know that BACT has been applied, that the air district has achieved the 1-hour ozone standard, and that the old 1991 inventory is significantly exaggerated.

In past years, Ventura has had similar situations where the 1994 SIP has been amended to allow for a transfer of credits from one strategy to another strategy. For example, the adhesives rule originally adopted by the local Air Pollution Control District had to be amended and credit from other programs was transferred to satisfy the targets originally planned. Such amendments are allowed by the Clean Air Act, and not unusual. This is not backsliding on the SIP commitment. It is an adjustment to the plan.

Our Request: amending the 1994 SIP is good for the economy and the environment

Your staff recommendation, reflected in Appendix H, proposed to revise the 1994 Ozone SIP to substitute 1.0 tpd of ROG emission reductions from California's on-going motor vehicle program, for 1.0 tpd of ROG emission reductions committed to for pesticides in the 1994 Ozone SIP in Ventura County.

After Appendix H was published, DPR published its proposed VOC regulation and supporting documentation. DPR's VOC Emissions Adjustment Memo (Table 23) shows that after BACT is utilized by 100% of the growers on 100% of the acres, that there is still a 1.348 tpd shortfall. This analysis was based on data from 2004. Growth has occurred since then. When adjusted with published data for 2007 acreage, the shortfall is 1.869 tpd. In other words, since Appendix H was published, DPR has published new technical data demonstrating that the correct amount to be transferred is 1.9 tpd.

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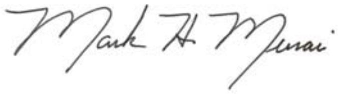
[5] Ventura County Star Editorial, June 10, 2007
[6] J. Duniway, July 2002 scientific paper

We request that you approve Appendix H with the corrected number of 1.9 tpd to be transfer from the motor vehicle program to the pesticide element.

Thank you for the opportunity to comment.

Sincerely,



Mark Murai
President

Mary-Ann Warmerdam
Director

Arnold Schwarzenegger
Governor

M E M O R A N D U M

TO: John S. Sanders, Ph.D., Chief
Environmental Monitoring Branch

FROM: Terrell Barry, Ph.D., Research Scientist III *Original signed by*
Frank Spurlock, Ph.D., Research Scientist III *Original signed by*
Randy Segawa, Agriculture Program Supervisor IV *Original signed by*
Environmental Monitoring Branch
(916) 324-4137

DATE: April 6, 2007

SUBJECT: PESTICIDE VOLATILE ORGANIC COMPOUND EMISSION ADJUSTMENTS FOR FIELD CONDITIONS AND ESTIMATED VOLATILE ORGANIC COMPOUND REDUCTIONS–INITIAL ESTIMATES

I. Summary

The purposes of this memorandum is to develop refined emission adjustment factors to account for the effect of application method on volatile organic compound (VOC) emissions from pesticides, with particular emphasis on fumigants, and to estimate the VOC reductions associated with changes to fumigant application methods. Each year, the Department of Pesticide Regulation (DPR) updates an inventory of pesticide VOC emissions for May–October for specified areas and compares the emissions on a relative basis to 1990 or 1991 as the base year. DPR currently assumes 100% of applied fumigants volatilize to the air. Field monitoring data shows that fumigant emissions are less than 100% and vary with application method.

There are several dozen field studies that measured fumigant emissions. Emissions vary from 9 to 100% of the amount applied, depending on the fumigant and application method. However, data is not available for all application methods in current use or in use during the 1990/91 base year. When no data is available, emissions have been estimated with surrogate data. In addition to emission estimates associated with each application method, DPR has estimated the frequency with which the various application methods were used during 1990/91 base year, as well as currently. Registrant data and pesticide use reports (PURs) were used for these estimates.

DPR used the emissions for each application method, and the frequency with which the various application methods are used to adjust its VOC emission inventory, as well as to estimate the possible emission reductions that would result from further changes to application methods. This analysis shows that application method changes between 1990/91 and 2004 are insufficient to achieve the required VOC reductions in the targeted areas. While application method changes since 1990/91 have lowered emission rates, increased fumigant use more than offsets the application method reductions. Moreover, even if all fumigant applications used “low-emission” methods, the VOC reductions would be insufficient to achieve the required levels in at least one

area. Limits on fumigant VOC emissions may be needed during May–October to ensure the required VOC reductions are achieved.

II. Background

Pesticide VOCs can contribute to the formation of ground-level ozone, which when present in high concentrations is harmful to human health and vegetation. The federal Clean Air Act requires each state to submit a state implementation plan (SIP) for achieving and maintaining federal ambient air quality standards, including the ozone standard. In 1994, California's Air Resources Board and DPR developed a SIP element to track and reduce pesticidal sources of VOCs in five regions that do not meet the 1-hour ozone standard (ozone nonattainment areas): Sacramento Metro, San Joaquin Valley, Southeast Desert, Ventura, and South Coast. On February 21, 2006, the U.S. District Court (Eastern District of California) ordered DPR to implement regulations by January 1, 2008, to achieve the VOC emission reduction goals.

In accordance with the 1994 SIP, DPR developed a method to track pesticide VOC emissions (VOC emission inventory). Each year, DPR estimates pesticide VOC emissions for May–October in each nonattainment area and compares the emissions on a relative basis to 1990 or 1991 as the base year. DPR initiated major revisions to the pesticide VOC emission procedures in 2002 (Spurlock, 2002a). Numerous updates and improvements to the VOC inventory calculation procedures have been made since that time (Spurlock, 2002b, 2004, 2005, 2006; Roush, 2006). The revisions have improved the accuracy of DPR's VOC inventory relative to earlier versions (e.g., Spurlock, 2002c).

The potential emission for a pesticide application is currently calculated as:

VOC emission (pounds) = pounds pesticide product applied x emission potential (EP)

where the EP is the EP of the pesticide product. The EP is a measure of the VOC content of a product. However, additional factors beyond product composition affect emissions under actual use conditions. In recognition of this, the 1994 pesticide element of California's SIP contains a provision for incorporating new knowledge into pesticide VOC emissions estimation procedures.

"The 1990 baseline year and subsequent year estimates may be further adjusted by additional VOC Emission Factors if additional information becomes available regarding the reactivity of compounds, the impact of temperature, moisture, deposition substrate, method of application, and other factors. Any additional VOC Emission Factor(s) will be pesticide product specific." (DPR, 1994).[1]

[1] On February 21, 2006, the United States District Court (Eastern District of California) ordered DPR to use the 1991 inventory as a surrogate for the 1990 baseline year.

Fumigants are among the highest VOC contributors due to both their high levels of use and their high-EPs. For the fumigants 1,3-dichloropropene (1,3-D), chloropicrin, and methyl bromide EPs of 100% are assumed. Thus, current VOC estimation procedures assume that all of these applied fumigants are eventually released to the troposphere. In the case of metam-sodium and N-methyl dithiocarbamate (metam-potassium) products, EPs assume 100% conversion to methyl isothiocyanate (MITC) followed by eventual release of 100% of MITC to the air. Similarly, for products containing sodium tetrathiocarbonate, EPs assume 100% conversion to carbon disulfide followed by release of 100% of carbon disulfide to the air. DPR has conducted numerous fumigant field monitoring studies over the last 15 years (e.g. <http://www.cdpr.ca.gov/docs/dprdocs/methbrom/pubs.htm>). Other researchers have also published fumigant field study results in peer-reviewed literature. Those studies demonstrate that the assumption of 100% fumigant emission to the air is inaccurate in most cases. This memorandum describes development of emission adjustment factors accounting for the effect of application method on VOC emissions from pesticides, with particular emphasis on fumigants. Using application method adjustment factors, the potential emission for a pesticide application is calculated as:

VOC emission (pounds) =
pounds product applied x EP x application method adjustment factor

The fumigant application method adjustment factors developed here are expressed as a proportion of the amount of applied fumigant that is emitted to the air. The adjustment factors are application method- and fumigant-specific, based on measured data, and yield more refined estimates of fumigant VOC emissions than current assumptions. Section II describes the available emission data and development of the application method adjustment factors.

In California, all agricultural and commercial pesticide applications must be reported. County agricultural commissioners and DPR compile these PURs into a database. DPR uses pounds of product applied recorded in this database to calculate the VOC emissions for each pesticide application included in the pesticide VOC emission inventory, as shown in the equations above. Specific application methods are not recorded on PURs. Therefore, a second adjustment is needed to account for the use of each fumigant application method. Section III describes the pounds of product applied associated with each fumigant application method (method use fraction).

Without the application method adjustment factors, fumigants account for more than 50, 80, and 90% of the pesticide VOC emissions in the San Joaquin Valley, Southeast Desert, and Ventura nonattainment areas, respectively. Moreover, these are the 3 nonattainment areas where DPR does not currently achieve the 20% pesticide VOC reduction of the 1991 base year required by the Court order. DPR is considering two regulation strategies to achieve pesticide VOC reductions from fumigants, particularly in the nonattainment areas. One strategy is to require use of “low-emission” fumigant application methods and/or prohibit certain “high-emission” fumigant application methods. A second strategy is to establish limits on VOC emissions from fumigants within the nonattainment areas. Regulations that incorporate one or both of these strategies will be effective in 2008. Section IV assesses these regulatory strategies by: (1) estimating the pesticide VOC emissions for the 1990/91 base year for each nonattainment area, with the application method and method use fraction adjustment factors; (2) estimating the VOC reductions that would have occurred if low-emission fumigant application methods had been used in 2004 for each nonattainment area; and (3) estimating the limit on fumigant emissions in each nonattainment area that would achieve the VOC emission reductions required.

This document describes the initial VOC adjustments based on the data currently available to DPR. Additional data should become available later this year and we may be unaware of some data that should be incorporated. Section V describes DPR’s future activities and process to revise the estimates.

III. Estimates of Volatile Organic Compound Emissions Under Field Conditions (Application Method Adjustment Factors)

In this context, an application method adjustment factor is the emissions of fumigant to the air under field conditions, expressed as a proportion (percentage) of applied fumigant, and is fumigant- as well as application method-specific. Fumigant emissions have been measured with several methods, both in the laboratory and in the field. Fumigant emission under field conditions is a complex process that likely varies with method of application, soil characteristics (e.g., particle size, moisture, organic content), weather conditions, and other factors. Due to this complexity, laboratory measurements may not provide an accurate estimate of fumigant emissions under field conditions. Therefore, DPR relies almost exclusively on field measurements to estimate emissions. Additionally, DPR prescribes many of the application procedures and equipment used for the monitoring studies as regulatory requirements. For example, DPR prescribes requirements for maximum application rate, application depth, tarpaulin type, soil moisture, and other critical parameters based on application equipment, procedures, and conditions of the monitoring studies. These parameters are summarized here, and full descriptions are provided in the original study reports.

The reason DPR has not incorporated application method adjustment factors previously is the need to estimate emissions using a consistent process for the 1990/91 base year as well as currently. Due to exposure concerns, fumigant application methods changed substantially beginning in 1993, and very few field studies have measured fumigant emissions associated with application methods prior to this date. This section summarizes the available emission data and the assumptions used to estimate emissions for methods that have no data.

A. Methyl Bromide

DPR proposes application method adjustment factors for three main groups of methyl bromide field application methods: methods that use tractor shanks to inject methyl bromide into pre-formed beds and are covered with a tarpaulin, methods that use tractor shanks to inject methyl bromide into flat fields (broadcast) and are covered with a tarpaulin, and methods that use tractor shanks to inject methyl bromide into flat fields (broadcast) without a tarpaulin. In addition, there are some non-field application methods. This approach is consistent with DPR's current regulations for methyl bromide.

1. Methyl Bromide Emission Studies

DPR's data set includes 30 field studies utilizing current application methods (Table 1). DPR's analysis of these data shows that the nine bed fumigations monitored had very high 24-hour emissions (average of 81% of amount applied, coefficient of variation [CV] 38%). The 13 broadcast applications with a tarpaulin show peak 24-hour emissions that average 24% of the amount applied (CV 52%). Broadcast applications without a tarpaulin show peak 24-hour emissions that average 37% of the amount applied (CV 47%). Methyl bromide is injected at different depths below the soil surface depending on the crop, with 6–12 inches classified as shallow injection, and 18–30 inches classified as deep injection. Analysis of the data (Barry 1999) shows that depth of application had no significant effect on the highest 24-hour emissions. While in concept there should be a depth effect, it is likely in practice that application-to-application variability is too large to detect that effect.

Five journal articles contained methyl bromide data most appropriate for developing application method adjustment factors: Majewski et al. (1995), Gan et al. (1996), Yates et al. (1996a), Yates et al. (1996b), and Gan et al. (1997). These articles report either direct flux (emission) measurements (e.g., aerodynamic method) in the field or measured soil column results. No flux chamber estimates of mass loss are included because there are significant technical issues associated with flux chamber estimates (Yates 2006). Table 2 summarizes these studies and shows emission estimates for Broadcast Tarp and Broadcast Nontarp methods. Shallow and deep injections are pooled within these two categories due to the lack of significant difference associated with injection depth observed in the DPR data set. The average emission for Broadcast Tarp application method in these studies is 40%. The average emission for Broadcast Nontarp application method in these studies is 66%.

2. Methyl Bromide Application Method Adjustment Factors

The average peak 24-hour emissions for the three groups are used as the basis for the DPR application method adjustment factors. Majewski et al. (1995) conclude that about 50% of the total emissions occur in the first 24 hours for applications. Therefore, the 24-hour emissions from the DPR data set can reasonably be doubled to provide an estimate of the application method adjustment factors. The application method adjustment factor for methyl bromide broadcast applications with a tarpaulin is 48% (both shallow and deep injection). The application method adjustment factor for methyl bromide broadcast applications without a tarpaulin is 74% (both shallow and deep injection). Due to the high 24-hour emissions for bed applications with a tarpaulin, 100% loss should be assumed. Of the two field studies described in the journal articles, Majewski et al. (1995) was a joint study with DPR, and its results are accounted for in DPR's emission estimates shown in Table 1. The emissions measured in the remaining field study (Yates et al. 1996b) were consistent with the 13 DPR and registrant studies of that same application method that are used for the current methyl bromide regulations (Table 1). This last study has not been included in the determination of the application method adjustment factors because it has a negligible effect when grouped with 13 other studies, and to maintain consistency between the application method adjustment factors and current methyl bromide regulations.

The data described support application method adjustment factors for current fumigation methods. Methods in use during 1990/91 were significantly different, particularly in the types of tarpaulins that were used. Low-density polyethylene tarpaulins were commonly used in 1990/91. No field data for applications with low-density tarpaulin is available. However, laboratory data shows that these are more permeable than the tarpaulins currently used. Due to the lack of data, the application method adjustment factor for methyl bromide methods used in the 1990/91 base year are assumed to have the same emissions as current methods without a tarpaulin (74%). This assumption accounts for the permeable low-density tarpaulins that were in use at the time.

In 1990/91 as well as currently, methyl bromide has uses as a space fumigant for both structures and harvested commodities. Methyl bromide emissions from these application methods are assumed to be 100% of the amount applied.

The methyl bromide registrants submitted proposed application method adjustment factors to DPR (Stangellhini 2006a; Appendix 1), based on the Gan et al. (1997) study. Some of the registrants' adjustment factors are similar to those proposed by DPR. However, several are inconsistent with DPR's analysis of the available data (Appendix 2).

Based on the emission data shown in Table 1 and the assumptions discussed above, the application method adjustment factors for methyl bromide are:

Shallow injection w/ high permeability tarp or no tarp-broadcast	74%
Shallow injection w/ low permeability tarp-broadcast	48%
Shallow injection w/ high permeability tarp or no tarp-bed	100%
Shallow injection w/ low permeability tarp-bed	100%
Deep injection w/ high permeability tarp or no tarp-broadcast	74%
Deep injection w/ low permeability tarp-broadcast	48%
Nonfield soil (structural/post-harvest)	100%

B. 1,3-Dichloropropene

DPR proposes application method adjustment factors for five 1,3-D field application methods: methods that use tractor shanks to inject 1,3-D at shallow depths, methods that use tractor shanks to inject 1,3-D at deep depths, methods that include post-fumigation water treatments for both shallow injection and deep injection, and chemigation with drip irrigation systems.

1. 1,3-Dichloropropene Emission Studies

Appendix 3 is a recent analysis of six 1,3-D field monitoring studies. Four studies employed a shank injection at varying depths and two studies employed drip application. In contrast to methyl bromide, 1,3-D studies appear to show differing emissions with depth of injection, but standard high-density tarpaulins have little or no effect on 1,3-D emissions (Yates et al. 2002). In order to fully utilize the four studies, they were combined by linear interpolation to estimate the flux at two standard depths: 18 inches and 12 inches.

Use of 1,3-D was suspended in early 1990 due to high ambient air concentrations monitored in Merced. In researching mitigation measures to reduce emissions, the registrant conducted a flux study using elevated soil moisture (Knuteson et al. 1992). This soil moisture mitigation measure is now a part of the shank application methodology.

Gao and Trout (2007) used flux chambers to estimate emissions for several chloropicrin and 1,3-D application methods, including high-density polyethylene tarpaulin, high-density polyethylene tarpaulin with pre-irrigation, single post-fumigation water treatment, multiple post-fumigation water treatments (intermittent watering-in), and virtually impermeable film. Those researchers reported problems maintaining a seal between the soil and the chamber. Other researchers have concluded that the chamber methodology does not accurately measure emissions under field conditions (Yates 2006). Consequently predictions of 1,3-D emission reductions due to post-fumigation water treatments are subject to considerable uncertainty because the Gao and Trout (2007) study is the only information available for 1,3-D on this mitigation measure. However, reductions observed in their study are qualitatively consistent with demonstrated reductions in MITC emissions for post-fumigation water treatments.

2. 1,3-Dichloropropene Application Method Adjustment Factors

Appendix 3 summarizes and estimates the 1,3-D emissions for the application methods currently used, based on the available field studies and the emission adjustments (application factors) described in DPR's recommended conditions for 1,3-D restricted materials permits (DPR 2002). Field studies for 1,3-D have been conducted during the fall and spring seasons only. DPR's recommended permit conditions (2002) include an ad hoc adjustment factor for 1,3-D applications during the summer. We have chosen not to include the summer adjustment factor for 1,3-D application methods in these VOC emission estimates for three reasons. One, the summer adjustment factors are ad hoc, and not based on any scientific data or evaluation. Two, DPR does not use a seasonal adjustment for its regulatory emission values for any of the other fumigant. Three, the revised method for estimating VOC emissions described here is based on assigning a single field adjustment factor for each application method and fumigant combination; a seasonal emission adjustment would greatly increase the complexity of the VOC calculations.

DPR will assume that reductions in 1,3-D emissions for three post-fumigation water treatments is approximately one-third less than an untarped application. Other application methods that appear to reduce chloropicrin emissions, such as pre-irrigation and virtually impermeable film may be problematic due to labeling requirements and other factors (Gao and Trout, 2007). Therefore, these application methods are not recommended at this time.

In 1990/91 there were virtually no applications of 1,3-D during the ozone season so no application method adjustment factors are needed for methods in those years.

Based on the emission data shown in Table 3 and the assumptions discussed above, the application method adjustment factors for the 1,3-D are:

Shallow injection w/ high permeability tarp or no tarp-broadcast	61%
Shallow injection w/ 3 water treatments	41%
Deep injection w/ high permeability tarp or no tarp-broadcast	41%
Deep injection w/ 3 water treatments	27%
Drip w/ high permeability tarp or no tarp	29%

C. Chloropicrin

The majority of chloropicrin is applied as a mixture with either methyl bromide or 1,3-D; a few applications use chloropicrin as the sole fumigant. The same application methods that are used for methyl bromide or 1,3-D will be used for chloropicrin, but with different application method adjustment factors.

1. Chloropicrin Emission Studies

Chloropicrin registrants measured chloropicrin emissions from several field applications (Beard et al. 1996). This study provides adequate data to characterize chloropicrin emissions for most of the current application practices. Emissions measured in this study showed relative differences similar to methyl bromide, with lower emissions associated with tarped broadcast applications and higher emissions associated with untarped broadcast and bed applications (Table 4). However, the study did not measure emissions for deep injection application methods, so the effect of injection depth is unknown. Data presented by the chloropicrin registrants yield similar conclusions, except the two studies Gillis and Smith (2002) and Lee et al. (1994) are either not of sufficient quality or do not include sufficient data to judge the quality to support their use in the DPR estimation of the adjustment factors. Chloropicrin registrants also measured emissions associated with chemigation of chloropicrin through a drip irrigation system (Rotonardo, 2004). This study provides adequate data for the emissions from the drip application method, and shows substantially lower emissions than injection methods (Table 4).

Gao and Trout (2007) used flux chambers to estimate emissions for several chloropicrin and 1,3-D application methods, including high-density polyethylene tarpaulin, high-density polyethylene tarpaulin with pre-irrigation, single post-application water treatment, multiple post-application water treatments (intermittent watering-in), and virtually impermeable film. Those researchers reported problems maintaining a seal between the soil and the chamber. Other researchers have concluded that the chamber methodology does not accurately measure emissions under field conditions (Yates 2006). Consequently, predictions of chloropicrin emissions associated with the intermittent watering-in application method are subject to considerable uncertainty because the Gao and Trout (2007) study is the only information available for chloropicrin on this mitigation measure. However, reductions observed in their results are qualitatively consistent with demonstrated reductions in MITC emissions for intermittent watering-in methods.

2. Chloropicrin Application Method Adjustment Factors

The Beard et al. (1996) and Rotonardo (2004) studies will be used to produce the DPR application method adjustment factors. The emissions from Beard et al. (1996) are shown in Table 4. Similar to the proposed methyl bromide factors (Barry, 2006), the proposed chloropicrin factors only distinguish between tarpaulin and no tarpaulin. No depth factor will be included. All broadcast tarpaulin method emission results will be combined to produce an average estimate.

The chloropicrin data set is small, as a result it is impossible to reliably distinguish between emissions for bed and broadcast applications. Thus, no separate field adjustment factor for bed methods will be estimated. Instead, based on the known high-emission characteristics of methyl bromide bed applications (Barry, 1999), the chloropicrin emission estimates for bed will be combined with the no tarpaulin method.

The drip application method is separated because although only one acceptable study exists for that method (Rotonardo, 2004) the emissions appear to be substantially lower than the shank injection methods.

As with methyl bromide, chloropicrin applications methods in 1990/91 used more permeable low-density polyethylene tarpaulins. Stangellhini (2006b, Appendix 1) proposes, and DPR agrees, that 1990/91 chloropicrin applications should be assigned the application method adjustment factor for applications without a tarpaulin.

DPR will assume that reductions in chloropicrin emissions for intermittent watering-in consisting of three post-fumigation water treatments is approximately one-third less than an untarped application. Other application methods that appear to reduce chloropicrin emissions, such as pre-irrigation and virtually impermeable films may be problematic due to labeling requirements and other factors (Gao and Trout, 2007). Therefore, these application methods are not recommended at this time.

Based on the emission data shown in Table 4 and the assumptions discussed above, the application method adjustment factors for chloropicrin are:

Shallow injection w/ high permeability tarp or no tarp-broadcast	64%
Shallow injection w/ low permeability tarp-broadcast	44%
Shallow injection w/ high permeability tarp or no tarp-bed	64%
Shallow injection w/ 3 water treatments	20%
Shallow injection w/ low permeability tarp-bed	64%
Deep injection w/ high permeability tarp or no tarp-broadcast	64%
Deep injection w/ low permeability tarp-broadcast	44%
Deep injection w/ 3 water treatments	20%
Drip w/ low permeability tarp	15%

C. Metam-sodium and Metam-potassium

Metam-sodium and metam-potassium fumigant action and VOC emissions are due to the hydrolysis product MITC, which is generated when sufficient water is applied to either metam-sodium or metam-potassium. The two active ingredients display essentially identical chemical behavior. In the remainder of this document metam be used to collectively refer to both metam-sodium and metam-potassium. EPs for products containing these chemicals are expressed on an MITC equivalent basis (Spurlock, 2002a, 2005). Here emission factors are also derived on an MITC emission basis.

DPR proposes application method adjustment factors for eight metam field application methods:

Using tractor shanks to inject metam at shallow depths
Chemigation through sprinkler irrigation systems
Post-fumigation water treatments for both shank injection and sprinkler applications
Spraying metam on the soil surface and incorporate using a rototiller
Spraying metam on the soil surface and cover with additional soil (soil capping)
Chemigation through flood irrigation systems
Chemigation with drip irrigation systems

1. Metam-Sodium Emission Studies

The Metam-sodium Task Force submitted results from field studies conducted under their 1997-2001 Field Program. The earliest studies monitored MITC air concentrations associated with standard sprinkler and standard shank injection applications (Merricks, 1999). Standard sprinkler and standard shank injection methods include water treatments immediately following completion of the application. Field study results were also submitted for shank injection and sprinkler applications employing new post-fumigation water treatments as mitigation measures aimed at suppressing MITC emissions (Merricks, 2001; Merricks, 2002). The post-fumigation water treatments consist of water applied immediately following the application but also additional water, usually at sunset of the first and second evenings following completion of an application. Emission profiles developed for all four of these application methods have been used previously by DPR to develop MITC buffer zones (Barry, 2006).

DPR has three metam-sodium drip method and one rototiller method emission profiles developed using results from three field studies (Levine et al, 2005; Li et al., 2006; Wofford 2005).

Table 5 shows the total MITC emissions over the 96-hour flux profiles for each of the application methods. The total MITC available for emission was calculated assuming a maximum, immediate conversion of metam-sodium to MITC of 95% (Wales, 2000) and adjusting for difference in molecular weight between metam-sodium and MITC.

2. Metam Application Method Adjustment Factors

The metam-sodium data set is small, as a result it is impossible to reliably distinguish between emission rates for sprinkler and shank injection methods. However, relative to the standard application methods, the emissions are substantially lower for post-fumigation water treatments of both sprinkler and shank injection. Thus, sprinkler and shank injection methods are combined but standard and post-fumigation water treatments are separated. The drip and rototiller application methods are separated because the emissions observed in Levine et al. (2005) and Wofford (2005) are substantially lower than observed for other application methods.

Other application methods were commonly used in 1990/91 as well as currently, but the emissions have not been measured either in the laboratory or in the field. Specifically, no emission data is available for methods that consist of spraying metam on the soil surface and covering with additional soil (soil capping) or for methods that consist of chemigating using flood irrigation systems. In order to account for the emissions from these application methods in 1990/91, DPR assumes that emissions from the soil capping method are the same as rototiller, and emissions from flood chemigation are the same as sprinkler.

All of the metam studies and emissions described above were daylight applications. Unlike other fumigants, metam applications commonly have higher emissions at night compared to the day, particularly if applications occur at night. Wofford et al. (1994) measured emissions of nearly 100% from a night sprinkler application. It is likely that other metam application methods also have higher emissions when done at night. Except for the standard sprinkler method, the emissions for metam night applications are unknown. The frequency of night applications is also unknown. Therefore, DPR does not currently account for the emission difference between day and night applications.

Based on the emission data shown in Table 5 and the assumptions discussed above, the application method adjustment factors for metam (as a percentage of MITC) are:

Shallow injection w/ high permeability tarp or no tarp-bed	77%
Shallow injection w/ 3 water treatments	21%
Rotovate/rototill	14%
Soil capping	14%
Sprinkler	77%
Sprinkler w/ 3 water treatments	21%
Flood	77%
Drip w/ high permeability tarp or no tarp	9%
Drip w/ low permeability tarp	9%

D. Dazomet

Similar to metam-sodium and metam-potassium, dazomet fumigant action and VOC emissions are due to the hydrolysis product MITC, which is generated when sufficient water is applied to dazomet. In addition to their chemical differences, dazomet is formulated as granules while metam-sodium and metam-potassium are formulated as liquids. The EP for dazomet is expressed on an MITC equivalent basis (Spurlock, 2002a, 2005). Here application method adjustment factors are also derived on an MITC emission basis.

DPR proposes application method adjustment factors for two dazomet application methods: methods for which dazomet is applied to the soil surface followed by post-fumigation water treatments, and methods for which dazomet is incorporated into the soil followed by post-fumigation water treatments.

1. Dazomet Emission Studies

The data set for dazomet consists of three studies, two surface applied and one incorporated (Table 5). The registrants for a dazomet product submitted study results that included air concentrations and emission calculations for a surface and an incorporated application (Certis, 2004). There is significant uncertainty in the emission estimates for both the surface and the incorporated application methods due to the very calm wind conditions during the studies. Out of 18 sampling periods for each study only three sampling periods from the incorporated application and none of the sampling periods from the surface application resulted in statistically significant regressions used to estimate the emission rate. A third study conducted by DPR (Fan, in progress) monitored a surface application to small plots of dazomet. The regression analysis used to estimate emissions was statistically significant, but resulted in an emission calculation that was a factor of ten higher than the registrant studies. Because of the discrepancies in the emission estimates between the three studies, DPR and the registrant jointly initiated a fourth study. The analysis of the data from that study is in progress. Additionally, all of the available studies may underestimate VOC emissions from dazomet because of other VOCs formed by its degradation. The available studies only measured MITC, but other degradation products may also have significant VOC emissions (Subramanian, et al. 1996).

2. Dazomet Application Method Adjustment Factors

The available data set for dazomet is small and the emission factors vary by a factor of ten, so an average of the fraction of MITC emitted from all of the studies is used as the interim application method adjustment factor for all applications of dazomet products. DPR may revise this adjustment factor once the third and fourth studies are completed. DPR may also revise this adjustment factor after further evaluation of the other dazomet degradation products. The interim application method adjustment factor for all dazomet application methods is 17%.

E. Sodium Tetrathiocarbonate

Sodium tetrathiocarbonate fumigant action and VOC emissions are due to the hydrolysis product carbon disulfide, which is generated when sufficient water is applied to sodium tetrathiocarbonate. The EP for sodium tetrathiocarbonate is expressed on a carbon disulfide equivalent basis (Spurlock, 2002a, 2005). Here application method adjustment factors are also derived here on a carbon disulfide emission basis.

DPR proposes application method adjustment factors for three sodium tetrathiocarbonate application methods: chemigation using drip irrigation systems, chemigation using mini-sprinkler systems, and flood/furrow chemigation.

1. Sodium Tetrathiocarbonate Emission Studies

Evaluations by DPR staff concluded that mini-sprinklers potentially result in higher off-site carbon disulfide air concentrations relative to the other application methods (Haskell, 1995). Thus, this method may also represent worst-case emissions of carbon disulfide. DPR has one direct flux (emission) study characterizing emissions of carbon disulfide following application of sodium tetrathiocarbonate by mini-sprinklers (Pilling, 1996). This study was the basis for buffer zones on the current labels. Emissions were characterized by the integrated horizontal flux method (Wilson and Shum, 1992) for 34.2 hours consisting of: (1) the application, (2) follow-up irrigation (watering-in), and (3) an additional 24 hours after completion of watering-in. The emission estimates indicate that 9.6% of the carbon disulfide generated by the sodium tetrathiocarbonate product was emitted during the 34.2 hours sampled. The emission profile shows the peak emissions occurred during the application process and then dropped rapidly to low emissions that were relatively uniform in value between 0.41 micrograms per square meter-second (ug/m^2sec) and 1.02 ug/m^2sec. However, on the morning of the second day emissions began to rise. At 0900 hours on the second day the emission estimate was 1.23 ug/m^2sec and the last 4-hour interval (mid-point time 1700 hours) showed an emission estimate of 2.6 ug/m^2sec. The emission profile for the second night is unknown. Based upon emission profiles for standard shank and standard sprinkler application methods of metam-sodium, it is possible that without watering-in on the second night the emission of carbon disulfide would have continued to rise. Thus, the 9.6% estimate of total carbon disulfide emissions may underestimate the true total emissions.

2. Sodium Tetrathiocarbonate Application Method Adjustment Factors

We assume that the emissions from drip and flood/furrow chemigation are the same as mini-sprinkler. Based on the 9.6% emission rate measured in the study described above, the application method adjustment factors for sodium tetrathiocarbonate are:

Drip	10%
Sprinkler	10%
Flood	10%

F. Other pesticides

Fumigants are the dominant contributors to pesticide VOCs, generally responsible for at least 50–60% of emission in most California nonattainment areas. The next largest class of high-contributing pesticides is liquid formulations such as emulsifiable concentrates. In some cases, emissions calculated directly from the thermogravimetric analyses measurements without accounting for application method may over-estimate actual field emissions for some of these products. This may be especially true for products that are incorporated into the soil. In other cases, such as high solvent formulations that are foliar applied, it is unlikely that field processes reduce emissions significantly. In any event, there is little, if any data available that would allow estimation of application method-based emission factors for nonfumigant pesticides. Consequently, emission factors for nonfumigants are assumed to be 100% in all years. DPR may reconsider these nonfumigant field adjustment factors as further data becomes available.

IV. Estimated Frequency of Use for Each Fumigant Application Method During May–October (Method Use Fractions)

In California, all agricultural and commercial pesticide applications must be reported. County agricultural commissioners and DPR compile these PURs into a database. The PUR database includes the identity of the product applied, the amount applied, location, date, crop/site treated, and other information. DPR uses the pounds of product applied recorded in the PUR database to calculate the VOC emissions for each pesticide application included in the pesticide VOC emission inventory. The PUR database contains general information about the application method (i.e. air, ground, or other), but it does not indicate the specific application method. Therefore, another adjustment is needed to account for the use of each fumigant application method.

In general, different crops use different fumigant application methods. Roush (2006) found that the different nonattainment areas have different crops responsible for the majority of pesticide

VOC emissions. Therefore, each nonattainment area should have a different set of adjustment factors to characterize the use of fumigant application methods. While the application method depends on the crop to be planted, other factors such as soil type, cost, and equipment availability also influence the choice of application method. For example, strawberries always use a shallow application method. However, the tarp broadcast and tarp bed application methods are both commonly used for strawberries, and these application methods have different emissions. Therefore, the type of crop is an unreliable surrogate to identify the fumigant application method in some cases.

DPR proposes to use a variety of methods to estimate the use of each of the fumigant application methods (method use fraction). The method for 1,3-D is the most accurate. As required under DPR's 1,3-D management plan, the registrants maintain records of the specific application method for all 1,3-D applications. Johnson (2006) describes the May–October method use fractions, based on the registrants' data.

Lawson (2006) provides a survey of metam-sodium practices by several dozen growers and applicators in certain areas of the state. This survey includes a compilation of the application methods. The survey includes specific information for three nonattainment areas, as well as the top ten counties. DPR uses the percentage breakdown described in Lawson (2006) on the use of the various metam-sodium applications for the San Joaquin Valley, Southeast Desert, and Ventura nonattainment areas. DPR uses the breakdown for the top ten counties described in Lawson (2006) as a surrogate for the Sacramento Metro nonattainment area, and Ventura as a surrogate for the South Coast nonattainment area.

Similar to the approach described by Stangellhini (2006a, 2006b; Appendix 1), DPR uses information from the PURs to estimate the May–October method use fractions for methyl bromide and chloropicrin based on the following assumptions:

- For 1990/91 methyl bromide and chloropicrin applications, all row, vegetable, and nursery crops (except strawberries) were fumigated using a shallow injection broadcast method with a high permeability tarpaulin or no tarpaulin.
- For 1990/91 methyl bromide and chloropicrin applications, one-half of the strawberry applications were conducted with a shallow injection broadcast method and a high permeability tarpaulin, and one-half of the strawberry applications were conducted with a shallow injection bed method and a high permeability tarpaulin.
- For 1990/91 methyl bromide and chloropicrin applications, all tree and vine crops were fumigated using a deep injection method with a high permeability tarpaulin or no tarpaulin.
- For 2004 methyl bromide applications, all row, vegetable, and nursery crops (except strawberries) were fumigated using a shallow injection broadcast method with a low permeability tarpaulin.

- For 2004 methyl bromide applications, one-half of the strawberry applications were conducted with a shallow injection broadcast method and a low permeability tarpaulin, and one-half of the strawberry applications were conducted with a shallow injection bed method and a low permeability tarpaulin.
- For 2004 methyl bromide applications, all tree and vine crops were fumigated using a deep injection method with a low permeability tarpaulin.
- For 2004 chloropicrin applications, all row, vegetable, and nursery crops (except strawberries and Inline® applications) were fumigated using a shallow injection broadcast method with a low permeability tarpaulin. Inline® applications were conducted with a drip chemigation method.
- For 2004 chloropicrin applications, strawberry Inline product applications were conducted with a drip chemigation method. For the remaining strawberry applications, one-half were conducted with a shallow injection broadcast method and a low permeability tarpaulin, and one-half were conducted with a shallow injection bed method and a low permeability tarpaulin.
- For 2004 chloropicrin applications, all tree and vine crops were fumigated using a deep injection method with a low permeability tarpaulin.

NOTE: 2004 is the most recent year for which DPR has calculated a VOC emission inventory.

The method use fractions for dazomet have no effect on the total emission estimates because the application method adjustment factor is 17% for both application methods. Similarly, the method use fractions for sodium tetrathiocarbonate have no effect on the total emission estimates because the application method adjustment factor for all 3 application methods is 10%.

The information from the 1,3-D registrants, Lawson (2006), and PURs is adequate for estimating the method use fractions during the 1990/91 base year and currently. Tables 6–10 show the method use fractions during the 1990/91 base year in each nonattainment area. Tables 11–15 show the method use fractions for 2004 in each nonattainment area. Tables 16–20 show the predicted method use fractions if all applications switched to a “low-emission” method for each nonattainment area. This last set of method use fractions was predicted by assuming that all “high-emission” methods switch to the most similar “low-emission” method. For example, Table 11 shows that 45% of the metam applications were conducted using the standard sprinkler (high-emission) method in the Sacramento Metro area during 2004. As shown in Table 16, DPR predicts that applicators using the standard sprinkler method change to the sprinkler with three water treatments (low-emission) method to reduce emissions.

V. Estimated Effect of Fumigant Application Method Adjustments on the Volatile Organic Compound Inventory

Previously, DPR did not include application method adjustment factors and method use fractions as part of its pesticide VOC emission calculations. Historically, DPR assumed all application method adjustment factors were 100%, and that fumigant use is equivalent to fumigant VOC emission. Table 21 summarizes the current May–October emission inventory (assuming 100% fumigant VOC emissions) for 1990, 1991, and 2004 in each nonattainment area, and shows an overall increase in fumigant use and emissions for most nonattainment areas.

This memorandum derives various fumigant- and application method-specific adjustment factors to refine the accuracy of the VOC inventory. Table 22 summarizes the application method adjustment factors associated with each fumigant and application method combination, and shows that most current application methods have substantially lower emissions than methods used in 1990/91.

Tables 6–20 summarize the May–October method use fractions during 1990/91, 2004, and the predicted method use fractions if all applications switched to a “low-emission” method for the 2008 regulations. The predicted method use fractions under the proposed regulations were determined using best professional judgment and the application methods used during 2004.

Estimated pesticide VOC emissions for May–October that account for fumigant application methods are calculated by multiplying the unadjusted VOC emissions shown in Table 21, by the application method adjustment factors shown in Table 22 and the corresponding method use fractions in Tables 6–20. Table 23 shows the results of these calculations and provides estimates of the adjusted VOC emissions during the 1990/91 base year and 2004. Table 23 indicates that application method changes between 1990/91 and 2004 are insufficient to achieve the required VOC reductions in the San Joaquin Valley, Southeast Desert, and Ventura nonattainment areas. While application method changes since 1990/91 have lowered emission rates, increased fumigant use more than offsets the application method reductions.

Table 23 also includes an estimate of the lowest pesticide VOC emissions currently feasible through changes in fumigant application methods. This was estimated by assuming that all field fumigations in 2004 used “low-emission” methods. Table 23 shows that even if all fumigant applications used “low-emission” methods, the VOC reductions will be insufficient to meet the SIP obligations for Ventura and possibly insufficient for San Joaquin Valley and Southeast Desert. If future fumigant use decreases relative to 2004, the San Joaquin Valley and Southeast Desert nonattainment areas will likely achieve the required VOC reductions by switching to “low-emission” methods. Conversely, if future fumigant use increases, these two areas are unlikely to achieve the required VOC reductions by relying solely on changing to “low-emission” methods. The Ventura nonattainment area will likely require a substantial decrease in use during May–October in order to achieve the required VOC reduction, even if all applications changed to “low-emission” methods.

Limits on fumigant emissions during May–October within each nonattainment area could achieve the required VOC reductions. Table 24 shows the maximum fumigant emissions that would achieve the required reductions, assuming VOC emissions from nonfumigant pesticides remain the same as 2004. If there are also no changes to the 2004 fumigation practices (i.e. no low-emission methods are adopted), acres fumigated and/or application rates during the May–October period would need to decrease approximately 40–50% in the San Joaquin Valley, Southeast Desert, and Ventura nonattainment areas in order to achieve the required VOC reductions (Table 24). The Sacramento Metro and South Coast nonattainment areas easily achieve the required reductions with current practices. It is likely that some combination of application method changes and emission limits is necessary to achieve the required VOC reductions for several nonattainment areas.

VI. Future Activities and Revised Estimates

These initial estimates of application method adjustment factors, method use fractions, and resulting VOC emission reductions support DPR’s proposed regulations for field fumigations. As required by law, DPR will submit this document and the proposed regulations for peer review and public comment. It is likely, if not certain, that DPR will revise its application method adjustment factors, method use fraction estimates, and the proposed regulations based on the peer review and public comment. DPR anticipates that the comments will include information not previously available to DPR. Moreover, additional field emission studies should be completed later this year.

Research is also in progress on methods to more accurately estimate VOC emissions from nonfumigant pesticides, such as emulsifiable concentrates. If this work is completed in time, it may provide the basis for DPR to develop adjustment factors for other pesticides.

DPR will make revisions after the peer review and public comment period, and incorporate any new data. These revisions will include updates of the application method adjustment factors, method use fractions, and estimated VOC emissions. The revisions will also include an estimate of the pesticide VOC emissions for 2005, based on the 2005 PUR data.

Accuracy of the application method adjustment factors varies. In many cases, the application method adjustment factors are based on preliminary studies or studies for similar application methods, such as the chloropicrin post-fumigation water treatments. Some uncertainties will remain after the review and revisions because the studies in progress will not provide data for all of the uncertain application method adjustment factors. We recommend that DPR conduct monitoring of commercial fumigant applications in 2008 and/or 2009 to determine the effectiveness of the regulations and to update the VOC reduction estimates.

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Table 1. Summary of methyl bromide emission estimates from DPR and registrant field studies. The methyl bromide application method adjustment factors are twice the average emission values shown, based on the assumption that the peak 24-hour emissions are one-half the total emissions.

Study ID[1]	**Bed/Broadcast**	**Tarpaulin Type**	**Chisel Type**	**Injection Depth (inches)**	**Date Applied**	**Peak Emissions in 24 hrs (%)**	**Average Emissions (%)**	**CV (%)**
SE1.1	Bed	None	Rearward curved	12	8/19/92	34	37	47
SE1.2	Bed	None	Rearward curved	12	9/24/92	56		
SE1.3/EH127-2	Bed	None	Rearward curved	12	10/27/92	40		
SE2.2	Broadcast	None	Forward curved	20	10/21/92	62		
EH164-7	Broadcast	None	Forward curved	20	1/22/98	32		
S104.2-1	Broadcast	None	Forward curved	24	3/8/93	44		
S100B1.1	Broadcast	None	Forward curved	24	3/13/93	22		
S110.1	Broadcast	None	Forward curved	24	10/31/95	8.4		
TC199	Broadcast	High barrier	Nobel Plow	12	6/30/92	26	24	52
EH127-1	Broadcast	High barrier	Nobel Plow	12	10/26/92	16		
EH150-6	Broadcast	High barrier	Nobel Plow	12	2/13/97	9.8		
EH163-2	Broadcast	High barrier	Nobel Plow	12	8/21/97	40		
EH164-5	Broadcast	High barrier	Nobel Plow	12	11/1/97	36		
EH164-10A	Broadcast	High barrier	Nobel Plow	12	6/5/98	36		
EH164-10C	Broadcast	High barrier	Nobel Plow	12	6/5/98	30		
EH164-10E	Broadcast	High barrier	Nobel Plow	12	6/7/98	17		
EH164-10G	Broadcast	High barrier	Nobel Plow	12	6/7/98	17		
TC324.1	Broadcast	High barrier	Nobel Plow	12	7/25/98	6.8		
EH163-4	Broadcast	High barrier	Nobel Plow	12	9/2/98	26		
BR787.1A	Broadcast	High barrier	Nobel Plow	12	6/24/99	20		
BR787.2A	Broadcast	High barrier	Nobel Plow	12	6/30/99	48		
S110F1	Bed	High barrier	Rearward curved	6	7/13/93	6.2	81	38
EH164-2	Bed	High barrier	Rearward curved	6	9/8/97	68		
EH164-11	Bed	High barrier	Rearward curved	6	10/6/98	100		
BR787.1B	Bed	High barrier	Rearward curved	6	6/24/99	100		
BR787.1C	Bed	High barrier	Forward curved	6	6/24/99	100		
BR787.2B	Bed	High barrier	Forward curved	6	6/30/99	76		
BR787.2C	Bed	High barrier	Rearward curved	6	6/30/99	76		
EH150-2	Bed	High barrier	Rearward curved	6	12/12/96	100		
EH164-6	Bed	High barrier	Rearward curved	6	12/17/97	100		

[1] Study IDs beginning with EH are DPR studies, all others are registrant studies.

Table 2. Summary of methyl bromide emission estimates from the literature.

Broadcast Tarp						
Reference	**Study Type**	**Soil Type**	**Depth (cm)**	**Emissions (%)**	**Average (%)**	**CV (%)**
JEQ Vol 24:742	Field	Silty Clay Loam	25	32	40	35
JEQ Vol 25:185	Field	Sandy Loam	25	63		
JEQ Vol 26:310	Column	Sandy Loam	30	43		
JEQ Vol 26:310	Column	Sandy Loam	30	37		
JEQ Vol 26:310	Column	Sandy Loam	60	26		
Broadcast Nontarp						
Reference	**Study Type**		**Depth (cm)**	**Emissions (%)**	**Average (%)**	**CV (%)**
JEQ Vol 24:742	Field	Silty Clay Loam	25	89	66	34
JEQ Vol 26:310	Column	Sandy Loam	20	82		
JEQ Vol 26:310	Column	Sandy Loam	30	71		
JEQ Vol 26:310	Column	Sandy Loam	60	38		
ES&T Vol 30:1629	Column	Sandy Loam	30	77		
ES&T Vol 30:1629	Column	Loamy Sand	30	77		
ES&T Vol 30:1629	Column	Clay	30	37		

Table 3. Summary of 1,3-D emission estimates.

Reference	Application Method	Location	Measured Emissions (%)	Emissions (%) interpolated to 18 inches	Average Emissions (%) (interpolated to 18 inches)	CV (%)	Average Emissions (%) (interpolated to 12 inches)	CV (%)
Gillis and Dowling (1998)	Shank Broadcast - 14" depth	Salinas, CA	65	55	41[1]	32	61[2]	32
Gillis and Dowling (1998)	Shank Bed - 12" depth	Salinas, CA	65	48				
Knuteson et al. (1995)	Shank Broadcast - 20-22" depth	Firebaugh, CA	26	37				
Knuteson et al. (1992)	Shank Broadcast - 18" depth	Salinas, CA	25	25				
Knuteson et al. (1999)	Drip	Salinas, CA	29	NA	---	---	---	---
Wesenbeeck & Phillipps (2000)	Drip	Douglas, GA	29	NA	---	---	---	---

[1] Deep application 18 inches
[2] Shallow application 12 inches

Table 4. Summary of chloropicrin emission estimates.

Reference	Application Method	Location	Emissions (%)	Average (%)	CV (%)
Beard (1996)	Broadcast/No Tarp	Arizona	62.5	64.2	6.0
Beard (1996)	Broadcast/No Tarp	Arizona	61.4		
Beard (1996)	Bed/Tarp	Arizona	68.6		
Beard (1996)	Broadcast/Tarp	Arizona	62.3	44.2	35.6
Beard (1996)	Broadcast/Tarp	Washington	33.8		
Beard (1996)	Broadcast/Tarp	Florida	36.5		
Rotonardo (2004)	Drip		15	15	

Table 5. Summary of MITC emission estimates. All calculations are on a 1-acre basis. See text for description of the application methods.

Metam-Sodium Studies					
Reference	**Application Method**	**MITC Emissions (lbs)**	**Total MITC (lbs)**	**Emissions (%)**	**Average Emissions (%)**
Merricks (1999)	Standard Sprinkler	139	172	81	78
Merricks (1999)	Standard Shank	63	86	73	
Merricks (2001)	Sprinkler w/ 3 Water Treatments	39	172	23	21
Merricks (2001)	Shank w/ 3 Water Treatments	16	86	19	
Levine, et al. (2005)	Nontarp drip	0.92	21	4.4	9.1
Levine, et al. (2005)	Nontarp/intermittent drip	0.64	26.2	2.4	
Li, et al. (2006)	Tarp drip	3.58	16	20.5	
Wofford (2005)	Rototill			14	14
Dazomet Studies					
Reference	**Application Method**	**MITC Emissions (lbs)**	**Total MITC (lbs)**	**Emissions (%)**	**Average Emissions (%)**
Certis (2004)	Surface	6.26	137	4.57	17
Fan, in progress	Surface	45	105	42.9	
Certis (2004)	Surface incorporated	6.04	269	2.3	

Table 6. 1990/91 frequency of fumigation methods used (method use fractions) in the Sacramento Metro nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D[1]	Chloropicrin	Methyl Bromide	Metam[3]	Dazomet[3]	Na Tetrathio-carbonate[4]
Shallow injection w/ high permeability tarp or no tarp-broadcast		84	73			
Shallow injection w/ low permeability tarp-broadcast						
Shallow injection w/ high permeability tarp or no tarp-bed				18		
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast		16	14			
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping				2	100	
Sprinkler				55		33
Sprinkler w/ 3 water treatments						
Flood				10		33
Drip w/ high permeability tarp or no tarp				10		34
Drip w/ low permeability tarp				5		
Nonfield soil (structural/post-harvest)			13			

[1] Fumigation methods are described in detail in the text.
[2] Negligible amounts of 1,3-D were applied during 1990/91.
[3] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[4] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 7. 1990/91 frequency of fumigation methods used (method use fractions) in the San Joaquin Valley nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D[1]	Chloropicrin	Methyl Bromide	Metam[3]	Dazomet[3]	Na Tetrathio-carbonate[4]
Shallow injection w/ high permeability tarp or no tarp-broadcast		58	58			
Shallow injection w/ low permeability tarp-broadcast						
Shallow injection w/ high permeability tarp or no tarp-bed				33		
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast		42	42			
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping				3	100	
Sprinkler				60		33
Sprinkler w/ 3 water treatments						
Flood						33
Drip w/ high permeability tarp or no tarp				2		34
Drip w/ low permeability tarp				2		
Nonfield soil (structural/post-harvest)						

[1] Fumigation methods are described in detail in the text.
[2] Negligible amounts of 1,3-D were applied during 1990/91.
[3] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[4] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 8. 1990/91 frequency of fumigation methods used (method use fractions) in the Southeast Desert nonattainment area.

Fumigation Method[1]	**% of Amount Applied**					
	1,3-D[1]	**Chloropicrin**	**Methyl Bromide**	**Metam**[3]	**Dazomet**[3]	**Na Tetrathio-carbonate**[4]
Shallow injection w/ high permeability tarp or no tarp-broadcast		100	69			
Shallow injection w/ low permeability tarp-broadcast						
Shallow injection w/ high permeability tarp or no tarp-bed				10		
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping					100	
Sprinkler				30		33
Sprinkler w/ 3 water treatments						
Flood				50		33
Drip w/ high permeability tarp or no tarp				5		34
Drip w/ low permeability tarp				5		
Nonfield soil (structural/post-harvest)			31			

1 Fumigation methods are described in detail in the text.
2 Negligible amounts of 1,3-D were applied during 1990/91.
3 DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
4 DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 9. 1990/91 frequency of fumigation methods used (method use fractions) in the Ventura nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D[1]	Chloropicrin	Methyl Bromide	Metam[3]	Dazomet[3]	Na Tetrathio-carbonate[4]
Shallow injection w/ high permeability tarp or no tarp-broadcast		50	49			
Shallow injection w/ low permeability tarp-broadcast						
Shallow injection w/ high permeability tarp or no tarp-bed		50	49	20		
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping					100	
Sprinkler				50		33
Sprinkler w/ 3 water treatments						
Flood						33
Drip w/ high permeability tarp or no tarp				15		34
Drip w/ low permeability tarp				15		
Nonfield soil (structural/post-harvest)			3			

[1] Fumigation methods are described in detail in the text.
[2] Negligible amounts of 1,3-D were applied during 1990/91.
[3] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[4] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 10. 1990/91 frequency of fumigation methods used (method use fractions) in the South Coast nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D[1]	Chloropicrin	Methyl Bromide	Metam[3]	Dazomet[3]	Na Tetrathio-carbonate[4]
Shallow injection w/ high permeability tarp or no tarp-broadcast		50	3			
Shallow injection w/ low permeability tarp-broadcast						
Shallow injection w/ high permeability tarp or no tarp-bed		50	3	20		
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping					100	
Sprinkler				50		33
Sprinkler w/ 3 water treatments						
Flood						33
Drip w/ high permeability tarp or no tarp				15		34
Drip w/ low permeability tarp				15		
Nonfield soil (structural/post-harvest)			95			

[1] Fumigation methods are described in detail in the text.
[2] Negligible amounts of 1,3-D were applied during 1990/91.
[3] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[4] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 11. 2004 frequency of fumigation methods used (method use fractions) in the Sacramento Metro nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D	Chloropicrin	Methyl Bromide	Metam[2]	Dazomet[2]	Na Tetrathio-carbonate[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast						
Shallow injection w/ low permeability tarp-broadcast		56	11			
Shallow injection w/ high permeability tarp or no tarp-bed				21		
Shallow injection w/ low permeability tarp-bed		33	6			
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast	100					
Deep injection w/ low permeability tarp-broadcast			11			
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping				15	100	
Sprinkler				45		33
Sprinkler w/ 3 water treatments						
Flood						33
Drip w/ high permeability tarp or no tarp				9		34
Drip w/ low permeability tarp		11		10		
Nonfield soil (structural/post-harvest)			71			

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 12. 2004 frequency of fumigation methods used (method use fractions) in the San Joaquin Valley nonattainment area.

Fumigation Method[1]	**% of Amount Applied**					
	1,3-D	**Chloropicrin**	**Methyl Bromide**	**Metam**[2]	**Dazomet**[2]	**Na Tetrathio-carbonate**[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast	2					
Shallow injection w/ low permeability tarp-broadcast		96	79			
Shallow injection w/ high permeability tarp or no tarp-bed				21		
Shallow injection w/ low permeability tarp-bed		2	1			
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast	98					
Deep injection w/ low permeability tarp-broadcast		1	16			
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping				20	100	
Sprinkler				35		33
Sprinkler w/ 3 water treatments						
Flood						33
Drip w/ high permeability tarp or no tarp				14		34
Drip w/ low permeability tarp				10		
Nonfield soil (structural/post-harvest)		1	4			

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 13. 2004 frequency of fumigation methods used (method use fractions) in the Southeast Desert nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D	Chloropicrin	Methyl Bromide	Metam[2]	Dazomet[2]	Na Tetrathio-carbonate[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast	4					
Shallow injection w/ low permeability tarp-broadcast		69	77			
Shallow injection w/ high permeability tarp or no tarp-bed				6		
Shallow injection w/ low permeability tarp-bed		19	19			
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast			1			
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping					100	
Sprinkler				75		33
Sprinkler w/ 3 water treatments						
Flood						33
Drip w/ high permeability tarp or no tarp	96			7		34
Drip w/ low permeability tarp		10		12		
Nonfield soil (structural/post-harvest)		2	3			

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 14. 2004 frequency of fumigation methods used (method use fractions) in the Ventura nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D	Chloropicrin	Methyl Bromide	Metam[2]	Dazomet[2]	Na Tetrathio-carbonate[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast	2					
Shallow injection w/ low permeability tarp-broadcast		48	63			
Shallow injection w/ high permeability tarp or no tarp-bed						
Shallow injection w/ low permeability tarp-bed		28	37			
Shallow injection w/ 3 water treatments				25		
Deep injection w/ high permeability tarp or no tarp-broadcast	4					
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping					100	
Sprinkler						33
Sprinkler w/ 3 water treatments				20		
Flood						33
Drip w/ high permeability tarp or no tarp	94			5		34
Drip w/ low permeability tarp		24		50		
Nonfield soil (structural/post-harvest)						

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 15. 2004 frequency of fumigation methods used (method use fractions) in the South Coast nonattainment area.

Fumigation Method[1]	**% of Amount Applied**					
	1,3-D	**Chloropicrin**	**Methyl Bromide**	**Metam**[2]	**Dazomet**[2]	**Na Tetrathio-carbonate**[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast						
Shallow injection w/ low permeability tarp-broadcast		40	61			
Shallow injection w/ high permeability tarp or no tarp-bed				25		
Shallow injection w/ low permeability tarp-bed		36	31			
Shallow injection w/ 3 water treatments						
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping					100	
Sprinkler				20		33
Sprinkler w/ 3 water treatments						
Flood						33
Drip w/ high permeability tarp or no tarp	100			5		34
Drip w/ low permeability tarp		24		50		
Nonfield soil (structural/post-harvest)			8			

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 16. Predicted fumigation methods if only “low-emission” methods used (predicted method use fractions) in the Sacramento Metro nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D	Chloropicrin	Methyl Bromide	Metam[2]	Dazomet[2]	Na Tetrathio-carbonate[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast						
Shallow injection w/ low permeability tarp-broadcast		89	14			
Shallow injection w/ high permeability tarp or no tarp-bed						
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments				36		
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast		11	12			
Deep injection w/ 3 water treatments	100					
Rotovate/rototill/soil capping					100	
Sprinkler						33
Sprinkler w/ 3 water treatments				45		
Flood						33
Drip w/ high permeability tarp or no tarp				9		34
Drip w/ low permeability tarp				10		
Nonfield soil (structural/post-harvest)			74			

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 17. Predicted fumigation methods if only “low-emission” methods used (predicted method use fractions) in the San Joaquin Valley nonattainment area.

Fumigation Method[1]	**% of Amount Applied**					
	1,3-D	**Chloropicrin**	**Methyl Bromide**	**Metam**[2]	**Dazomet**[2]	**Na Tetrathio-carbonate**[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast						
Shallow injection w/ low permeability tarp-broadcast		98	85			
Shallow injection w/ high permeability tarp or no tarp-bed						
Shallow injection w/ low permeability tarp-bed			13			
Shallow injection w/ 3 water treatments	2			41		
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments	98					
Rotovate/rototill/soil capping					100	
Sprinkler						33
Sprinkler w/ 3 water treatments				35		
Flood						33
Drip w/ high permeability tarp or no tarp				14		34
Drip w/ low permeability tarp		2		10		
Nonfield soil (structural/post-harvest)			2			

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 18. Predicted fumigation methods if only “low-emission” methods used (predicted method use fractions) in the Southeast Desert nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D	Chloropicrin	Methyl Bromide	Metam[2]	Dazomet[2]	Na Tetrathio-carbonate
Shallow injection w/ high permeability tarp or no tarp-broadcast						
Shallow injection w/ low permeability tarp-broadcast		89	100			
Shallow injection w/ high permeability tarp or no tarp-bed						
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments	4			6		
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping					100	
Sprinkler						33
Sprinkler w/ 3 water treatments				75		
Flood						33
Drip w/ high permeability tarp or no tarp	96	11		7		34
Drip w/ low permeability tarp				12		
Nonfield soil (structural/post-harvest)						

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 19. Predicted fumigation methods if only "low-emission" methods used (predicted method use fractions) in the Ventura nonattainment area.

	% of Amount Applied					
Fumigation Method[1]	**1,3-D**	**Chloropicrin**	**Methyl Bromide**	**Metam[2]**	**Dazomet[2]**	**Na Tetrathio-carbonate[3]**
Shallow injection w/ high permeability tarp or no tarp-broadcast						
Shallow injection w/ low permeability tarp-broadcast		76	100			
Shallow injection w/ high permeability tarp or no tarp-bed						
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments	2			25		
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments	4					
Rotovate/rototill/soil capping					100	
Sprinkler						33
Sprinkler w/ 3 water treatments				20		
Flood						33
Drip w/ high permeability tarp or no tarp	94	24		5		34
Drip w/ low permeability tarp				50		
Non-field soil (structural/post-harvest)						

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 20. Predicted fumigation methods if only "low-emission" methods used (predicted method use fractions) in the South Coast nonattainment area.

Fumigation Method[1]	% of Amount Applied					
	1,3-D	Chloropicrin	Methyl Bromide	Metam[2]	Dazomet[2]	Na Tetrathio-carbonate[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast						
Shallow injection w/ low permeability tarp-broadcast		76	94			
Shallow injection w/ high permeability tarp or no tarp-bed						
Shallow injection w/ low permeability tarp-bed						
Shallow injection w/ 3 water treatments				25		
Deep injection w/ high permeability tarp or no tarp-broadcast						
Deep injection w/ low permeability tarp-broadcast						
Deep injection w/ 3 water treatments						
Rotovate/rototill/soil capping					100	
Sprinkler						33
Sprinkler w/ 3 water treatments				20		
Flood						33
Drip w/ high permeability tarp or no tarp	100			5		34
Drip w/ low permeability tarp		24		50		
Nonfield soil (structural/post-harvest)			6			

[1] Fumigation methods are described in detail in the text.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 21. Estimates of pesticide VOC emissions without application method adjustment factors (unadjusted standard EPs) for 1990, 1991, and 2004. The 1991 goal is a 20% reduction of the 1991 emissions.

Nonattainment Area	Year	Unadjusted VOC Emissions, May – October (tons/day)							
		1,3-D	**Chloropicrin**	**Methyl Bromide**	**Metam**	**Dazomet**	**Na Tetrathio-carbonate[1]**	**Other Pesticides**	**Total Emissions**
Sacramento Metro	1990	0.000	0.036	0.400	0.022	0.000	0.000	2.402	2.860
	1991	0.000	0.035	0.319	0.013	0.000	0.000	2.749	3.116
	2004	0.087	0.007	0.061	0.009	0.000	0.000	1.199	1.363
	1991 goal								2.493
San Joaquin Valley	1990	0.005	0.208	5.158	2.017	0.000	0.006	15.081	22.475
	1991	0.000	0.301	7.493	1.461	0.000	0.000	12.853	22.108
	2004	4.550	0.320	2.364	6.280	0.025	0.113	11.658	25.310
	1991 goal								17.686
Southeast Desert	1990	0.000	0.011	0.902	0.010	0.000	0.000	0.309	1.232
	1991	0.002	0.014	0.414	0.019	0.000	0.000	0.381	0.830
	2004	0.025	0.094	0.296	0.832	0.011	0.005	0.238	1.501
	1991 goal								0.664
Ventura	1990	0.000	0.929	2.785	0.160	0.000	0.001	0.620	4.495
	1991	0.000	0.745	2.531	0.085	0.000	0.000	0.554	3.915
	2004	1.543	3.322	3.317	0.482	0.009	0.000	0.637	9.310
	1991 goal								3.132
South Coast	1990	0.000	0.174	9.248	0.004	0.000	0.000	1.397	10.823
	1991	0.005	0.166	3.489	0.040	0.000	0.000	1.466	5.166
	2004	0.198	0.449	0.669	0.042	0.024	0.000	1.199	2.581
	1991 goal								4.133

[1] Sodium (Na) tetrathiocarbonate.

Table 22. Summary of fumigant application method adjustment factors.

Fumigation Method[1]	% of Amount Applied					
	1,3-D	Chloropicrin	Methyl Bromide	Metam[2]	Dazomet[2]	Na Tetrathio-carbonate[3]
Shallow injection w/ high permeability tarp or no tarp-broadcast	61	64	74	not applicable	not applicable	not applicable
Shallow injection w/ low permeability tarp-broadcast	not applicable	44	48	not applicable	not applicable	not applicable
Shallow injection w/ high permeability tarp or no tarp-bed	not applicable	64	100	77	not applicable	not applicable
Shallow injection w/ low permeability tarp-bed	not applicable	64	100	not applicable	not applicable	not applicable
Shallow injection w/ 3 water treatments	41	20	not applicable	21	not applicable	not applicable
Deep injection w/ high permeability tarp or no tarp-broadcast	41	64	74	not applicable	not applicable	not applicable
Deep injection w/ low permeability tarp-broadcast	not applicable	44	48	not applicable	not applicable	not applicable
Deep injection w/ 3 water treatments	27	20	not applicable	not applicable	not applicable	not applicable
Rotovate/rototill/soil capping	not applicable	not applicable	not applicable	14	100	not applicable
Sprinkler	not applicable	not applicable	not applicable	77	not applicable	33
Sprinkler w/ 3 water treatments	not applicable	not applicable	not applicable	21	not applicable	not applicable
Flood	not applicable	not applicable	not applicable	77	not applicable	33
Drip w/ high permeability tarp or no tarp	29	not applicable	not applicable	9	not applicable	34
Drip w/ low permeability tarp	not applicable	15	not applicable	9	not applicable	not applicable
Nonfield soil (structural/post-harvest)	not applicable	not applicable	100	not applicable	not applicable	not applicable

[1] Fumigation methods are described in detail in DPR's proposed regulations.
[2] DPR assumes 100% conversion of metam and dazomet to MITC and percentages are relative to the amount of MITC applied.
[3] DPR assumes 100% conversion of sodium (Na) tetrathiocarbonate to carbon disulfide and percentages are relative to the amount of carbon disulfide applied.

Table 23. Estimates of pesticide VOC emissions with application method adjustment factors for 1990, 1991, 2004, and predicted 2004 emissions if only "low-emission" methods are used under the 2008 regulations. The goal is a 20% reduction of the 1991 emissions.

Nonattainment Area	Year	Field Adjusted VOC Emissions, May – October (tons/day)							
		1,3-D	Chloropicrin	Methyl Bromide	Metam	Dazomet	Na Tetrathio-carbonate[1]	Other Pesticides[2]	Total Emissions
Sacramento Metro	1990	0.000	0.023	0.309	0.012	0.000	0.000	2.402	2.746
	1991	0.000	0.022	0.247	0.007	0.000	0.000	2.749	3.025
	2004	0.036	0.003	0.054	0.005	0.000	0.000	1.199	1.297
	2004 low[3]	0.023	0.003	0.053	0.002	0.000	0.000	1.199	1.280
	Goal (1991)								2.420
San Joaquin Valley	1990	0.005	0.133	3.817	1.136	0.000	0.001	15.081	20.173
	1991	0.000	0.192	5.545	0.823	0.000	0.000	12.853	19.413
	2004	1.883	0.144	1.189	3.019	0.004	0.011	11.658	17.908
	2004 low[3]	1.241	0.139	1.319	1.050	0.004	0.011	11.658	15.422
	Goal (1991)								15.530
Southeast Desert	1990	0.000	0.007	0.740	0.007	0.000	0.000	0.309	1.063
	1991	0.002	0.009	0.340	0.013	0.000	0.000	0.381	0.745
	2004	0.008	0.044	0.176	0.533	0.002	0.000	0.238	1.001
	2004 low[3]	0.007	0.039	0.142	0.156	0.002	0.000	0.238	0.584
	Goal (1991)								0.596
Ventura	1990	0.000	0.594	2.434	0.090	0.000	0.000	0.620	3.738
	1991	0.000	0.477	2.212	0.048	0.000	0.000	0.554	3.291
	2004	0.465	1.421	2.224	0.069	0.002	0.000	0.637	4.818
	2004 low[3]	0.450	1.231	1.592	0.069	0.002	0.000	0.637	3.981
	Goal (1991)								2.633
South Coast	1990	0.000	0.111	9.188	0.002	0.000	0.000	1.397	10.698
	1991	0.005	0.106	3.466	0.022	0.000	0.000	1.466	5.065
	2004	0.058	0.164	0.455	0.017	0.004	0.000	1.199	1.897
	2004 low[3]	0.058	0.166	0.342	0.006	0.004	0.000	1.199	1.775
	Goal (1991)								4.052

[1] Sodium (Na) tetrathiocarbonate.
[2] VOC emissions for other pesticides (nonfumigants) use the EPs without any adjustment for field conditions.
[3] 2004 low shows the predicted 2004 emissions if all fumigant applications used a "low-emission" application method.

Table 24. Maximum fumigant emissions (fumigant emission limit) that would achieve the goal of a 20% reduction of the 1991 pesticide VOC emissions, assuming VOC emissions from nonfumigant (other) pesticides remain the same as 2004. The 2004 fumigant emissions and the percentage reduction of these emissions needed to achieve the emissions goal are also shown.

Nonattainment Area	**Field Adjusted VOC Emissions, May–October (tons/day)**				**Additional 2004 Fumigant Emissions Reduction Needed to Achieve Goal (%)[2]**
	Emissions Goal	**2004 Emissions From Other Pesticides**	**Max Fumigant Emissions That Achieve Goal[1]**	**2004 Fumigant Emissions**	
Sacramento Metro	2.420	1.199	1.221	0.098	-1146 (goal achieved)
San Joaquin Valley	15.530	11.658	3.872	6.250	38
Southeast Desert	0.596	0.238	0.358	0.763	53
Ventura	2.633	0.637	1.996	4.181	52
South Coast	4.052	1.199	2.853	0.698	-308 (goal achieved)

[1] Maximum Fumigant Emissions That Achieve Goal calculated by subtracting the 2004 Emissions From Other Pesticides from the Emissions Goal.

[2] % reduction based on the difference between the Max Fumigant Emissions That Achieve Goal and the 2004 Fumigant Emissions, and assuming emissions from other pesticides remain the same as 2004. Examples: The 2004 fumigant emissions in Sacramento Metro could increase by 1146% and still meet the emissions goal. The 2004 fumigant emissions in San Joaquin Valley must decrease by 38% in order to meet the emissions goal.

Link: http://www.cdpr.ca.gov/docs/pressrls/2007/070518.htm

DPR PROPOSES FUMIGANT RULES TO CLEAR THE AIR

SACRAMENTO – The Department of Pesticide Regulation today proposed rules to sharply reduce fumigant air emissions that contribute to smog. Acting under federal court order, DPR will begin allocating fumigant use in areas with poor air quality.

The rules also would eliminate some fumigation methods that permit high emissions of volatile organic compounds (VOCs) into the air. While farm chemicals comprise only about 2 percent of California's overall VOC emissions, pesticides are among the top ten VOC sources in the San Joaquin Valley and Ventura air attainment areas. The Southeast Desert area also fails to meet pesticide VOC goals.

The Department predicts its plan will reduce emissions by more than 4.5 tons per day statewide. Proposed rules would reduce fumigant emissions from about 38 to more than 50 percent within the three areas.

"DPR is committed to improving California's air quality," said Director Mary-Ann Warmerdam. "We believe that pesticide emissions should be reduced in a way that protects people and their environment, while preserving the agricultural economy that is critical to so many livelihoods.

"Our strategy requires careful balance and close cooperation with environmental and economic stakeholders," said Warmerdam, "but we are determined to succeed, because there is no acceptable alternative to providing clean air for all Californians."

DPR's regulatory action complies with a 2006 federal court order. The order requires DPR to enforce a 20 percent reduction in pesticide VOCs, compared to 1991 levels. Rules must take effect by January 1, 2008. The court order stemmed from a lawsuit that claimed the state failed to meet its obligations under the federal Clean Air Act.

To achieve timely compliance with the court order, DPR targeted fumigants because of their high VOC emissions. From May to October, fumigants account for 35 percent of VOCs in the San Joaquin Valley area, and 76 percent or more in the Southeast Desert and Ventura areas. (Sacramento Metropolitan and South Coast areas are in compliance with pesticide VOC limits.)

DPR would set an overall fumigant use allocation (or "cap") for each non-attainment area from May to October, based on the court-ordered goal. To remain within allotment and emission limits, fumigant registrants would track and report applications. They also would calculate emissions from each application method used, at DPR's direction.

Statewide, farm fumigants account for about 20 percent of all pounds applied, and the proposed rules apply to all seven of them: methyl bromide, metam-sodium, 1-3 Dichloropropene, chloropicrin, dazomet, metam-potassium, and sodium tetrathiocarbonate.

As part of the rulemaking process, an economic analysis estimated it could cost growers $10 million to $40 million a year for low-emission application methods. DPR expects San Joaquin and the Southeast Desert to hit their VOC target levels using low-emission methods.

But in the Ventura area, low-emission applications alone would not meet the VOC target. Based on 2004 pesticide use reports, one-third of Ventura's 30,000 fumigated acres might go untreated to meet the target. Depending upon cropping and alternate land use, the economic loss could range from zero to $80 million, in a worst-case scenario.

Last year, DPR launched an initiative to develop a comprehensive, long-term strategy to reduce pesticide air emissions without disrupting the agricultural economy. That strategy included a data call-in that required registrants to submit plans on how to reduce VOCs for about 600 products. Almost all have responded, and data evaluation is underway.

On another front, DPR's proposed budget for 2007-08 includes $780,000 to revive Pest Alliance grant partnerships with the private sector, to seek alternatives to fumigants and other reduced-risk strategies.

DPR will sponsor a Pesticide VOC Research Symposium May 22-23 in Sacramento.

Formal hearings for the VOC regulations have been scheduled July 10 in Ontario and July 12 in Parlier, Fresno County. (See the proposed regulations)

One of six departments and boards within the California Environmental Protection Agency, DPR regulates the sale and use of pesticides to protect people and t he environment.

APPENDIX EE

Symposium

Methyl Bromide Alternatives – Meeting the Deadlines

Status of Chemical Alternatives to Methyl Bromide for Pre-Plant Fumigation of Soil

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ABSTRACT

Duniway, J. M. 2002. Status of chemical alternatives to methyl bromide for pre-plant fumigation of soil. Phytopathology 92:1337-1343.

None of the chemical alternatives currently registered and available has the full spectrum of activity and versatility of methyl bromide as a pre-plant soil fumigant. Chloropicrin and 1,3-dichloropropene (Telone) can provide significant control of many plant pathogens in soil and growth stimulation in annual crops. These compounds, however, provide limited control of weeds or other residual plant materials in soil of concern in nursery production systems, and some perennial replant diseases. Methyl isothiocyanate generators such as metam sodium have broad biocidal activity in soil, but are more difficult to apply effectively. In most soil applications, the available alternatives are likely to be used in combinations, either as mixtures (e.g., 1,3-dichloropropene and chloropicrin) or sequentially (e.g., chloropicrin followed by metam sodium). They may also be supplemented with other more specific pesticides and cultural controls. Among the alternatives currently under active development but not yet available, methyl iodide and propargyl bromide probably have activity that most closely parallels that of methyl bromide in soil. However, all of the chemical alternatives to methyl bromide will be subject to continuing review and more regulation. Furthermore, we do not know the actual prospects for registration of the new fumigants currently under development and there is a risk that registered fumigants will not be available for large-scale use in soil indefinitely.

Methyl bromide has been used as a pre-plant soil fumigant for over 40 years. It has activity in soil against a wide spectrum of plant pathogens and pests, including fungi, nematodes, insects, mites, rodents, weeds, and some bacteria. In addition, methyl bromide is sufficiently volatile to penetrate soils for some distance from the points of application. Although methyl bromide is acutely toxic, methods of soil fumigation with methyl bromide have evolved to meet current registration and safety requirements. In agricultural practice, it is versatile, highly effective, and relatively easy to use. Approximately 20,000 metric tons are applied annually to soils in the United States, making it one of the most used pesticides in the country (23).

The states with the highest use of methyl bromide in soil are California and Florida, and the crops with the largest use in soil include tomatoes, strawberries, peppers, ornamentals, nurseries, tobacco, grapes, and melons (23). Most of the methyl bromide use is in high-input, high-value horticultural production systems in which the expense of fumigation is a small part of the whole and returns are potentially large. Because of the input costs, however, the risks of large monetary losses in these systems without fumigation are high. Furthermore, much of the land involved is of relatively high value and requires continuous production of high-value crops to make farming profitable. Where certain high-value crops such as strawberries and tomatoes are replanted on the same ground, pre-plant fumigation of soil with methyl bromide gives the largest benefits (19,30). While certain annual cropping systems are the largest users on an annual basis, pre-plant fumigation of soil with methyl bromide is also important to the control of replant diseases in perennial crops and for nursery propagation of pathogen-free, quality planting materials of many kinds. The extent to which methyl bromide has been used in soil and the predicted losses following its pending phase-out show the importance of this pesticide to U.S. agriculture (3).

The process leading to the phase-out of methyl bromide in the United States was initiated in 1993 when the U.S. Environmental Protection Agency (EPA) officially determined that methyl bromide is a Class I Stratospheric Ozone Depleting Substance. Effective 1 January 1994, domestic production was capped at 1991 levels and methyl bromide use was scheduled to be eliminated by 2001 under provisions of the U.S. Clean Air Act (23). Regulations in the United States have since been changed to conform with the current provisions of the Montreal Protocol for the international reductions and phase-out of methyl bromide in developed countries, i.e., 25, 50, 70, and 100% reductions (relative to 1991) in 1999, 2001, 2003, and 2005, respectively (2). For developing countries, the reductions are more gradual and the phase-out is delayed until 2015. While the Montreal Protocol allows for some critical and quarantine use exemptions after 2005, the circumstances under which methyl bromide use in soil would be allowed are likely to be highly restricted (2). With a continued demand for methyl bromide and reduced supply, growers will soon not be able to obtain sufficient amounts of methyl bromide to meet previous needs. Therefore, there is a pressing need for effective alternatives to methyl bromide fumigation of soil. Unfortunately, nonchemical alternatives are not sufficiently developed or effective to meet current needs and growers will be turning to one or more of the known chemical alternatives to methyl bromide for fumigation of soil for the near future. This has already begun, for example, in Australia where chloropicrin use has increased as methyl bromide use declined in recent years (22). This review will emphasize those chemical alternatives for which there is sufficient information to suggest that they will be effective in soil and possibly available for agricultural use in the foreseeable future. Further-

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more, the focus here is on chemical alternatives to methyl bromide under investigation for strawberry production in California. Brief reviews of alternatives in other regions or other crops can be found elsewhere (16,22).

Strawberry cultivation in California has evolved over the last 40 years into a highly productive system that relies heavily on soil fumigation with methyl bromide (30). Although a variety of crop production systems have relied on methyl bromide for soil fumigation (23), in recent years, there has been more research on the alternatives to methyl bromide for strawberry than for any other crop production system. Although specific pests and pathogens targeted by soil fumigation vary between cropping systems and locations, the alternative fumigants that are found to work for strawberry production are also likely to have activity and applications in other production systems. Since about 1965, well over 90% of the land used for strawberry production in California has been fumigated with mixtures of methyl bromide and chloropicrin before each crop is planted, both for fruit production and for runner plant production in nurseries (30). The resulting high level of control of soilborne pathogens has allowed breeders to concentrate on developing cultivars with very high yield potential and berry quality, and has allowed horticulturists to further optimize California's annual production system (30,37). As a result, average berry yields have increased from 11 to 13 tons/ha in the era before fumigation to over 45 tons/ha in more recent years (30). California now produces roughly 80% of the U.S. fresh market strawberries and about 20% of the total worldwide. In 1999, strawberries were produced on over 9,700 ha and had a farm gate value over $800 million. In addition, there is a large nursery industry producing several hundred million runner plants each year, many of which are exported. Soil fumigation remains central to this production system. A recent summary analysis of 45 studies, in which strawberry yields in California were compared with and without standard methyl bromide-chloropicrin fumigation of soil, showed that on average fumigation increased yield 94% (25).

Benefits of soil fumigation. Soil fumigation was first developed for strawberries in California because of a pressing need to control Verticillium wilt and weeds (30,31). Similar to other cropping systems, the advantages of soil fumigation with methyl bromide and chloropicrin mixtures for control of other soilborne pathogens of strawberry, including important *Phytophthora* spp. and nematodes, soon became apparent (23,29,30). In addition, soil fumigation generally increases root health, growth, and fruit yields in strawberry even when major pathogens are not present in soil (30,37). Although the microbiology underlying this general growth response has been researched extensively (29), it has remained a fertile area of investigation. The growth response has been attributed in part to a temporary inhibition of nitrification and increased ammonia-N in soil (22,29,30), but other shifts in microbiology are surely important. Soil fumigation with mixtures of methyl bromide and chloropicrin reduces the incidence of *Pythium*, *Cylindrocarpon*, and binucleate *Rhizoctonia* spp. damaging to strawberry roots (17,18,30,32,34). Endomycorrhizae are reported to benefit strawberry (6), but they are also reduced following fumigation (J. Hao and J. M. Duniway, *unpublished data*). Although a reduction of pathogens in soil is a major benefit of fumigation, it is important to note that fumigation with methyl bromide and chloropicrin does not sterilize soil (29). For example, significant populations of bacteria survive fumigation and *Pseudomonas* spp. rapidly recolonize fumigated soils; some of these colonize strawberry roots in high numbers (33). Individual isolates of *Pseudomonas fluorescens*, *Pseudomonas putida*, and *Pseudomonas chlororaphis* from strawberry roots growing in fumigated soils increase the growth of strawberry significantly in natural soils in greenhouse experiments (33). Therefore, beneficial root colonizing bacteria may contribute to the favorable response of strawberry to soil fumigation. Whatever the underlying mechanisms turn out to be, the lack of economic yields in strawberry without fumigation is in part a replant problem. A survey of fumigation trials in California suggests that the benefits of soil fumigation on strawberry increased over the first 3 years of consecutive strawberry culture on the same ground (25). More specifically, when ground with no history of strawberry culture was first planted with strawberry for several consecutive years with and without annual fumigation of the same plots, the beneficial effects of fumigation on yield increased with years of repeated strawberry (Fig. 1) (J. M. Duniway, *unpublished data*). Unfortunately, because of high land costs and the need for high potential returns each year, many strawberry growers in California are forced to replant strawberries in the same fields yearly without rotation.

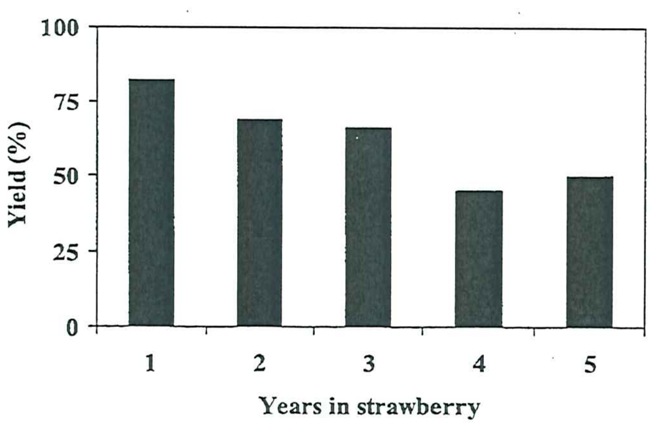

Fig. 1. Yield of fresh market strawberries in nonfumigated soil as a percentage of the yield obtained in fumigated soil, plotted as a function of years of consecutive strawberry cultivation on the same soil. Three replicate beds were either fumigated with 364 kg/ha of 67% methyl bromide and 33% chloropicrin or not fumigated each year and planted with cv. Selva strawberry. The plots were located in a field near Watsonville, CA, with no history of strawberry cultivation for the previous 12 years.

Chemical alternatives to methyl bromide. Table 1 lists most of the chemicals that have been discussed recently as possible alternatives to methyl bromide for soil fumigation (2). A majority of these chemicals were considered to be potential fumigants as soil fumigation technology evolved about 40 years ago, but methyl bromide rapidly became the preferred fumigant (29). While the list of possible alternatives seems long, sufficient information on activity in soil is available only for a minority of the chemicals listed, and still fewer are registered pesticides and available for agricultural use in the United States. Chemical alternatives that are available and that have known broad-spectrum activities in soil are chloropicrin, 1,3-dichloropropene (1,3-D), and the methyl isothiocyanate (MITC) generators, metam sodium and dazomet. Each may be used individually, but they are more likely to be used as mixtures (e.g., 1,3-D and chloropicrin) or in

TABLE 1. Chemical alternatives to methyl bromide for soil treatment

	Requiring further development	
Currently available	MBTOC[a]	Additions[b]
Chloropicrin	Methyl iodide	Other halogenated hydrocarbons
1,3-Dichloropropene	Propargyl bromide	Propylene oxide
Methyl isothiocyanate	Ozone	Sulfur dioxide
Generators	Formaldehyde	Peroxyacetic acid
Metam sodium	Sodium tetrathiocarbonate	Acrolein (2-propenal)
Dazomet	Carbon disulfide	Others to be developed
	Anhydrous ammonia	
	Inorganic azides	
	Natural compounds	

[a] Alternatives considered by the 1998 report of the Methyl Bromide Technical Options Committee, United Nations Environmental Programme (2).
[b] Alternatives added by J. M. Duniway.

sequential applications (e.g., chloropicrin followed by metam sodium). Fortunately, improved methods of application for these chemicals to soil are evolving at this time (1,36). While the available alternatives do not cause depletion of stratospheric ozone, relative to methyl bromide, they all have limitations in activity or versatility as soil fumigants. Among the chemical alternatives that are not registered, methyl iodide and propargyl bromide stand out for having good information on their level and broad spectrum of activity in soil. They are also not sufficiently stable in the atmosphere to cause significant stratospheric ozone depletion. The other chemical alternatives listed as requiring further development have either insufficient activity or feasibility for soil fumigation, or too little is known about them to suggest they might actually become a useful and registered replacements for methyl bromide. These, and other chemicals that may yet surface as prospective alternative fumigants in soil, are not likely to become available for general use for several years and, therefore, are not reviewed further here. In addition, a variety of more specific pesticides that target certain fungi, bacteria, nematodes, insects, or weeds might be used to supplement soil treatments with one or more of the chemical alternatives listed. These more specific pesticides are also not reviewed here, the concentration being on chemical fumigants with broad-spectrum activity in soil that might be available in the next few years.

Chloropicrin (trichloronitromethane). The early use and development of chloropicrin as a soil fumigant is reviewed elsewhere (19,29,30). Chloropicrin was first used for strawberry culture in California to control Verticillium wilt and it has strong fungicidal activities in soil (29–31). Chloropicrin also has beneficial nematicidal activity, but is much less nematicidal than methyl bromide or 1,3-D (13); it also has somewhat less activity on dormant weeds and seeds in soil. In the 1960s, the use of chloropicrin alone as a soil fumigant in strawberry production was rapidly replaced by mixtures of chloropicrin with methyl bromide. This occurred because the mixture has a broader spectrum of activity (e.g., including weeds) and because of the synergistic activity of methyl bromide and chloropicrin on control of *Verticillium dahliae* in soil (29–31). Various mixtures of methyl bromide with chloropicrin (e.g., 67/33 and 57/43%) have become the standard for strawberry production in California and elsewhere, although chloropicrin has been used less in Europe because of its stigma from use as tear gas in World War I (30). The odor and eye irritation caused by chloropicrin are perceptible at very low levels, and as a result, it is used as a warning agent in methyl bromide when the latter is used as a stand-alone fumigant.

More recent trials of chloropicrin as a stand-alone soil fumigant for strawberry production in California show that it is still effective. For example, in large replicated field experiments done near Watsonville, CA, broadcast fumigation with chloropicrin at 336 kg/ha gave 94 to 96% of the strawberry yields obtained with a standard mixture of methyl bromide and chloropicrin (Fig. 2) (9). Similar results were obtained in southern California near Oxnard (5; M. D. Coffey and A. O. Paulus, *unpublished data*). These experiments were done in commercial strawberry fields with histories of methyl bromide fumigation, but fumigation with the methyl bromide/chloropicrin standard each year increased yields 44 to 85% over those obtained in nonfumigated soil, even though *V. dahliae* and *Phytophthora* spp. were not present at damaging levels (5,9). Furthermore, the performance of chloropicrin relative to the methyl bromide/chloropicrin mixture did not diminish with repeated use on the same ground in a strawberry-lettuce rotation (9). Although chloropicrin can also be effective in bed applications that require less material, results for strawberry production at a coastal site near Watsonville have been variable. For example, shank applications of chloropicrin to two-row beds provided 117 and 77% of the yields obtained with methyl bromide and chloropicrin in 1997 and 1998, respectively (Fig. 3). Earlier treatments of the same plots with chloropicrin gave relative yields of 90 and 109% in 1995 and 1996, while the relative yields without fumigation ranged from 45 to 82% of that obtained with a methyl bromide/chloropicrin standard (10). All of the bed fumigation treatments in these experiments provided a high and equivalent level of Verticillium wilt control and other factors are likely to have contributed to the year-to-year variation in the relative effectiveness of chloropicrin (10). In other experiments, bed fumigation with chloropicrin at 224 or 280 kg/ha resulted in yields approximately 12% less than the standard methyl bromide/chloropicrin control (14). A survey of earlier fumigation trials for strawberry production in California suggests that soil fumigation with chloropicrin alone in place of methyl bromide mixed with chloropicrin will result in an average yield loss of 9.6% (25). The same survey suggests that high rates of chloropicrin are more effective and that the performance of chloropicrin may decline with consecutive years of use on the same ground for strawberries. While the latter result is doubtful, we clearly need better data on the minimum rates of chloropicrin needed for effective soil treatment, especially where major pathogens are present in soil. For example, elimination of *V. dahliae* in field soil at 15 cm depth required 140 kg/ha, but control equivalent to that obtained with methyl bromide and chloropicrin at 50 cm depth required 224 kg/ha (J. M. Duniway, *unpublished data*). Even the higher rate provided only partial control of buried inoculum of *Phytophthora cactorum* (G. Browne, *unpublished data*). Although chloropicrin is registered and available now for use as a soil fumigant in California, there is resistance by regulators in some counties to the use of the high rates known to be most effective and the actual regulations on its use are still evolving. In addition, methods to apply chloropicrin as an emulsion in water through drip irrigation systems are under development (27). Although chloropicrin has considerable utility as a stand-alone fumigant in soil, it is more likely to be used in mixtures with 1,3-D or in sequential applications with metam sodium (9,10,27).

1,3-D. This compound was initially developed to be a soil nematicide in a mixture with 1,3-dichloropropane (D-D) (13,19).

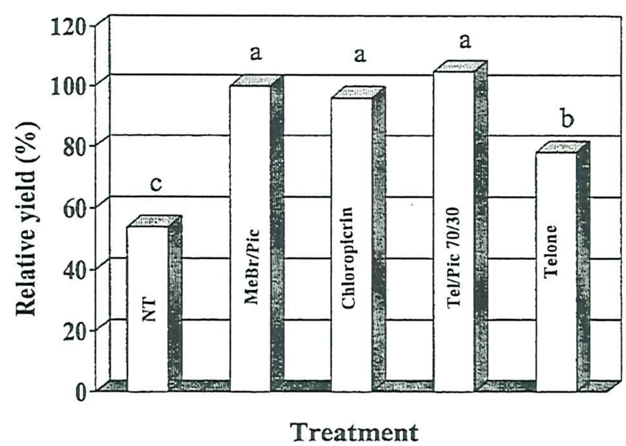

Fig. 2. Yields of fresh market strawberries obtained in 1996 from replicated field plots where the soil was not treated or was fumigated with 67% methyl bromide and 33% chloropicrin at 361 kg/ha, chloropicrin at 353 kg/ha, or 70% Telone II (1,3-dichloropropene) and 30% chloropicrin at 484 kg/ha, or Telone II at 340 kg/ha. Yields with different letters are significantly different at $P = 0.05$. Fumigants were injected at 20 cm depth (standard broadcast treatment), and the soil was immediately covered with polyethylene, which was removed after 5 days. Beds were raised, and strawberry cv. Selva was transplanted (two rows per bed) in November 1995. Conventional practices for annual strawberry production and pest management for the area were followed. Berries were picked for fresh market at least twice weekly for several months by normal grower practice. These plots were part of a larger set of experiments on alternatives to methyl bromide conducted over 4 years in commercial fields farmed with a strawberry-lettuce rotation just inland from Watsonville, CA (9).

Early in its development, however, D-D exhibited activity against some oomycota (13), and with additional use of 1,3-D as a fumigant, its known spectrum of activity has grown to include certain plant pathogenic fungi and bacteria (24). 1,3-D is available as a fumigant under the brand name Telone (Dow AgroSciences LLC, Indianapolis), either as a stand-alone fumigant (Telone II, 94% 1,3-D) or in mixtures with 17 or 35% chloropicrin (Telone C-17 and Telone C-35, respectively). As distributed in the United States, 1,3-D is a mixture of *cis* and *trans* isomers, with the *cis* isomer being the more biologically active of the two. Although 1,3-D is volatile and somewhat mobile in the soil as a gas, it is less volatile and mobile than methyl bromide.

Telone II is not likely to be used as a stand-alone soil fumigant in strawberry production. Nevertheless, the author and coworkers did apply it in one field experiment near Watsonville, CA, to determine if it would give general growth and yield increases in strawberry. When applied by standard broadcast methods at 340 kg/ha, Telone II increased subsequent strawberry yields significantly over those obtained without soil fumigation (Fig. 2) (9). Neither plant pathogenic nematodes, *V. dahliae*, nor *Phytophthora* spp. were significant factors affecting strawberry in this experiment and the results suggest that Telone II causes many of the shifts in soil microbiology associated with the positive response of strawberry to soil fumigation with methyl bromide and chloropicrin reviewed above. A mixture of 70% Telone II and 30% chloropicrin in the same experiment at 484 kg/ha, however, provided significantly higher yields than Telone II alone (Fig. 2). In fact, the Telone/chloropicrin mixture approximately doubled yields relative to nonfumigated soil in a manner similar to standard fumigation with methyl bromide and chloropicrin (Fig. 2) (9).

Although a survey of earlier fumigation trials for strawberry production in California suggests that soil fumigation with Telone mixed with chloropicrin is no better than fumigation with chloropicrin alone (25), more recent experiments with Telone C-35 have shown it to be a highly effective fumigant for strawberry production in California. For example, shank applications to preformed beds with Telone C-35 at 476 kg/ha (treated bed area) often resulted in yields equivalent to those obtained with methyl bromide/chloropicrin (Fig. 3) (10). Shank application to beds at a lower rate of 308 kg/ha nearly doubled yield over that obtained without fumigation, but the resulting yield was 12% less than the methyl bromide/chloropicrin standard (14). Relative to broadcast application, fumigation of preformed beds requires less chemical, e.g., approximately 40% less for two-row strawberry beds. Perhaps more important is the recent evolution of methods to emulsify Telone C-35 in water for delivery into preformed beds through drip irrigation systems under plastic mulch (27). This method was tried first in other cropping systems, but results from early trials in strawberries showed it to be highly effective. For example, when applied as an emulsion, Telone C-35 provided berry yields equivalent to those obtained with standard bed or broadcast fumigations with methyl bromide/chloropicrin (Fig. 3) (10). Numerous experiments and grower trials have now been conducted with drip and/or shank applied Telone C-35 for strawberry and it is likely to become one of the preferred alternatives to methyl bromide/chloropicrin for strawberry production in California. Furthermore, in part because of its strong nematicidal activity, Telone may also become an important component of soil fumigation practices for nursery production of runner strawberry plants in California. In addition, Telone C-17 is one of the likely alternatives to methyl bromide for tomato production in Florida, where nematode control is important; however, where nutsedge is a problem, an additional herbicide will be required (16).

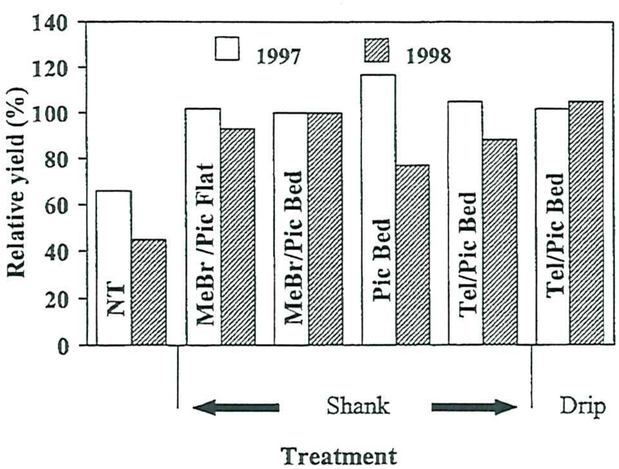

Fig. 3. Yields of fresh market strawberries obtained in 1997 and 1998 from replicated field plots at a coastal site near Watsonville, CA, where the soil was not treated or was broadcast or bed fumigated with 67% methyl bromide and 33% chloropicrin at 364 kg/ha, bed fumigated with chloropicrin at 336 kg/ha, or bed fumigated with Telone C-35 at 476 kg/ha. Strawberry was grown every year, *Verticillium dahliae* was present in the soil, and the broadcast fumigation treatment (rate per total ground area) was applied in September 1996 and 1997. Two-row beds were then shaped, fumigated by shank injection (two shanks per bed, 15 to 20 cm deep, rates given per unit of treated bed area), and covered with black plastic mulch. Telone C-35 was also applied to beds as a water emulsion through the drip irrigation lines after the plastic mulch was in place. 'Selva' was transplanted through the plastic mulch 1 month later and conventional practices for annual strawberry production and pest management for the area were followed. Berries were picked for fresh market at least weekly for several months by normal grower practice.

The complex history of recent regulatory reviews and requirements for reregistration of 1,3-D as a soil fumigant is reviewed elsewhere (24). Regulatory concerns include potential ground water contamination, worker exposure, air emissions for potential chronic exposure, and a California Proposition 65 listing as a carcinogen. As of this writing however, Telone II, Telone C-17, and Telone C-35 are all registered and available for use nationally and in California. An emulsified version of Telone C-35 is approaching registration under the brand name InLine (Trademark of Dow AgroSciences LLC). Although registered and available, some of the regulations to mitigate risks of human exposure are cumbersome and actually limit the utility of 1,3-D products. These include extensive buffer zone requirements (e.g., cannot be shank applied within 90 m of occupied structures), personal protective equipment to limit worker exposure, and in California, a cap on the amount of 1,3-D that can be applied in 1 year per township (93 km^2) to mitigate potential for chronic exposure. Large buffer zones are a limitation in many areas of strawberry production that are near or abut urban areas. Because of the heat at the usual time of soil treatment, the personal protective equipment requirements are difficult to implement in Florida. The township cap in California, which varies with the season and method of application, will restrict the availability of 1,3-D as a full replacement for methyl bromide in some areas of concentrated strawberry production (4). Fortunately, methods of application of 1,3-D products to soil are evolving that further reduce worker exposure (e.g., drip delivery of emulsified 1,3-D [1]) and air emissions (e.g., low permeability plastic mulches [36]). Even with the current restrictions in place, it is likely that 1,3-D, when used in combination with chloropicrin, will become one of the preferred alternatives to methyl bromide for strawberry production in California.

Methyl isothiocyanate. Metam sodium (sodium *N*-methyl dithiocarbamate) degrades rapidly to methyl isothiocyanate (MITC) in soil, and has been distributed as a soil fumigant in a stabilized aqueous solution under a variety of trade names since the 1950s (e.g., Vapam HL, 42% metam sodium, Amvac Chemical Corp., Newport Beach, CA). MITC is the primary active agent of metam sodium in soil and is a broad-spectrum fumigant with activity against plant pathogenic nematodes, weeds, oomycota, and a variety of plant pathogenic fungi (13). The behavior of metam sodium

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and MITC in soil has been investigated extensively (26), and current application practices rarely achieve an optimum distribution or the ideal conditions of soil temperature and moisture for MITC to kill all stages of plant pests and pathogens. Although metam sodium is registered, available to growers, and has been used widely, it has a reputation of being unreliable if not used carefully. Metam sodium and its active derivatives are not very mobile in soil and the product must be delivered to the volumes of soil targeted for treatment either by mechanical placement or by water infiltration. For most applications, water is used to move the material in soil, but this needs to be done without leaching too deeply or the volatilization of irritant and smelly vapors. Some sort of surface seal, either applied as water or plastic, is usually required.

Metam sodium has been used on a limited scale as a stand-alone fumigant for strawberry production in California for a long time, but the results have been variable and yields are generally significantly lower than those obtained with methyl bromide and chloropicrin. Whereas some of these applications have been done in part by sprinklers, most have delivered metam sodium into preformed beds through drip lines under plastic mulch. With this latter method, more recent studies have shown metam sodium at approximately 280 liters/ha of treated bed area to give about half the yield increase induced by standard fumigation with methyl bromide and chloropicrin (25,27). Unfortunately, metam sodium probably reacts with chloropicrin and 1,3-D in aqueous solutions and simultaneous or combined applications of metam sodium with these other fumigants have not been very successful (27). Sequential applications separated by several days in time, however, can be effective. For example, shank applications to beds of chloropicrin at 224 and 280 kg/ha or Telone C-35 at 308 kg/ha, when followed 2 weeks later by drip applications of metam sodium, provided strawberry yields nearly equivalent to those obtained following standard fumigation with methyl bromide and chloropicrin (14). Although sequential treatments take more time, they may facilitate soil treatments that are effective with less chloropicrin or 1,3-D. Furthermore, a sequential treatment with metam sodium can provide an added increment of weed and soilborne pathogen control, although these benefits are more likely following chloropicrin than Telone C-35 (G. T. Browne and J. M. Duniway, *unpublished data*).

MITC can also be generated in soil using the granular product dazomet (Trade name Basamid; BASF Corp., Mount Olive, NJ). As is the case for metam sodium, dazomet is not likely to be used as a stand-alone fumigant for strawberry production, but may be a useful addition to other fumigants in sequential applications. For example, applying Basamid at 168 to 224 kg/ha over the tops of beds and furrows, with an appropriate series of overhead sprinkler irrigations to activate the product and seal the soil, either before or after shank fumigations with Telone C-35 (314 to 400 kg/ha) increased strawberry yields somewhat, but more important, provided a high level of weed control (28). Although dazomet can potentially be used as a more general soil fumigant at higher rates, the optimum sequence of soil moisture for full activation following application without residual phytotoxicity is difficult to achieve. Furthermore, dazomet is currently registered in the United States only on nonbearing (e.g., nursery) crops. Experimentation is currently being done, however, to use dazomet in sequential applications with other fumigants for the production of runner strawberry plants in nurseries. The idea is to use other fumigants for general pathogen and nematode control in soil and use dazomet to augment control of weeds and volunteer strawberry plants in the upper layers of soil. Control of volunteer strawberry seedlings is needed to maintain trueness to type in runner plant production. Metam sodium and dazomet will continue to have useful applications in strawberry production, but most likely they will be used in conjunction with other soil fumigants that provide greater or more consistent pathogen control.

Chemical alternatives requiring further development. Among the growing list of chemicals proposed as alternatives to methyl bromide for soil fumigation (Table 1), methyl iodide and propargyl bromide currently stand out for having chemical reactivity and known spectrum of biological activity in soil that are similar to those of methyl bromide. Both were considered to be prospective fumigants several decades ago, but were overshadowed by the growing availability and utility of methyl bromide at that time. Neither methyl iodide nor propargyl bromide has significant potential for transport to the stratosphere and they are not considered to be stratospheric ozone depleting compounds (21). Methyl iodide can be applied to fumigate soil by conventional shank methods and both can be applied by evolving methods of delivery in water through drip systems. It is important to note, however, that neither methyl iodide nor propargyl bromide has been registered with the U.S. EPA as a pesticide or soil fumigant. As of this writing, there has been more development activity and there is more information available on methyl iodide than on propargyl bromide.

Methyl iodide. Considerable research is underway to further develop and register methyl iodide as a soil fumigant under the name Iodomethane or Midas (Tomen Agro Inc., now Arvesta Corp., San Francisco). The basic properties of methyl iodide are reviewed elsewhere (11,21). Although methyl iodide has efficacy equal to or better than methyl bromide against fungi, nematodes, and weeds on an equimolar basis (21), it also has a much higher molecular weight (142 versus 95) and may require higher rates on a weight basis. Although the toxicology data needed for registration of methyl iodide are still being gathered, its toxicology is likely to be similar to that of methyl bromide. Methyl iodide, however, is listed on the California Proposition 65 list as a carcinogen. Methyl iodide does have a safety advantage over methyl bromide in being liquid rather than gas at normal handling temperatures, but it is sufficiently volatile and mobile in soil to act as a true fumigant (11).

In one of the early trials of methyl iodide as a fumigant for strawberry production, when shank applied in beds at 403 to 448 kg/ha, methyl iodide worked as well as the methyl bromide/chloropicrin standard in increasing berry yields and controlling Verticillium wilt (7,8). Like methyl bromide, methyl iodide appears to have some synergy with chloropicrin in killing fungi (12), and most recent trials of methyl iodide for strawberry have used 50/50 mixtures of methyl iodide with chloropicrin. For example, when this mixture was drip applied into beds at 224 to 336 kg/ha, it gave berry yields almost equivalent to those obtained with standard methyl bromide/chloropicrin fumigation (H. Ajwa, *personal communication*). Similar drip applications also reduced the numbers of viable *V. dahliae* microsclerotia buried at depths of 15 and 30 cm, but control at deeper depths was somewhat less than with the methyl bromide (J. M. Duniway, *unpublished data*). However, in strawberry nursery experiments where a 50/50 mixture of methyl iodide and chloropicrin was shank applied by standard broadcast methods, it worked as well as the methyl bromide/chloropicrin standard in reducing inoculum of *V. dahliae* buried in soil and nearly as well for runner plant production (J. M. Duniway, *unpublished data*). There are numerous trials being done to further develop methyl iodide as a soil fumigant for strawberries and other crops. No doubt, methods for its application will be further optimized to improve pathogen control while reducing risks of residual phytotoxicity. Barring unforeseen complications, methyl iodide is likely to become an important alternative to methyl iodide for soil fumigation.

Propargyl bromide (3-bromopropyne). While there is considerable recent activity to further develop propargyl bromide as a soil fumigant (35), there are few published reports to date on its effectiveness in soil. Propargyl bromide is physically unstable and in recent years has been formulated in 20% toluene for handling, but more acceptable carriers are currently under development.

Recent trials show that propargyl bromide can be a very effective soil fumigant. For example, injections of propargyl bromide into soil microplots in Florida at 168 kg/ha controlled root knot nematode damage to tomato and increased yield in the same manner as methyl bromide applied at 448 kg/ha (20). Propargyl bromide has also been applied in water through drip systems for strawberry production in California. For example, in an experiment near Watsonville, application of 202 kg/ha to preformed beds by this method provided berry yields nearly equivalent to those obtained with methyl bromide/chloropicrin at 420 kg/ha; propargyl bromide also gave a high level of Verticillium wilt control in this experiment (H. Ajwa, *personal communication*). Given its very high level of activity as a biocide in soil, considerable development work is being done to further stabilize propargyl bromide for safe distribution, and field research is under way to further optimize it as a soil fumigant. However, the status of the toxicology information needed for U.S. EPA registration is unclear, and there are many hurdles to overcome for propargyl bromide to become a registered and available soil fumigant.

Concluding remarks. Among the known chemical alternatives to methyl bromide, chloropicrin, 1,3-D, and metam sodium are the only ones currently registered and available in the United States that have enough broad-spectrum activity to be considered as current replacements for methyl bromide in soil fumigation. None of these three, however, can be considered an equivalent replacement for methyl bromide in most soil applications, and they are likely to be used in mixed or sequential applications. Two additional alternatives, methyl iodide and propargyl bromide, have strong fumigant activities in soil that approach those of methyl bromide. Although these compounds are currently being developed as soil fumigants, they are not registered and we do not know when or even if they will actually become available as commercial fumigants. No doubt, the list of possible chemical alternatives to methyl bromide will continue to grow as other compounds and methods of soil treatment are explored. Any new chemical alternatives identified in the near future, however, are several years from commercial application and are not likely to help offset reductions in methyl bromide scheduled between now and 2005. Improved methods of soil fumigation (e.g., drip application and less permeable plastics) with the alternatives known at this time are more likely to be important in the next few years. The preferred fumigant and method of application, however, are likely to vary among cropping systems.

The phase-out of methyl bromide has heightened public awareness of fumigants in general, and the regulatory environment for the large-scale use of known and new fumigants is also changing at this time. Chloropicrin is registered, but guidelines for its use in California are still evolving and some county agricultural commissioners in California are not allowing applications at the higher rates known to be most effective. In the case of 1,3-D, the cumbersome worker protection and buffer zone requirements, as well as the township caps in California, have already been noted. There is also little doubt that metam sodium will come under further review, and new broad-spectrum fumigants such as methyl iodide and propargyl bromide are likely to face stiff resistance from some quarters. Unfortunately, much of the soil fumigation that is done for production of high-value horticultural crops is done in areas of mixed urban and agricultural land use. The growing proximity of urban populations, along with an increased awareness of the toxicology of soil fumigants, is likely to lead to further restrictions on the use of soil fumigants. Therefore, it is imperative that research continue to further improve fumigation technology to reduce human exposure and to further optimize agricultural productions systems that now rely on methyl bromide so that they can remain economically viable using less, and perhaps in some cases, no soil fumigants.

Hopefully the importance of soil fumigation for nursery production of certain planting materials is given sufficient consideration in the future development and regulation of soil fumigants. For example, the production of vigorous and largely pathogen-free runner strawberry plants on a few thousand acres of fumigated soils in California has very large and long-term benefits, including reductions of pesticide use, for strawberry production on nearly 10,000 ha within the state and additional acreage elsewhere. Furthermore, a large portion of this nursery production is for export to other countries and must meet strict phytosanitary requirements. Although nursery production of strawberry runner plants will likely always require some treatment of soil to reduce or eliminate harmful pathogens, chemical alternatives to methyl bromide are currently less developed for strawberry runner plant production than they are for berry production. Although there is information on strawberry runner production with chloropicrin and 1,3-D/chloropicrin (15), we currently know very little about the potential risks of pathogen damage and contamination of nursery materials grown without methyl bromide. Additional nursery research is underway, however, and some of the more active new fumigants, such as methyl iodide and propargyl bromide, may have important applications in nursery production systems. Although exemptions to allow continued use of methyl bromide in soil after 2005 will be hard to obtain (2), they should be considered for certain nursery situations where it will otherwise be difficult, if not impossible, to produce high quality, pathogen-free planting materials.

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