# Appendix 2
# Review of Registrant Proposed Field Adjustment Factors

## A. Methyl Bromide

Stangellhini (2006a) proposes field adjustment factors for methyl bromide based on laboratory and field studies of various application methods. Under Stangellhini's scheme, a field adjustment factor of 100% is assumed for all commodity and space fumigations. This is reasonable because nearly all applied methyl bromide from these applications are eventually released to the atmosphere. However, Stangellhini's soil application method groupings are inconsistent with those developed in DPR's analysis of 47 field methyl bromide studies (Segawa et al., 2000). Here we derive field adjustment factor estimates based on data cited in Stangellhini (2006a) and DPR's extensive methyl bromide data set of field studies. The field adjustment factors so derived are consistent with the DPR methyl bromide regulations.

### 1. Review of the Consortium of Methyl Bromide Registrants proposed adjustments

Stangellhini's (2006a) proposed field adjustment factors are based on a single soil column study (Gan et al., 1997) that is summarized in Yates et al. (1996a):

Shallow injection (6-15in.), bed or broadcast, no tarp, field adjustment factor = 82%
Shallow injection (6-15in.), bed or broadcast, LDPE tarp, field adjustment factor = 82%
Shallow injection (6-15in.), bed or broadcast, HDPE tarp, field adjustment factor = 43%
Deep injection (20+in.), bed or broadcast, no tarp, field adjustment factor = 38%
Deep injection (20+in.), bed or broadcast, LDPE tarp, field adjustment factor = 38%
Deep injection (20+in.), bed or broadcast, HDPE tarp, field adjustment factor = 26%

Where:

LDPE = Low Density Polyethylene Film Tarp
HDPE = High Density Polyethylene Film Tarp.

The Gan et al. study (1997) included documented analytical methods for bromide ion and methyl bromide, frequent sampling and mass balance recoveries near 100%. Consequently the study is acceptable in terms of data quality. However, with the exception of 30 cm injection depth, the results are single realizations of each test system, thus the results are unreplicated. Such column studies are highly controlled and do not reflect the variability in emissions typical of field applications.

### 1. DPR Methyl Bromide Soil Application Data Set

Stangellhini's (2006a) application method groupings are inconsistent with DPR's analysis of the methyl bromide field studies in the DPR database for two reasons: 1) the DPR database shows that all bed application methods, regardless of the type of tarp used, show very high 24 hour emission values and mass loss (81%), and 2) no significant effect on the highest 24 hour emissions due to depth of injection could be detected. Details of this analysis are given in Barry (1999) and that analysis supports a substantially different structure for application method groupings where bed and broadcast represent one level of classification, and “tarp” and “no tarp” application methods are a second level of classification. No classification based on depth is included because no differences due to depth of injection were observed in the highest 24-hour flux. 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.

DPR’s data set includes 31 field studies utilizing the application methods consistent with those described by Stangellhini. The mean peak 24-hour emissions from these studies are similar in magnitude as emissions over the entire loss period (approximately 2 weeks) described by Stangellhini (2006a). The DPR mean peak 24-hour emissions (emission ratios) are shown below:

| | |
|---|---|
| HDPE tarp/broadcast 24-hr emissions (emission ratio) = 24% | (n=13, CV = 52%) |
| No tarp/broadcast 24-hr emissions (emission ratio) = 37% | (n = 8, CV = 47%) |
| HDPE tarp/bed 24-hr emissions (emission ratio) = 81% | (n = 9, CV = 38%) |

In all cases the first 24 hours following application showed the highest 24-hour emission ratio. Since these emissions are for only the first 24 hours and are similar in magnitude to the Stangellhini (2006a) proposed field adjustment factors, these results indicate that it is likely the Stangellhini (2006a) field adjustment factors are too small.

### 2. Methyl Bromide Literature Reported Emissions

Mthyl bromide data appropriate for developing adjustment factors is found in 5 journal articles: Majewski et al. (1995), Gan et al. (1996), Yates et al. (1996b), Yates et al. (1996c), and Gan et al. (1997). These articles report either direct flux (emission) measurements (e.g. aerodynamic method) in the field or soil column results. No flux chamber estimates of mass loss are included because there are significant technical issues associated with flux chamber estimates (Yates et al., 1996b). Table 1 summarizes these studies and shows emission estimates for Broadcast Tarp and Broadcast Non-tarp methods. Shallow and deep injections are pooled within these two categories per the lack of significant difference associated with injection depth observed in the DPR data set. The mean emission for Broadcast Tarp application method is 40%. The mean emission for Broadcast Non-tarp application method is 66%.

### 3. Methyl Bromide Field Adjustment Factor Development

Comparison with the mean mass loss estimates in Table 1 indicates that these estimates are within the variation observed in the literature values. Use of these field adjustment factors is consistent with the methyl bromide regulations and permit conditions.

The Stangellhini (2006a) proposed generalized adjustment function is reasonable and can be implemented to adjust methyl bromide VOC emissions. Emission of 100% of mass applied for all applications not made to soil is reasonable. However, the grouping structure and field adjustment factors proposed for soil applications are not consistent with the structure supported by analysis of the studies in the DPR methyl bromide data set. Thus, the grouping structure has been changed to reflect the actual differences in emissions that were detectable in the DPR data set.

The mean peak 24-hour emissions (emission ratios) for the three groups are used as the basis for the DPR field adjustment factors. Majewski et al. (1995) conclude that about 50% of the total mass loss occurs in the first 24 hours for both tarp and non-tarp applications. Therefore, the well-characterized DPR regulatory emission ratios for Broadcast HDPE Tarp, Broadcast Non-tarp, and Bed Tarp can be reasonably doubled to provide an estimate of the field adjustment factor. Due to the large initial emission ratio for Bed Tarp, 100% loss should be assumed.

The adjustment for both 1990 and 2004 will need to account for fumigations that were likely made to beds. Those application records should assume 100% of the mass applied is lost. Consistent with the Stangellhini (2006a) proposal, the 1990/91 base year adjustment for soil applications not made to beds should assume the non-tarp mass loss of 74%. This assumption will account for the very permeable LDPE tarps that were in use at the time.

## B. Chloropicrin

The document “Analysis of Chloropicrin emissions in the San Joaquin Valley in 1990 and 2004” (Stangellhini, 2006b) proposes to adjust chloropicrin VOC emission estimates for soil applications according to the proportion of applied mass lost observed in field studies of various soil application methods. Emission of 100% of mass applied is assumed for all applications not made to soil. The conceptual basis for this proposal is sound. However, two of the studies used in the Stangellhini (2006b) proposal, Gillis and Smith (2002) and Lee et al. (1994), are not of sufficient quality to be included in the estimation of the adjustment factors. The proposed DPR field adjustment factors use only data judged acceptable by DPR.

### 1. Review of the Chloropicrin Manufacturers Task Force proposed adjustments

The chloropicrin field adjustment factors proposed by Stangellhini (2006b) are:

Shallow injection (6-15in.), broadcast, no tarp = 62%
Shallow injection (6-15in.), broadcast, LDPE tarp = 62%
Shallow injection (6-15in.), broadcast, HDPE tarp = 37%
Deep injection (20+in.), broadcast, no tarp = 62%
Deep injection (20+in.), broadcast, LDPE tarp = 62%
Deep injection (20+in.), broadcast, HDPE tarp = 37%
Drip-application, surface or buried, HDPE tarp = 9%

Where:

LDPE = Low Density Polyethylene Film Tarp
HDPE = High Density Polyethylene Film Tarp.

### 2. Chloropicrin Literature Reported Emissions

Gao and Trout (2007) used flux chambers to estimate emissions for several chloropicrin and 1,3-D application methods, including HDPE tarp, HDPE tarp with pre-irrigation, single watering-in, intermittent watering-in, and virtually impermeable film (VIF). 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 emission reductions due to intermittent watering-in methods are subject to considerable uncertainty, although such reductions are qualitatively consistent with demonstrated reductions in MITC emissions for intermittent watering-in methods.

### 3. Chloropicrin Field Adjustment Factor Development

The Stangellhini (2006b) proposed generalized adjustment function is reasonable and can be implemented to adjust chloropicrin VOC emissions. Emission of 100% of mass applied for all application not made to soil is reasonable. However, the grouping structure and field adjustment factors proposed for soil application methods are not consistent with that proposed by DPR.

The Beard et al. (1996) study will be used exclusively to produce the DPR field adjustment factors for the shank application method. The emissions from Beard et al. (1996) are shown in Table 2. Similar to the proposed methyl bromide factors, the proposed chloropicrin factors only distinguish between tarp and no tarp. No depth factor will be included. All broadcast tarp method mass loss results will be combined to produce a mean estimate.

The chloropicrin data set is small and, thus, 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 tarp 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 methods.

The Stangellhini (2006b) proposal argues that tarps used in 1990 were LDPE tarps and were highly permeable, thus the No Tarp loss rate was assigned to the LDPE applications. This assumption is reasonable.

DPR will assume that reductions in chloropicrin emissions for intermittent watering-in is similar to that observed for MITC, or approximately one-third of an untarped application.

Other application methods that appear to reduce chloropicrin emissions, such as pre-irrigation and VIF may be problematic due to labeling requirements and other factors (Gao and Trout, 2007). Therefore, these application methods are not recommended at this time.

The mean field adjustment factor of each group will be used as the DPR estimated field adjustment factor value. Results are shown below:

Broadcast/No tarp & Bed field adjustment factor = 64% (n = 3, CV = 6%)
Broadcast/Tarp field adjustment factor = 44% (n = 3, CV = 35%)
Broadcast/Tarp with intermittent watering-in = 20%
Drip/Tarp field adjustment factor = 15% (n = 1, CV = N/A)

The CV values for these chloropicrin groups are smaller than those observed for methyl bromide. However, this data set is substantially smaller.

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Table 1. Summary of methyl bromide mass loss estimates from the literature.

| **Broadcast Tarp** | | | | | | |
|---|---|---|---|---|---|---|
| **Reference** | **Study Type** | **Soil Type** | **Depth (cm)** | **Mass Loss (%)** | **Mean (%)** | **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 Non-tarp** | | | | | | |
| **Reference** | **Study Type** | | **Depth (cm)** | **Mass Loss (%)** | **Mean (%)** | **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 2. Mass loss (% of applied mass) for various chloropicrin application methods as measured in Beard et al. (1996).

| **Application Method** | **Location** | **Mass Loss (%)** | **Mean (%)** | **CV (%)** |
|---|---|---|---|---|
| Broadcast/No Tarp | Arizona | 62.5 | 64.2 | 6.0 |
| Broadcast/No Tarp | Arizona | 61.4 | | |
| Bed/Tarp | Arizona | 68.6 | | |
| Broadcast/Tarp | Arizona | 62.3 | 44.2 | 35.6 |
| Broadcast/Tarp | Washington | 33.8 | | |
| Broadcast/Tarp | Florida | 36.5 | | |

# APPENDIX 3

# Application Method Adjustment Factors and Method Use Fractions for 1,3-Dichloropropene

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SUBJECT: CALCULATION OF EMISSION POTENTIAL FACTORS FOR 1,3-DICHLOROPROPENE FOR FIVE AREAS FOR PERIODS FROM MAY 1 THROUGH OCTOBER 31

## Introduction

Emissions of volatile organic compounds from pesticide applications are estimated by the Department of Pesticide Regulation as follows:

$$\text{VOC emitted (lbs)} = \text{EP} * \text{lbs product applied} \qquad (1)$$

The Emission Potential (EP) is that fraction of a product that is assumed to contribute to tropospheric VOCs. Several methods have been used to measure or estimate EPs for different pesticide products. For many fumigants, including 1,3-dichloropropene (1,3-d) products, EPs have historically been assumed to be 100%. However, several studies have demonstrated that a portion of applied 1,3-d does not volatilize from soil after application. The purpose of this memorandum is to estimate EP for 1,3-d in five California regions during the May–October ozone season.

## Background

The fumigant 1,3-dichloropropene was suspended in April of 1990 when high air concentrations were found in Merced. Reintroduction occurred in 1995 following field studies which measured 1,3-d emissions. Initially, 1,3-d was applied only by shank injection. However, a subsequent formulation of 1,3-d called InLine was brought to market which was applied by drip irrigation. In this memorandum, I will first discuss development of factors for shank injection and then development of factors for drip application.

## Approach

This approach relies on two strands of analysis, which are combined to calculate the final factor. The first strand examines the injection and drip application methods and associated flux studies to estimate a non-summer and summer flux factor. The second strand examines by region the pounds of 1,3-d used in order to develop weights for combining the flux factors. The final calculation consists of the use-weighted aggregate factor (EP) for each region. You provided me with a list of four regions to calculate in addition to the San Joaquin region which I originally calculated. The five regions are San Joaquin Air Basin, Sacramento Metro, Southeast Desert, Ventura, and South Coast.

## Shank injection

A 1,3-d flux study (Knuteson et al. 1992) conducted as part of the research effort yielded a volatilization loss of 25%. In this study, 1,3-d was injected at a depth of 18 inches. Because this study was done under relatively cool conditions during fall, an ad hoc factor of 40% (40/25=1.6x) was considered more appropriate for emissions from summer time applications when warmer conditions may cause greater losses.

Several memoranda were written presenting simulation work and discussing the concept of regulating 1,3-d by restricting use on a township basis (Johnson 1995ab, 1996). For injection depths shallower than 18 inches, a linear interpolation scheme was used. This scheme assumed 100% volatilization at the soil surface (depth = 0) and 35% at a depth of 18 inches (Johnson, 1996). The 35% volatilization fraction was a weighted average of the summer and non-summer application volatilization fractions.

Current approaches to estimating volatilization flux for injected 1,3-d assume either linear or nonlinear relationships between flux and injection depth (Cryer, 2005). Gan et al. (1998) reported flux data from laboratory experiments using 1,3-d. Those data demonstrate a linear relationship between volatilization fraction and injection depth for uncovered treatments at 20, 30, and 40 cm injection depths.

Four field studies of 1,3-d flux from injection application are depicted in Figure 1 along with the linear interpolation line from 100% to 40% over 0 to 18 inch depth. The cumulative volatilization fraction calculations are based on measured flux from commercial-sized field applications.

Field studies typically display high variability. In our own experience, based largely on back-calculated values from commercial-sized field applications of methyl bromide, coefficients of variation ranged from 38% to 52% for 24-hour flux fractions over 3 kinds of applications (Barry 1999). Consequently, in consideration of what I believe would be relatively high variation (in the vertical direction) in field-to-field estimates inherent to Figure 1 and the observed linear relationship between volatilization fraction and depth observed in the laboratory (Gan et al. 1998), a linear interpolation is probably a reasonable representation of the depth-flux relationship as a generalization of commercial applications.

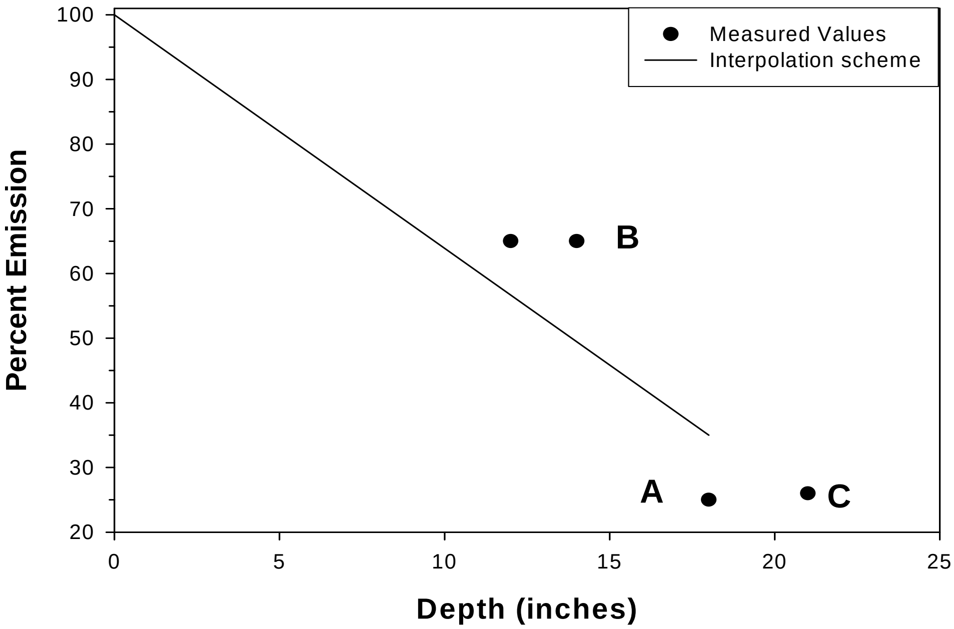

Figure 1. Measured values and interpolation scheme. A (Knuteson et al. 1992), B (two points, Gillis and Dowling (1998)), C (Knuteson et. al. 1995).

### Calculation of non-summer and summer injection factor

The volatilization factors are based on the following assumptions:

1. Linear interpolation can be used to estimate flux where 100% is assumed to volatilize at the surface and a study provides emissions based on the study injection depth.
2. The California Data Management System (CDMS) database contains two types of entries for injection: “Injected 18 inches or deeper” and “Injected 12 to 17 inches.” I will use an 18 inch depth for the deep injection and a 12 inch depth for the shallow injection.
3. Summer emissions are 1.6x higher than non-summer emissions.

The four studies depicted in Figure 1 are provided in tabular form (Table 1). The first column is the fraction volatilized during the study. The third column is the depth of injection. To interpolate for each study, a line is constructed running through (depth, fraction volatilized) from the study and (0 inch depth, 100% volatilized). The last column in Table 1 shows the calculated volatilization fraction at 18 inch depth using linear interpolation based on each study’s results. Equation 2 displays the formula used to calculate these entries.

**Table 1. Four flux studies of 1,3-d shank application.**

| Fraction Volatilized | Method | Injection depth in study (inches) | Bedded or not | Date of Application | Reference | Linear Interpolation to 18" Depth Fraction Volatilized |
|---|---|---|---|---|---|---|
| 0.65 | Shank | 14 | no bed | 10/29/1995 | Gillis and Dowling 1998 | 0.55 |
| 0.65 | Shank | 12 | bed | 11/15/1995 | Gillis and Dowling 1998 | 0.48 |
| 0.26 | Shank | 20-22 | bed | 5/5/1993 | Knuteson et al. 1995 | 0.37 |
| 0.25 | Shank | 18 | no bed | 9/25/1991 | Knuteson et al. 1992 | 0.25 |
| | | | | | **Average** | **0.41** |

$$F_{18} = \frac{\left(1.0 - F_{D_i}\right)}{\left(0 - D_i\right)}\left(18\right) + 1.0 \qquad (2)$$

In equation 2, $F_{18}$ is the estimated fraction volatilized at 18 inch depth, $F_{Di}$ is the fraction volatilized in study i at depth Di. The average volatilization factor at 18 inches was 0.41. I have ignored that two of the studies were bedded and two of the studies were broadcast. Incorporating the resulting average fraction at 18 inches into new equation results in

$$F_D = \frac{\left(1.0 - 0.41\right)}{\left(0 - 18\right)}\left(D\right) + 1.0 = -0.033D + 1.0 \qquad (3)$$

This equation applies from 0 to 18 inches depth of injection for non-summer shank applications. The symbols are $F_D$=fraction of applied active ingredient volatilized at depth, D, in inches. Using equation 3 at 12 inches depth yields a fraction of $0.61[= -0.033*12 + 1.0]$.

Since these studies were all conducted outside of summer season, the corresponding volatilization fraction during summer applications would be (1.6)*0.41=0.656, for the 18 inch depth and (1.6)*0.61=0.97 for the 12 inch depth.

**Calculation of non-summer and summer drip factor**

Two studies of tarped drip application were conducted (Table 2). Study results were mutually consistent and 29% of the applied 1,3-d volatilized. One study (Knuteson et al. 1999) was conducted in Salinas, California, while the other was conducted in Douglas, Georgia. Applying the 1.6 summer factor to 0.29 resulted in a factor 0.46 for summer drip. For drip formulations (Telone EC, InLine) about 6% by product weight consists of inert ingredients. No applications using Telone EC were listed in the 2004 CDMS database.

**Table 2. Two flux studies of 1,3-d drip application.**

| Fraction Volatilized | Method | Tarped | Bedded or not | Date of Application | Reference |
|---|---|---|---|---|---|
| 0.29 | Drip | Yes | bedded | 10/2/1998 | Knuteson et al. 1999 |
| 0.29 | Drip | Yes | bedded | 12/6/1999 | Wesenbeeck and Phillips 2000 |

Table 3 summarizes the drip and shank volatilization factors. Shallow shank refers to a 12 inch depth, while deep shank refers to an 18 inch depth (or deeper). Drip refers to tarped drip applications. Current label requirements mandate tarping for drip applications.

**Table 3. Factor summary**

| | Drip | Shallow Shank | Deep Shank |
|---|---|---|---|
| **Non-summer** | 0.290 | 0.610 | 0.410 |
| **Summer** | 0.464 | 0.970 | 0.656 |

**Calculation of non-summer and summer use weights for five basins**

The next step was to determine the fraction of pounds applied in the five basins for the three application methods, split between non-summer and summer months from May 1 through October 31. Summer was defined as from June 21 to Sept 21 inclusive. These factors were estimated using CDMS report of 2004 1,3-d use data. The fractions were based on pounds of 1,3-d applied. Applications listed in the CDMS system are classified by method. The five regions and associated counties that I used are San Joaquin (Fresno, Kern, Kings, Madera, Merced, San Joaquin, Stanislaus, and Tulare); Sacramento Metro (Sacramento, Solano, Yolo, Placer, and

El Dorado); Southeast Desert (Riverside and San Bernardino); Ventura (Ventura); South Coast (Los Angeles and Orange). The pounds were normalized to the total for each region. The regions are clearly varied in the use patterns ranging from the Sacramento-Metro region where 1,3-d is applied mostly as deep shank in non-summer to the south coast region which is all drip during the summer.

**Table 4. Regional use weights for non-summer and method of application for 1,3-d.**

| | | Drip | Shallow Shank | Deep Shank |
|---|---|---|---|---|
| **Sacramento-Metro** | **Non-summer** | 0.000 | 0.000 | 0.820 |
| | **Summer** | 0.000 | 0.000 | 0.180 |
| **SE Desert** | **Non-summer** | 0.122 | 0.019 | 0.000 |
| | **Summer** | 0.839 | 0.019 | 0.000 |
| **Ventura** | **Non-summer** | 0.210 | 0.022 | 0.036 |
| | **Summer** | 0.733 | 0.000 | 0.000 |
| **San Joaquin** | **Non-summer** | 0.002 | 0.004 | 0.466 |
| | **Summer** | 0.000 | 0.010 | 0.518 |
| **South Coast** | **Non-summer** | 0.000 | 0.000 | 0.000 |
| | **Summer** | 1.000 | 0.000 | 0.000 |

## Calculation of regional emission potentials for 1,3-d volatilization

The calculation of the factors for each region was accomplished by multiplying the method factors in Table 3 by the corresponding use weights in Table 4 within each region and adding the resulting products (Table 5). For example, in the Sacramento-Metro region, there were no drip or shallow shank applications. Hence the use weights were zero for drip and shallow shank. The emission potential therefore was calculated as 0.41*0.82+0.656*0.18=0.454. The emission potentials ranged from 0.43 to 0.54.

**Table 5. Regional emission potentials for 1,3-d.**

| | Emission Potential |
|---|---|
| **Sacramento-Metro** | 0.45 |
| **SE Desert** | 0.46 |
| **Ventura** | 0.43 |
| **San Joaquin** | 0.54 |
| **South Coast** | 0.46 |

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