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TO: Randy Segawa, Environmental Program Manager I
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FROM: Bruce Johnson, Ph.D., Research Scientist III   *Original signed by*
Environmental Monitoring Branch
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DATE: September 24, 2007

SUBJECT: RECALCULATION OF 1,3-DICHLOROPROPENE EMISSION FACTORS

A previous memorandum (Johnson 2006) calculated emission factors for shank-injected 1,3-dichloropropene based on two deep and two shallow flux studies (Gillis and Dowling, 1998; Knuteson et al., 1992; Knuteson et al., 1995). The method required assumption of a linear relationship between depth and cumulative flux. With that assumption, the four studies were combined to estimate a flux at 12 inches and 18 inches of depth. A simpler approach, and one not requiring the assumption of a linear relationship, is to divide the four studies into two groups: shallow and deep and take simple averages for the two groups.

Table 1 provides the revised calculations and along with the previously values for comparison. The result increased the shallow factor from 61% to 65% and increased the shallow with water treatments from 41% to 44%. The deep injection method decreased from 41% to 26%. The recalculation does not affect the drip method.

Table 1. Shank injection methods for 1,3-d, recalculation of emission factors.	Percentage based on Johnson (2006)	Revised Percentages	Notes:
Method			
Shallow injection	61	65	Based on average of 2 shallow studies
Shallow injection w/ 3 water treatments	41	44	Based on reducing shallow broadcast by 33%
Deep injection w/ high permeability tarp or no tarp-broadcast	41	26	Based on average of 2 deep studies

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

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TO: Randy Segawa, Agriculture Program Supervisor IV
              Environmental Monitoring Branch

FROM: Bruce Johnson, Ph.D., Research Scientist III   *Original signed by*
              Environmental Monitoring Branch
              (916) 324-4106

DATE: November 30, 2006

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:

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

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

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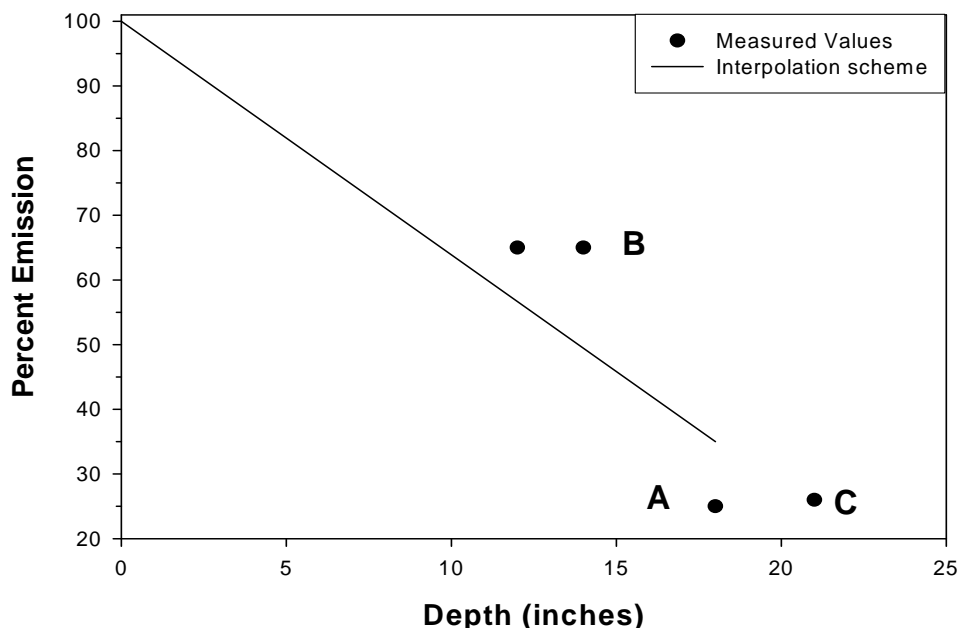
Figure 1. Measured values and interpolation scheme. A (Knuteson et al. 1992), B (two points, Gillis and Dowling (1998)), C (Knuteson et. al. 1995).

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.						Linear Interpolation to 18" Depth Fraction Volatilized
Fraction Volatilized	Method	Injection depth in study (inches)	Bedded or not	Date of Application	Reference	
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

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

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 D_i. 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

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

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

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

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 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).

Table 3. Factor summary

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

Drip refers to tarped drip applications. Current label requirements mandate tarping for drip applications.

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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     Terrell Barry, Ph.D., Research Scientist III

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