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Calculated Reentry Interval for Table Grape Harvesters Working in California Vineyards Treated with Methomyl

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Lannate® is an insecticide widely used by California grape growers to control leafhoppers and thrips. The active ingredient in Lannate® is methomyl [*S*-methyl-*N*-(methylcarbamoyl)-thioacetimidate], a compound of the oxime carbamate group. Methomyl has been classified as a pesticide of Category I (danger) toxicity, with dislodgeable foliar residues (DFR) persisting over a relatively short period. The maximum label rate allowed for foliar application of methomyl to grapes is 0.9 lb per acre. In late May 1988, methomyl residues from grape foliage were reported for the first time to be associated with cholinergic illness symptoms among California grape girdlers. The illness incident involved a crew of grape girdlers working in a California vineyard sprayed with methomyl 5 days earlier (O'Malley *et al.* 1991). The methomyl DFR in that vineyard ranged from 0.19 to 0.33 $\mu g/cm^2$, with a mean of 0.27 $\mu g/cm^2$ ($n = 4$). Depressed levels of both red blood cell and plasma [acetyl]cholinesterase (AChE) were observed in 12 of 13 girdlers tested.

Field data on methomyl dislodgeable dissipation were collected by the Cal/EPA Department of Pesticide Regulation (DPR) [formerly a division of the California Department of Food and Agriculture] one day after the illness incident and into later months of the same year. More substantial data of this type were collected in 1989, which were recently published by Reeve *et al.* (1992). These data all indicated a reproducible pattern in which methomyl DFR dissipated much more rapidly in May/June/July (with a half-life of approximately 2 days) than in later months of the year (with a half-life of approximately 4 days). As a result, a state regulation (DPR 1989) was developed which imposed a reentry interval of 7 days post-application for methomyl applications made in California prior to August 15 of each year, and a longer reentry of 21 days for those made after that date. That regulation, which is still in effect today, was based on the calculated expectation that the methomyl residues would reduce to the safe reentry level (SRL) of 0.1 $\mu g/cm^2$ or less by day 7 in the early season, and by day 21 in the late season. That SRL was adopted following a separate field observation by DPR that no AChE inhibition or related illness was seen in California grape girdlers working in another vineyard with a mean methomyl DFR of 0.1 $\mu g/cm^2$ (O'Malley *et al.* 1991).

Routine observation demonstrated that growers in California frequently remove the canes and leaves around the table grape clusters prior to harvesting. This common agricultural practice suggests that the exposure potential during table grape harvesting, which normally takes place in the late season, would be substantially lower than that during grape girdling or other grape harvesting not under this type of canopy management. It was this routine observation that had prompted California grape growers as well as DPR

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to reconsider the reentry interval for table grape harvesters working in a vineyard under canopy management. This communication is to provide a detailed discussion on the rationale and mathematical justification for a shorter reentry for workers who would harvest table grapes maintained under canopy management.

MATERIALS AND METHODS

To establish the reentry interval for table grape harvesters, we began with an equality function which involves the use of SRL and dermal transfer factor (TF). In reentry studies, TF is an empirical multiplier frequently used to extrapolate hourly dermal exposure from plant residues monitored in treated fields. This multiplier is normally expressed in units of hourly dermal exposure (μg/hr) *per* unit of DFR (μg/cm^2). Nigg *et al.* (1984), Popendorf and Leffingwell (1982), and Zweig *et al.* (1984, 1985) were among the first to describe the use of TF as a conversion factor for calculating worker reentry exposure. Further analysis indicated, however, that the derivation of a proper TF might actually be more complex than initially anticipated (Krieger *et al.* 1991).

By definition, the widely used toxicity index NOEL (no observable effect level) for dermal exposure can be approximated by the product of SRL x TF. Following this assertion, we then have

$$SRL_{tgh} \times TF_{tgh} = SRL_{gg} \times TF_{gg} = \text{dermal NOEL},$$

where the subscripts *tgh* and *gg* denote table grape harvesting and grape girdling, respectively.

Upon dividing both sides with the same term (*ie* with TF_{tgh}), we can rewrite the above equality function as

$$SRL_{tgh} = SRL_{gg} \times [TF_{gg}/TF_{tgh}].$$

Currently the safe reentry level for grape girdling as well as for all grape cultural practices is set at 0.1 μg/cm^2. As noted earlier, this SRL_{gg} was adopted following a field study in which a grape girdling crew was monitored for AChE levels before and after working in a vineyard with a mean methomyl residue level of 0.1 μg/cm^2. To this date there have been no field studies conducted by DPR to estimate the TF_{gg}/TF_{tgh} ratio. However, a reentry exposure study submitted by DuPont (Merricks 1990) indicated that this ratio was at least 2.2 (see Table 1). The DuPont study was performed in compliance with current data requirements set forth by the U. S. Environmental Protection Agency (1985) for protection of workers from reentry exposure. Using the conservative DuPont ratio of 2.2 (*ie* 18/8) and the SRL_{gg} of 0.1 μg/cm^2, we calculated from the above equality function a comparable, conservative SRL of 0.22 μg/cm^2 for table grape harvesters.

To make use of the calculated SRL_{tgh}, we generalized a dissipation curve of methomyl dislodgeables over time with the published 1989 data. (Note that throughout this paper more emphasis was given to the 1989 data than to those collected in 1988; this is because the latter were based on a sampling regimen that was less thought out due to time constraints.) This dissipation curve, which is shown in Figure 1, was subsequently used to estimate the safe reentry interval (time) for workers who would harvest table grapes maintained under canopy management.

The dissipation curve in Figure 1 was constructed using a conservative half-life ($t_{1/2}$) of 6 days. The mean $t_{1/2}$ of methomyl dislodgeables was estimated to be approximately 4 days in the late season, based on the published 1989 data. As common practice, a first-

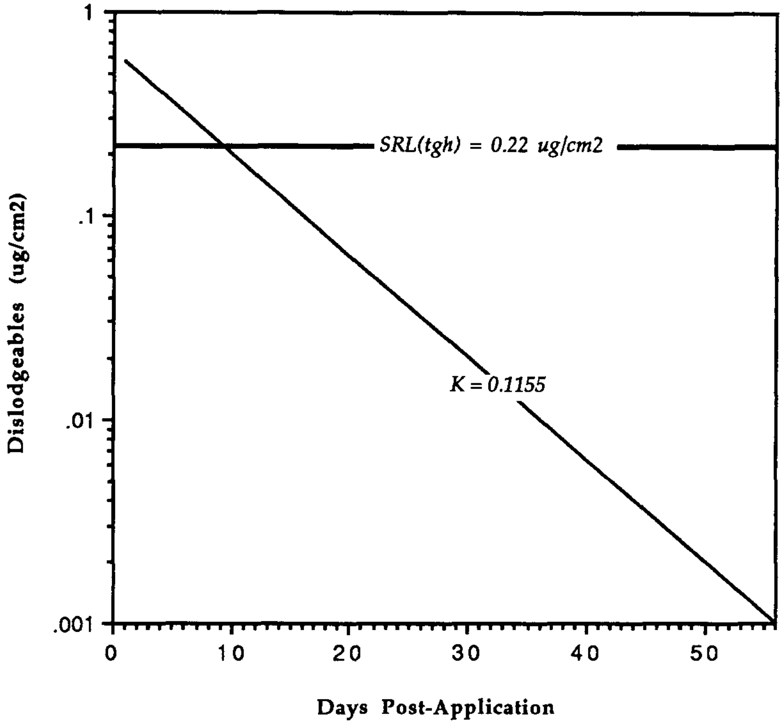

Figure 1. Decline of methomyl foliar dislodgeables over time, based on the published 1989 data (see the present text for notations and assumptions used).

Table 1. Ratios of methomyl dermal exposure (DE) to methomyl foliar dislodgeables (DFR)[a,b]

Cultural Practice	Study Reentry Days	Hourly Dermal Exposure (μg/hr)	Methomyl DFR (μg/cm^2)	TF x 10^3
GGO	7 - 8	315 - 1,215	0.013 - 0.018	18 - 93
TGH	10 - 11	211 - 226	0.027 - 0.086	3 - 8

[a] reproduced from Worker Health and Safety Branch Brief No. 020, which was based on the reentry exposure study submitted by DuPont (Merricks 1990).

[b] GGO = grape girdling operation; TGH = table grape harvesting; TF (transfer factor) = DE/DFR.

order exponential decay model was assumed for methomyl dissipation; many of the individual 1989 data sets also supported this assumption. The first-order exponential model asserts the following mathematical relation between $t_{1/2}$ and the first-order reaction constant K:

$$K = -\ln 2 \times (t_{1/2})^{-1} = -0.6932 \times (t_{1/2})^{-1},$$

where K is also the slope of the log-linear curve specified by the decay model. In this case where $t_{1/2}$ = 6 days, the value of K was estimated to be approximately - 0.1155 units (on natural log scale) of methomyl dislodgeables dissipated *per* day. The methomyl dislodgeables in this curve were assumed to be completely dissipated in 56 days, based on the observation that all of the methomyl dislodgeables (even those from vineyards treated at the maximum rate) was seen to have reduced to the minimum detection limit of 0.001 $\mu g/cm^2$ in 8 weeks post-application (see Table 2). It is of note that for any given day in the dissipation curve, its DFR can be calculated directly from the definition of the slope

$$K = (\ln Y_i - \ln Y_{56}\ \mu g/cm^2)/(i - 56\ \text{days}),$$

where $\ln Y_i$ is the natural log of the DFR value expected on day i post-application and Y_{56} = the minimum detection limit (0.001 $\mu g/cm^2$).

Dong *et al.* (1991) recently have exemplified the procedure for the generalization of both a global Y-intercept (*ie* initial deposition) and a global slope common to all individual regression lines being considered. This procedure was not used here to construct the dissipation curve, however, because the 1989 data revealed (qualitatively) a shorter half-life (and hence a more rapid decay) during the initial (typically within the first 24 or 36 hours) stage of methomyl dissipation. We have found that many of the DFR measured during the first 24 hours were above their regression line, and that their inclusion by and large yielded a statistically less desired coefficient of determination (r^2). This type of bi-phasic decay is by no means a rare representation of pesticide dissipation on foliage. In 1955 Gunther and Blinn described many pesticides having two to three phases of decay, with the first stage normally having a shorter half-life. (Note that here only the second phase of dissipation would be considered the time frame of interest, insofar as the reentry interval in question was concerned.)

RESULTS AND DISCUSSION

The dissipation curve shown in Figure 1 clearly indicates that 10 days post-application is a reasonable reentry for workers harvesting table grapes maintained under canopy management, instead of the current 21 days. The vast majority of the dissipation data collected in 1989 also confirmed our mathematical justification that by day 10 post-application, the methomyl dislodgeable levels from foliar application would reduce to 0.22 $\mu g/cm^2$ or less.

There existed a few aberrant values in the 1989 data that reflected some exceptional upper extremes of half-life and DFR at day 10. We deliberately excluded these values from our reentry analysis or consideration because we considered them to be overly deviant. For example, the half-life for the DFR collected at Field 32 in 1989 (see Table 2) was calculated to be 7.7 days with a r^2 of 0.76 (n = 5). This was the only half-life in the 1989 data that exceeded 6 days. We did not use this extreme as the conservative half-life in our analysis because the associated r^2 was considered to be below our standard. According to Snedecor and Cochran (1980), the Student's t statistic for independence between two regression variables is mathematically equivalent to the quantity $r(n - 2)^{0.5}/(1 - r^2)^{0.5}$ (where n is the sample size). In this case where r^2 = 0.76, the test statistic t was calculated to be 3.08 with a p-value of > 0.05; this suggests that one cannot reject the null hypothesis, at α = 5%, that the regression coefficient (slope) calculated for Field 32 could be zero (or was not significantly different from zero). Another reason for not using 7.7 days as the conservative half-life in our analysis is footnoted in Table 2.

Note that by a conservative half-life we mean a half-life which would yield a slope that is less steep (*ie* a smaller rate constant K). As shown in Figure 1, this in turn would result in

Table 2. Half-lives of methomyl dislodgeables and their last observed residue values[a]

Field	Half-Life	r^2	Last Observation in Each Field Study: Days Post-Application	Last Observation in Each Field Study: Mean DFR ($\mu g/cm^2$)[b]
		June 1989		
1	2.2	0.99	16	0.002
2	2.4	0.98	16	0.002
3	2.3	0.98	12	0.005
4	1.4	0.99	11	0.002
5	2.8	0.93	14	0.004
6	2.7	0.97	14	0.004
7	1.7	0.92	14	0.003
8	1.8	0.98	7	0.080
9	2.1	0.94	7	0.108
		July 1989		
10	1.7	0.99	20	0.001
11	2.2	0.96	21	0.002
12	1.8	0.99	11	0.022
13	3.4	0.96	28	0.001
14	1.5	0.91	36	ND
15	1.5	0.99	36	ND
16	2.0	0.93	26	ND
17	1.4	0.98	19	ND
18	1.0	0.97	27	0.001
19	1.5	0.82	27	ND
20	1.7	0.99	27	0.001
21	2.3	0.97	27	ND
22	1.9	0.93	33	ND
		August 1989		
23	3.5	0.95	26	0.005
24	3.8	0.91	19	0.017
25	4.7	0.93	19	0.032
26	3.8	0.92	25	0.001
27	1.6	0.97	25	0.001
28	2.3	0.99	18	0.002
29	5.8	0.92	23	0.007
		September 1989		
30	2.0	0.81	7	0.021
31	2.3	0.98	14	0.001
32[c]	7.7	0.76	23	0.032
		October 1989		
33	5.0	0.98	30	0.016
34	3.8	0.91	23	0.015
35	5.1	0.92	23	0.048
36	4.6	0.99	23	0.054

[a] an extension of the results published by Reeve *et al.* (1992).

[b] ND ≡ below the minimum detection limit (*ie* non-detectable).

[c] with the lowest r^2 partly because the mean DFR (0.024 $\mu g/cm^2$) on Day 14 (the second to the last observation) was less than the last observed mean; if the last observation were unavailable or excluded from the regression analysis, the half-life would have been 4.6 days with a $r^2 = 0.92$.

a longer (more conservative) reentry interval for table grape harvesting (and a longer time for complete dissipation). Figure 1 also shows that if the time assumed for complete dissipation were shorter than 56 days post-application with the slope or half-life being the same, the reentry interval would be shorter (less conservative).

Finally, two additional points are noteworthy here. The first is that insofar as grape cultural practices are concerned, methomyl-related illnesses have been confirmed in California only among grape girdlers working on day 5 post-application (Maddy *et al.* 1990, O'Malley *et al.* 1991). To this date this type of illness has not been confirmed among California grape harvesters or any workers not engaged in grape girdling.

The other final point worth considering here is the extent to which canopy management can actually reduce the amount of grape foliage contacted by table grape harvesters. The job of a grape girdler in California typically involves the following tasks: a) removing the plant trash from the base of a grapevine; b) cutting a girdle around the base of the vine; and c) stripping the bark down the vine from the girdle cut. Their job is thus considered to be far more contact intensive than that of a worker who would harvest table grapes maintained under canopy management. As part of canopy management, a table grape harvester working in a California vineyard would simply cut or trim a bunch of grapes from the vine *on the side of the trellis where canes have already been cut.* Therefore, hour for hour the amount of grape foliage contacted by the body surface of a (typical) California grape girdler is expected to be more than twice the amount contacted by the body surface of a (typical) California grape harvester. Those who have some field experience in dealing with vineyard work would agree with this estimate for the TF_{gg}/TF_{tgh} ratio. As expected, the use of any ratio estimate greater than the assumed (conservative DuPont) value of 2.2 would yield a reentry shorter than the 10 days calculated in this reentry analysis.

REFERENCES

Department of Pesticide Regulation, Cal/EPA (1989) Reentry intervals. California Code of Regulations Title 3, Chapter 6, Section 6772

Dong MH, Saiz SG, Mehler LN, Ross JH (1991) Determination of crop-specific parameters used in foliar mass to area conversion: I. For selected varieties of grapes. Bull Environ Contam Toxicol 46:542-549

Gunther FA, Blinn RC (1955) Analysis of insecticides and acaricides. Interscience Publishers, New York, pp.141-142

Krieger RI, Blewett C, Edmiston S, Fong HR, Meinders DD, O'Connell LP, Schneider F, Spencer J, Thongsinthusak T, Ross JH (1991) Gauging pesticide exposure of handlers (mixer/loaders/applicators) and harvesters in California agriculture. La Medicina del Lavoro 81:474-479

Maddy KT, Edmiston S, Richmond D (1990) Illness, injuries, and death from pesticide exposures in California 1949 - 1988. Rev Environ Contam Toxicol 114:57-123

Merricks DL (1990) Lannate insecticide - field worker exposure study in grape girdling and harvesting operations. California Department of Pesticide Regulation Pesticide Registration Document No. 253-192

Nigg HN, Stamper JH, Queen RM (1984) The development and use of a universal model to predict tree crop harvester pesticide exposure. Am Ind Hyg Assoc J 45:182-186

O'Malley MA, Smith C, O'Connell LP, Ibarra M, Acosta I, Margetich S, Krieger RI (1991) Illness among grape girdlers associated with dermal exposure to methomyl. The Worker Health and Safety Branch, California Department of Pesticide Regulation, Publication HS-1604

Popendorf WJ, Leffingwell JT (1982) Regulating OP pesticide residues for farm worker protection. Residue Rev 82:125-201

Reeve MW, O'Connell LP, Bissell S, Ross JH (1992). Characterization of methomyl dissipation on grape foliage. Bull Environ Contam Toxicol *(July, in press)*
Snedecor GW, Cochran WG (1980) Statistical methods. The Iowa State University Press, Ames, Iowa, p.185
United States Environmental Protection Agency (1985) Pesticide assessment guidelines, subdivision K (exposure: reentry protection). PB85-120962, National Technical Information Service (5285 Port Royal Road, Springfield, VA 22161)
Zweig G, Gao RY, Witt JM, Popendorf WJ, Bogen K (1984) Dermal exposure to carbaryl by strawberry harvesters. J Agr Food Chem 32:1232-1236
Zweig G, Leffingwell JT, Popendorf WJ (1985) The relationship between dermal pesticide exposure by fruit harvesters and dislodgeable foliar residues. J Environ Sci Health B20:27-59

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