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DATE: July 10, 2007

SUBJECT: EVALUATION OF THE GROUND WATER CONTAMINATION POTENTIAL OF PROPOSED FUMIGANT USE REGULATIONS

Summary

The California Department of Pesticide Regulation (DPR) is proposing fumigant use regulations that would require post-application water treatments to reduce volatilization of the fumigants to the atmosphere. An empirical model was developed to assess whether or not the proposed mitigation measures shifted potential contamination from the air to the ground water environment. The fate and transport of four fumigants–methyl bromide, chloropicrin, methyl isothiocyanate (MITC), and 1,3-dichloropropene (1,3-D)–were evaluated in a leaching-vulnerable Fresno, California soil.

To provide a worst-case scenario for potential ground water contamination, the model did not explicitly account for fumigant losses by volatilization or from sorption of the residues to the soil even though volatilization, especially, is well-known to be one of the primary routes of fumigant dissipation in the field. Furthermore, the maximum application rate and longest reported degradation half-life for each pesticide was used in the evaluation. Fumigants known to have contaminated ground water–1,2-dichloropropane (1,2-D), 1,2-dibromoethane (EDB), and 1,2-dibromo-3-chloropropane (DBCP)–were also analyzed and the results were compared to both the results for the four current fumigants and to well monitoring data for the known contaminants. This comparison was performed to confirm that the modeling evaluation used was, in fact, overestimating the predicted concentrations.

Under extreme irrigation conditions that produced large amounts of percolating water and a high potential for residue leaching, the empirical model predicted low or zero flux of current fumigants to ground water, and predicted essentially zero concentration after accounting for

fumigant residence time in the aquifer. The current fumigants have much shorter soil degradation and hydrolysis half-lives resulting in a much lower potential to contaminate ground water than the fumigants known to previously contaminate ground water. The modeling approach used in this evaluation predicted well water contamination by 1,2-D, EDB, and DBCP at levels that exceeded actual concentrations by two to three orders of magnitude, confirming our expectation that the modeling procedure purposefully over-estimated concentrations. While this evaluation methodology cannot predict the actual concentrations that a pesticide would reach in ground water and well water, it is an accurate screening tool to determine if further evaluation is needed.

Introduction

Methyl bromide, chloropicrin, MITC, and 1,3-D are soil fumigants used before planting to control a wide range of pests including weeds, nematodes, and diseases in numerous crops. MITC is a breakdown product of metam sodium, metam potassium, and dazomet. In an effort to reduce volatile organic compounds (VOCs) that contribute to ground-level ozone formation, DPR has developed proposed regulations to reduce the overall emissions of the fumigants. One of the mitigation measures proposed is a post-application irrigation treatment to reduce volatilization of the fumigants to the atmosphere. Assuming the soil water content is at a minimum of 50% field capacity at application, DPR would require the following sprinkler irrigation schedule:

- 0.25 inches of water applied within 30 minutes of the completion of the fumigation
- 0.25 inches starting no earlier than one hour prior to sunset the day of fumigation
- 0.25 inches starting no earlier than one hour prior to sunset one day after fumigation
- 0.25 inches starting no earlier than one hour prior to sunset two days after fumigation

Since additional water applications present a potential for ground water contamination in a leaching-vulnerable California soil, an evaluation was conducted using an empirical-based, probabilistic Monte Carlo procedure to determine if the four fumigants–methyl bromide, chloropicrin, MITC, and 1,3-D–would move to ground water and be detectable in well water.

Methods

The following equations were used in the Monte Carlo procedure to model the movement of fumigants to ground water and well water.

Equation 1:

$$Ground\ Water\ Concentration\ (ppb) = \frac{R \times 0.5^{(Nt)}}{D_w}$$

Equation 2:

$$Well\ Water\ Concentration\ (ppb) = \frac{R \times 0.5^{(Nt + Na)}}{D_w}$$

where:

$$N_t = \frac{D_g \times 365\ d}{V \times D_t}$$

$$N_a = \frac{A \times 365\ d}{H}$$

R = pesticide application rate (mg/m^2) at 75 cm soil application depth (Table 1)
D_w = depth of annual ground water recharge = 0.5 m (Table 2)

and where:

N_t = Number of half-lives each fumigant was subjected to during transport in the vadose zone from the point of application in the soil profile to the water table; degradation half-lives in this first transport segment were taken from aerobic metabolism or terrestrial field dissipation (TFD) data

N_a = Number of half-lives each fumigant was subjected to in the aquifer from entry into the water table to arrival at a well screen; degradation half-lives in this second transport segment were assumed equal to fumigant hydrolysis half-lives

D_g = A random variable; the transport depth to ground water measured as the vertical distance from the point of fumigant application to the water table surface (m, Table 2)

V = transport velocity of the solute center of mass = 5.6 m/y (Table 2)

D_t = longest reported degradation half-life (d, Table 1)

A = A random variable; the ground water residence time (y) measured as the elapsed time from the entry of a water parcel into the water table to subsequent uptake at a well screen (Table 2)

H = hydrolysis half-life (d, Table 1)

Table 1. Fumigant specific values used in modeling scenario.

Fumigant Active Ingredient (AI)	Maximum Application Rate, lb AI/acre/y (*R*)	Longest Degradation Half-life, d (D_t)	Hydrolysis Half-life, d (*H*)	References
Current Fumigant				[1] soil aerobic half-life [2] terrestrial field dissipation half-life [3] DPR, 2007a [4] Vogue et al., 1994 [5] Katz, 1993 [6] WHO, 2003 [7] U.S. EPA, 2000 [8] Cohen et al., 1983 [9] Wilkerson et al., 1985
Methyl bromide	400	19.9 [1,3]	10 [3]	
Chloropicrin	400	5.13 [1,3]	191 [3]	
MITC	239	19.2 [2,3]	20.4 [3]	
1,3-D	332	52.4 [2,3]	7.2 [3]	
Old Fumigant				
1,2-D	625 [8]	700 [1,4]	1,400 [6]	
EDB	106 [9]	350 [1,5]	5,475 [5]	
DBCP	663 [9]	180 [1,4]	13,140 [7]	

Table 2. Additional variables used in modeling scenario.

Variable	Parameters	Variable Type	Values
Depth of Annual Ground Water Recharge, m (D_w)	Spurlock et al., 2000	Constant	0.5 m
Range of Transport Depths, m (D_g)	Lognormal distribution, location 3.5358, scale 0.31157	Random, 40,000 samples	3.09 – 130.83 m
Mean Transport Velocity, m/y (*V*)	243 mm rainfall, 1,375 mm irrigation, 25 mm supplemental irrigation	Constant	5.6 m/y
Range of Ground Water Residence Times, y (*A*)	Gamma distribution, location 2.97, scale 10.37, shape 0.566756	Random 40,000 samples	2.97 – 148.65 y

Pesticide applications were simulated at maximum label rates (Table 1). To simulate a deep shank injection the fumigants were applied 75 cm below the soil surface. Since there are three fumigants that produce MITC, dazomet was used to provide a worst-case scenario because at the highest legal application rate it produces the greatest amount of MITC. The results for the four fumigants were compared to the results for three previously used fumigants that are known to contaminate ground water–1,2-D, EDB, and DBCP. The analysis generally assumed that these highly volatile compounds did not undergo volatilization, were fully solubilized in water upon application, and had no soil sorption capabilities, reflecting a scenario that would overestimate the potential movement of the fumigants to ground water and well water. In the case of 1,3-D and MITC, terrestrial field dissipation (TFD) half-lives were found to be longer than aerobic metabolism half-lives, therefore, TFD half-lives were used for the degradation half-life. Technically, since the TFD half-life reflects, in part, volatilization, the half-lives used for MITC and 1,3-D implicitly include volatilization. However, the modeling itself did not explicitly include volatilization. Since the longer of the two values (aerobic metabolism or TFD) were used (Table 1), this analysis is biased towards the materials reaching groundwater. Pesticide degradation half-lives were considered constant with soil depth. Studies have shown that pesticide degradation half-lives increase significantly with depth (Frank and Sirons, 1985; Johnson and Levy, 1994; Kruger et al., 1993). Currently, however, there is insufficient information to model degradation half-lives as a function of soil depth.

In a modeling exercise predicting simazine and diuron concentrations in Fresno County ground water, Spurlock et al. (2006) determined that ground water residence time and depth to ground water were among the most important variables affecting predicted concentrations of well water contaminants. In their analysis, these two parameters accounted for most of the variation in modeled well water concentrations as opposed to solute aerobic, TFD, and hydrolysis half-life data. A Monte Carlo approach was used in our analysis to account for this variability.

The time elapsed during transport in the vadose zone from application depth (75 cm) to ground water depth was determined by dividing this distance (D_g) by the mean transport velocity (V). Ground water depths were obtained from well measurements in a 1,500 km^2 area of Fresno County with course soil and shallow ground water where at least one pesticide detection had occurred. Approximately 90 ground water depths were obtained. A lognormal distribution was chosen to fit the data and 40,000 ground water depths were randomly sampled from the distribution using Crystal Ball (Decisioneering Inc, 2000). To account for the deep fumigation, 75 cm was subtracted from each ground water depth to obtain the transport depth. The range of transport depths used in the calculation is specified in Table 2. A transport velocity of 5.5 m/y was estimated by calibrating the LEACHM pesticide transport model to field data in a leaching-vulnerable soil in Fresno, California (Hutson and Wagenet, 1992; Spurlock et al., 2006). Under the study conditions movement of bromide, a tracer for water movement, was based on average annual rainfall of 243 mm for the area and 1,375 mm of irrigation water, approximately 160% of evapotranspiration for a sprinkler irrigated grape crop. This irrigation efficiency indicates that approximately 60% of the applied water is lost to percolation and reflects inefficiencies noted in some surface delivery systems (California Agricultural Technology Institute, 1988; Snyder et al., 1986). The additional 25 mm of water required by the proposed regulations increased the transport velocity slightly to 5.6 m/y (Spurlock, 2007). To quantify the difference the additional 25 mm of water would make in predicted concentrations, 1,2-D and 1,3-D were modeled using both the 5.5 m/y and 5.6 m/y transport velocities.

The time elapsed during transport to ground water was divided by the longest reported half-life for each compound (D_t) (Table 1) to yield the number of half-lives the fumigant was subjected to in the vadose zone (N_t). The number of half-lives was used in combination with the fumigant application rate (R) to establish the fumigant mass just before entry into the aquifer. Initial pesticide loading of the aquifer was calculated by dividing the residues remaining after transport to ground water depth by the historical net annual ground water recharge depth of 0.5 m/y in the study area (D_w) (Spurlock et al., 2000) (Equation 1).

The concentration of pesticide that reaches ground water is not necessarily indicative of the concentration that will reach a well because wells are screened below the water table, resulting in the continued degradation of pesticide residues as they move through the aquifer (Spurlock et al., 2000). The elapsed time from initial pesticide loading of the aquifer to subsequent detection at a well is considered the ground water residence time (Kundel and Wendland, 1997; Böhlke and Denver, 1995) and is one of the most important factors for predicting pesticide concentrations in well water (Spurlock et al., 2006). Eighteen ground water residence times have been reported for wells in the upper, unconfined aquifer in this study area (Spurlock et al., 2000). A gamma distribution best fit the data and 40,000 ground water residence times were randomly sampled from the distribution using Crystal Ball (Decisioneering Inc, 2000). Each ground water residence time (*A*) was divided by the hydrolysis half-life (*H*) of each fumigant (Table 1) to yield the number of half-lives the fumigant was subjected to in the aquifer (N_a). The number of half-lives in the aquifer was randomly combined with the estimated concentration of each fumigant entering the aquifer to estimate a concentration at the well (Equation 2).

Utilizing the 40,000 half-lives in the vadose zone, the ground water recharge depth, and the pesticide application rate, the solution of Equation 1 established a distribution of initial pesticide loading of the aquifer. The solution of Equation 2 randomly combines the solutions to Equation 1 and the 40,000 half-lives in the aquifer to establish a distribution of potential well water concentrations for each fumigant. A probabilistic assessment of potential ground water and well water concentrations of each fumigant was then conducted. Since the calculated results of the assessment would always produce a positive concentration of pesticide, no matter how small, a self-imposed censoring limit of $1x10^{-9}$ ppb was implemented for simplicity. This censoring limit is one million times lower than the lowest method detection limit (MDL) of 0.001 ppb for the fumigants know to contaminate ground water (DPR, 2007b).

Results and Discussion

The predicted concentrations of each fumigant potentially entering ground water are listed in Table 3 and the predicted concentrations in well water are listed in Table 4. The fumigants under proposed regulation were not predicted to be detectable in California well water above our self-imposed censoring limit of $1x10^{-9}$ ppb whereas the known ground water contaminants 1,2-D, EDB, and DBCP were predicted to be present in well water up to levels of 61,400 ppb, 12,600 ppb, and 57,800 ppb, respectively (Table 4). According to DPR’s Well Inventory Database (2007b), the maximum concentrations of 1,2-D, EDB, and DBCP actually detected in California wells were 160 ppb, 4.7 ppb, and 166 ppb, respectively, which are two to three orders of magnitude lower than the predicted values (Table 5). Although there were some predicted concentrations for the current fumigants reaching ground water at levels above our censoring limit (Table 3), the evaluation purposefully predicted high concentrations because losses to volatilization and sorption to soil were not explicitly modeled. Consequently, the results for the current fumigants are also likely an overestimation of their true potential concentrations.

Table 3. Predicted fumigant concentrations in ground water.

Current Fumigant	Maximum (ppb)	95th Percentile (ppb)	75th Percentile (ppb)	50th Percentile (ppb)	25th Percentile (ppb)	Minimum (ppb)
Methyl Bromide	81.0	§	§	§	§	§
Chloropicrin	1.39×10^{-7}	§	§	§	§	§
MITC	37.5	§	§	§	§	§
1,3-D	5,200	0.00714	4.39×10^{-6}	1.45×10^{-8}	§	§
1,3-D ∗	4,950	0.00532	2.86×10^{-6}	8.51×10^{-9}	§	§
Old Fumigant						
1,2-D	116,000	42,400	24,400	15,900	9,430	30.6
1,2-D ∗	116,000	41,400	23,600	15,300	8,980	26.2
EDB	16,200	2,140	708	301	106	0.00112
DBCP	69,400	1,360	158	30.0	3.95	§

§ Predicted values were < 1×10^{-9}

∗ Predicted values were calculated using 5.5 m/y transport velocity and did not account for additional 25 mm of irrigation water required by the proposed regulations.

Table 4. Predicted fumigant concentrations in well water.

Current Fumigant	Maximum (ppb)	95th Percentile (ppb)	75th Percentile (ppb)	50th Percentile (ppb)	25th Percentile (ppb)	Minimum (ppb)
Methyl Bromide	§	§	§	§	§	§
Chloropicrin	§	§	§	§	§	§
MITC	§	§	§	§	§	§
1,3-D	§	§	§	§	§	§
1,3-D ∗	§	§	§	§	§	§
Old Fumigant						
1,2-D	61,400	17,400	8,490	4,220	1,510	7.08×10^{-8}
1,2-D ∗	61,200	17,000	8,190	4,040	1,440	6.90×10^{-8}
EDB	12,600	1,540	486	199	67.6	8.83×10^{-4}
DBCP	57,800	1,150	133	25.3	3.36	§

§ Predicted values were < 1×10^{-9}

∗ Predicted values were calculated using 5.5 m/y transport velocity and did not account for additional 25 mm of irrigation water required by the proposed regulations.

Table 5. Concentrations of fumigants detected in California wells (DPR, 2007b).

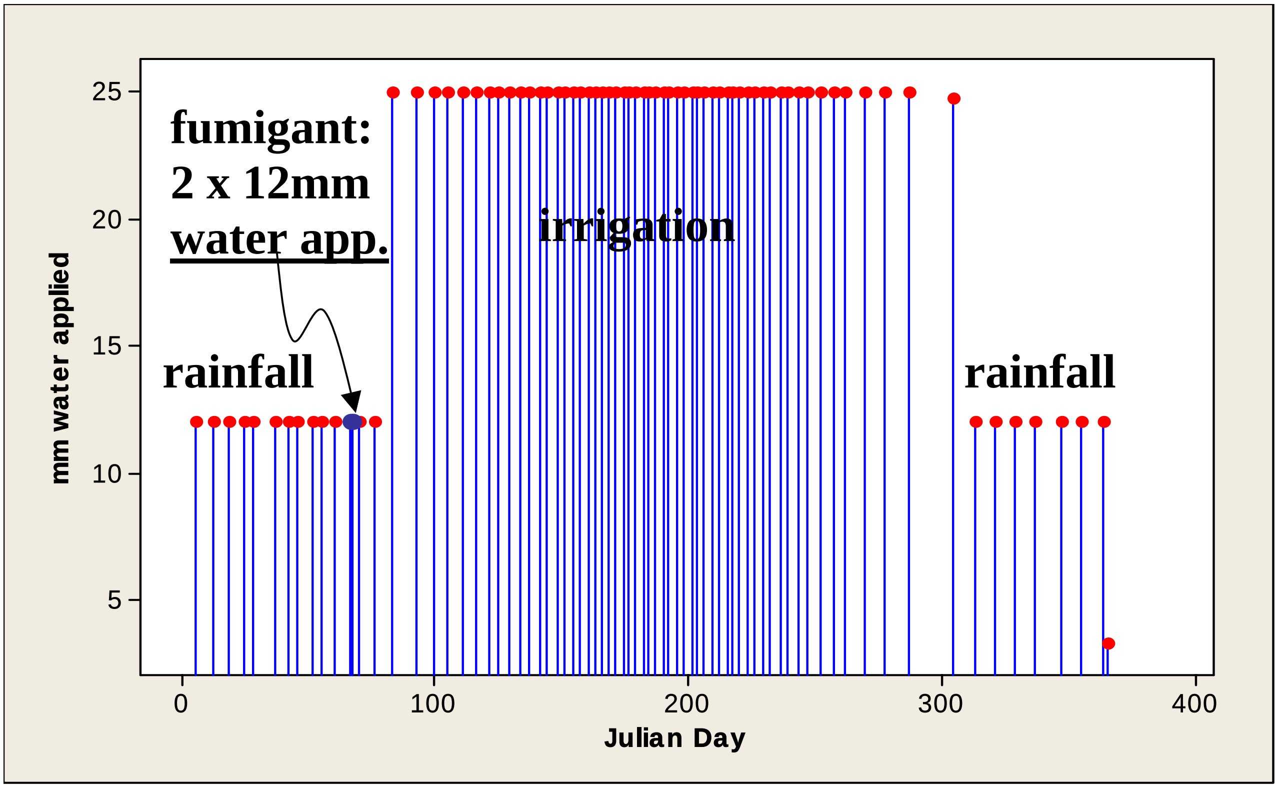
Fumigant	Maximum Conc. (ppb)	Median Conc. Positive Detections [1] (ppb)	Median Conc. All Wells Sampled [1] (ppb)	MDL [2] (ppb)	% Wells with Positive Detections	# Wells Sampled
California						
1,2-D	160	0.80	0	2.5	1.4	12,095
EDB	4.7	0.013	0	0.5	2.1	8,250
DBCP	166 [4]	0.26	0	0.05	25.0	12,244
Fresno [3]						
1,2-D	33	1.52	0	10	3.3	242
EDB	1.1	0.02	0	0.5	7.8	256
DBCP	51	1.2	0.19	0.05	65	1,649

[1] Based on mean concentration when a well had multiple analyses.
[2] 99.5% of the MDLs were less than or equal to this value.
[3] From monitoring data in the 16-township course soil area in Fresno County.
[4] Two higher values were reported in the Well Inventory Database but they are suspect.

The additional 25 mm of water required by the proposed regulations was a very small fraction of the 1,618 mm of annual irrigation and rainfall modeled (Figure 1). At the 95th percentile the predicted well water concentration of 1,2-D was 17,400 ppb when accounting for the additional water applications. The predicted concentration of 1,2-D without the additional water applications was slightly less at 17,000 ppb (Table 4). The additional water had a miniscule effect especially when compared to the orders of magnitude difference between (1) the predicted concentrations for the current fumigants and the known contaminants and (2) the predicted concentrations for the known contaminants and the maximum levels measured in wells.

The main physical-chemical differences between the previously and currently used soil fumigants are the shorter soil degradation half-lives and hydrolysis half-lives. The soil degradation half-lives and hydrolysis half-lives for the current fumigants were both significantly lower (p=0.0259, Mann-Whitney Test) than those for the known contaminants (Table 1) resulting in predicted ground water and well water concentrations that are orders of magnitude lower than the known ground water contaminant concentrations (Table 4). Two ground water monitoring studies provide further anecdotal evidence for the difference in contamination potential between the previously and currently used soil fumigants (Knuteson et al., 1992a; Knuteson et al., 1992b). The concentrations of 1,3-D and 1,2-D were monitored in divergent locations where Telone (1,3-D) had previously been applied. 1,2-D was monitored because it was previously present as an impurity in Telone comprising approximately 2% of the product by weight. Residues of 1,3-D were not detected whereas 1,2-D was detected at levels below 0.6 ppb, indicating that the residues for 1,2-D are more recalcitrant than 1,3-D residues.

Figure 1. Amount of rainfall, irrigation water, and additional water required by proposed regulations over one year.



Conclusions

Using an empirical Monte Carlo modeling procedure, the fumigants methyl bromide, chloropicrin, MITC, and 1,3-D were predicted to be undetectable in wells in a leaching-vulnerable California soil due to the proposed fumigant post-application irrigation treatments. The method used to assess the fumigants greatly overestimated the concentration of the fumigants 1,2-D, DBCP, and EDB, which are known ground water contaminants. The physical-chemical properties of the known contaminants contrasted greatly with those of the current fumigants, reflecting greater environmental persistence (Table 1). The results of this modeling exercise indicate that the proposed regulations for current fumigants will not increase the likelihood that fumigants will move to California ground waters or well waters.

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