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Potential for Methomyl Movement to California Groundwater as a Result of Agricultural Use

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Summary

In this evaluation, a deterministic model was used to assess the potential for the insecticidal active ingredient methomyl to contaminate groundwater under a worst-case modeling scenario. The scenario included two applications per year of methomyl, with each application at the maximum label rate for each year over a 30-year simulation period. Under the scenario, the model estimated a negligibly small methomyl concentration of 3.76×10^{-18} ug/L in groundwater from a hypothetical water well. The estimated methomyl concentration was multiple orders of magnitude lower than DPR's current pesticide reporting limit in groundwater of 0.05 ug/L. The negligibly small simulated methomyl concentration was corroborated by the lack of an actual confirmed detection of methomyl in more than 18,000 analyzed groundwater samples from approximately 7,500 unique wells as collected by various local, state, and federal agencies in California since the mid-1980s. In addition, no verifiable detections of methomyl in groundwater in other states outside of California were found by DPR through a survey of national databases. Based on the modeling analysis, it is concluded that methomyl does not have a significant potential to contaminate groundwater in California when applied at its label-specified maximum annual application rate over a long-term multiple-year period.

Introduction

The Exposure Assessment Group of the Department of Pesticide Regulation (DPR) Human Health Assessment Branch has requested assistance from the Groundwater Protection Program (GWPP) in evaluating the potential for methomyl movement to groundwater under California conditions. They have also requested results from groundwater monitoring studies conducted for methomyl.

The GWPP utilizes modeling data and groundwater monitoring studies for evaluating the potential for pesticide active ingredients to contaminate California groundwater under agricultural use conditions. Applications of the GWPP's model have included evaluating the potential impact on groundwater of new pesticide active ingredients submitted to DPR for California registration, reevaluating pesticides with existing California registrations, identifying management practices to mitigate residue movement to groundwater, prioritizing pesticides for groundwater monitoring, and determining water input management in field studies. The groundwater model has been calibrated to simulate pesticide movement in soils vulnerable to leaching and to predict residue concentrations in well water. The model has been verified against well monitoring data obtained from pesticide monitoring studies conducted in areas of California where the groundwater has been impacted by pesticides.

Groundwater monitoring by DPR for certain pesticide active ingredients is mandated by the Pesticide Contamination Prevention Act of 1985. Active ingredients of agricultural use pesticides, including methomyl, are evaluated based on their physical and chemical properties and use patterns to determine whether they should be placed on the Groundwater Protection List (Title 3 of the California Code of Regulations (CCR), section 6800[b]) for groundwater monitoring. Pesticide active ingredients are placed on this list if they "exceed" threshold values of certain physical/chemical properties and if products containing these active ingredients are: 1) intended to be applied to or injected into the soil by ground-based application equipment, or 2) intended to be applied to or injected into the soil by chemigation, or 3) the label of the pesticide requires or recommends that the application be followed, within 72 hours, by flood or furrow irrigation (Dias, 2013).

Modeling Methodology and Parameterization

The LEACHP computer model (Hutson and Wagenet, 1992) is used by the GWPP to simulate pesticide fate and transport in the soil root zone. The model is mechanistic in nature and simulations account for the influence of developing plant structures, evapotranspirative processes, depth-dependent soil texture and organic matter content; chemical adsorption, degradation and transformation processes; soil water movement, solute convection and dispersion, and heat flow and profile temperatures in the soil. Soil texture, organic carbon content and bulk density data used to define the California conditions modeling scenario represent coarse, loamy-sand soils located in eastern Fresno County, California, in an area that is considered vulnerable to leaching of pesticide residues to groundwater. Troiano et al. (1993) measured the high leaching potential of this soil in a field study that determined the effect of method and amount of irrigation water application on the movement of atrazine and bromide in soil. Data from that study were later used by Spurlock (2000) to calibrate the LEACHP model to the study area by establishing estimates for several soil hydraulic properties required for modeling of pesticides in soil. The calibrated LEACHP model was then coupled to an empirical-based model for use in a Monte Carlo probabilistic procedure to investigate the effect of irrigation management on leaching of known groundwater contaminants in California. The modeling scenario was verified by good agreement between simulated output and pesticide residue concentrations measured in domestic drinking water wells located in the study area (Spurlock, 2000).

For this current analysis, deterministic and probabilistic modeling approaches were initially considered to estimate potential concentrations of methomyl in domestic drinking water wells. However, the physical and chemical properties of methomyl indicated that it is only moderately persistent in the soil environment, especially when compared to the properties of those pesticides that have been found in California groundwater as a result of agricultural use such as those listed in Title 3 CCR 6800(a). Consequently, the computing-intensive probabilistic modeling approach was deferred in favor of conducting a single deterministic simulation to evaluate the extent of methomyl fate and movement in soil and potential to reach groundwater. With this approach, the LEACHP model was configured to simulate an idealistic, worst-case modeling scenario by selecting physical and chemical model parameter values for methomyl most conducive to its persistence and movement in soil, chemical application directly to the soil surface at maximum label rates across consecutive years, soil conditions vulnerable to leaching residues, shallow groundwater, and excessive irrigation inputs producing large amounts of percolating water. The GWPP’s groundwater modeling scenario utilizes a second, empirical-based model coupled to the primary LEACHP model that simulates residue movement below the deepest simulated LEACHP soil depth of 3 meters. Simulated residues passing through this depth are transitioned to the empirical-based model for simulation in the deep vadose and saturated zones and finally to a well where residue concentrations are estimated. More detailed methodology of the GWPP’s modeling scenario utilizing LEACHP and the empirical-based model, including model parameterization, has been previously documented (Troiano and Clayton, 2009).

Water inputs to the modeling scenario were consistent with those to support grape production, which is a typical crop grown in the study area in the coarse-textured soils of eastern Fresno

County. A 6-month irrigation period was simulated from mid-April to mid-October. Irrigation events were simulated at fixed-depth increments of 100 millimeters (mm) with the frequency of application determined by crop water demand and irrigation efficiency. Water applications were made at 160% of crop demand, which represented typical California agricultural irrigation efficiencies of approximately 60% for non-pressurized, surface delivery methods such as basin, border and furrow-type systems (California Agricultural Technology Institute, 1988; Snyder et al., 1986). Rainfall events were simulated during the non-irrigation season from November through April and were applied when the long-term mean daily precipitation accumulated to 12 mm since the previous water input. Mean long-term daily temperature, precipitation, and reference evapotranspiration (ETo) values were obtained from the California Irrigation Management Information System weather station #80 at California State University, Fresno (http://www.ipm.ucdavis.edu/WEATHER/wxretrieve.html) and calculated over a consecutive 20-year period. Water demand for the simulated grape crop was calculated from the long-term mean daily ETo and crop coefficients, the latter of which for grapes ranged from 0 to 0.85 depending on the stage of canopy development. Simulated irrigation applications were subsequently based on the product of this crop water demand and the excess demand factor of 1.6 to account for irrigation application inefficiencies.

The deterministic modeling approach for methomyl consisted of methomyl-specific parameter selection based on a worst-case scenario reflecting the longest terrestrial field dissipation (TFD) half-life and lowest carbon-normalized soil adsorption coefficient (Koc) values. Since data from these studies involve chemical interactions with soil, the results can be variable due to the heterogeneous nature of soil, especially when compared to other study types that are conducted in a more uniform matrix such as air and water for volatility and solubility studies, respectively. Accordingly, for each active ingredient DPR typically receives several TFD and soil adsorption studies from which dissipation half-life and Koc values are calculated, respectively, thereby providing some indication in the variability of these parameters. For methomyl, only two TFD studies were on file with DPR which provided dissipation half-life values of 5.2 and 54.4 days, respectively. No other field-derived dissipation half-life values for methomyl were found in the Pesticide Properties DataBase (PPDB) maintained by the Agriculture and Environment Research Unit at the University of Hertfordshire, UK (Lewis et. al., 2016). Therefore, the half-life value of 54.4 days was selected for this current evaluation of methomyl to comply with the worst-case modeling scenario. For methomyl solubility, a single value of 54,700 milligrams per liter (mg/L) was present in DPR's Pesticide Chemistry Database. A similar methomyl solubility value of 55,000 mg/L was found in the PPDB. To comply with the worst-case modeling scenario, the methomyl solubility of 55,000 mg/L was selected for the model input. These parameter values and others utilized for deterministic modeling in this current evaluation are given in Table 1, with the LEACHP model input file given in Appendix 1.

Table 1. Methomyl-specific LEACHP model input data. Where multiple values were available those values identified by ‘*’ were selected.

Modeling parameter	Value	Source
Active ingredient application rate (mg/m^2/year)	1,614[x]	DuPont Lannate® SP Insecticide label[z]
Koc (cm^3/g)	60.0 41.7 38.3 33.3*	DPR pesticide chemistry database
TFD dissipation half-life (day)	13.5 54.4*	DPR pesticide chemistry database
Aqueous solubility (mg/L)	54,700 55,000*	DPR pesticide chemistry database PPDB, University of Hertfordshire, UK
Vapor density (mg/L)	4.3E-04	DPR pesticide chemistry database
Molecular diffusion coefficient in water (mm^2/day)	120[y]	Spurlock (2000)
Molecular diffusion coefficient in air (mm^2/day)	4.300E+05[y]	Spurlock (2000)
Air diffusion coefficient enhancement to account for atmospheric pressure fluctuations (mm^2/day)	1.400E+05[y]	Spurlock (2000)

[x]Maximum application rate of 7.2 pounds of methomyl per acre per crop (807 mg/m^2/crop) for cabbage, cauliflower, celery, Chinese cabbage, and lettuce. Model input of 1,614 mg/ m^2/year represents maximum application rate (807 mg/m^2/crop) applied to two crops grown in the same year on same piece of land.

[z]Active registration in California since 3/10/97.

[y]Universal values utilized for most non-volatile pesticides.

Methomyl is the active ingredient in several insecticide products used to control various aphids, worms, and beetles in field and vegetable crops, fruit and citrus orchards, melons, and commercial turf (sod farms). The highest (maximum) application rate of methomyl is 7.2 pounds (lbs) per acre per crop (807 mg/m^2/crop) for the crops cabbage, cauliflower, celery, Chinese cabbage, and lettuce.

Other crops with labeled use have lower maximum application rates. In some areas of California, multiple crops are grown on the same piece of land within a single year. For example, in Monterey County use of methomyl has been reported on spring-grown lettuce followed by methomyl use on fall-grown celery on the same piece of land and within the same calendar year. To reflect potential maximal use of methomyl in such cropping systems, the maximum label rate of methomyl (807 mg/m^2/crop) in this modeling evaluation is applied twice per year (i.e., a total methomyl application of 1,614 mg/ m^2/year) for each year simulated by the model.

The LEACHP simulation period for standard evaluations by the GWPP is 5 years whereby applications of the active ingredient are made annually at maximum label rates to the soil surface. Simulations for the 5-year period typically result in near steady-state conditions where the annual rate of chemical application and the sum of the dissipation losses approach equilibrium. Since two annual applications of methomyl at its maximum application rate were implemented for this evaluation, the model was executed for a 30-year period in order to achieve a quasi-steady-state mass flux of methomyl exiting below the simulated 3-meter soil root zone. After the 30-year simulation period, annual loading and distribution of residues in the soil profile and residue movement below the 3-meter deep soil profile are essentially stable. The empirical-based modeling phase utilizes this stabilized annual mass of residue movement below the LEACHP profile to estimate a residue concentration in well water.

Modeling Results

Under the defined worst-case scenario, the LEACHP model was executed for a 30-year simulation period in order for the mass flux of methomyl residues leaching below the modeled 3-meter soil root zone to reach a quasi-steady-state value. A summary of the simulated annual inputs and outputs in the modeled 3-meter soil root zone is given in Table 2. Given a total annual application of 1,614 mg/m^2 of methomyl in the model, LEACHP estimated a cumulative annual loss of 296.6 mg/m^2 of methomyl through the bottom of the 3-meter soil root zone. This cumulative annual loss was inputted into the following empirical-based modeling function to simulate methomyl residue aging in the deep vadose and saturated zones and to subsequently produce an estimate of methomyl concentration in a hypothetical water well:

$$Well\ Water\ Concentration\ (mg/m^3\ or\ \mu g/L) = \frac{R \times 0.5^{(Nt+Ns)}}{D_w}$$

where:

- R = annual cumulative total methomyl loss below LEACHP root zone (mg/m^2)
- N_t = number of dissipation half-lives methomyl experienced during transport in the deep vadose zone
- N_s = number of dissipation half-lives methomyl experienced in the saturated zone
- D_w = depth of annual groundwater recharge (m)

The empirical-based modeling function yielded a negligibly small methomyl concentration in well water of 3.76 x 10^{-18} micrograms per liter (ug/L). This estimated water well concentration for methomyl is multiple orders of magnitude lower than the GWPP's current pesticide reporting limit of 0.05 ug/L. It is worth noting that despite the negligibly small simulated concentration of methomyl in well water by the model, placement of methomyl on the Groundwater Protection List (Title 3 of the California Code of Regulations (CCR), section 6800[b]) is defined by the guidelines outlined by Dias (2013) and is independent of the results of the GWPP's deterministic and probabilistic modeling approaches.

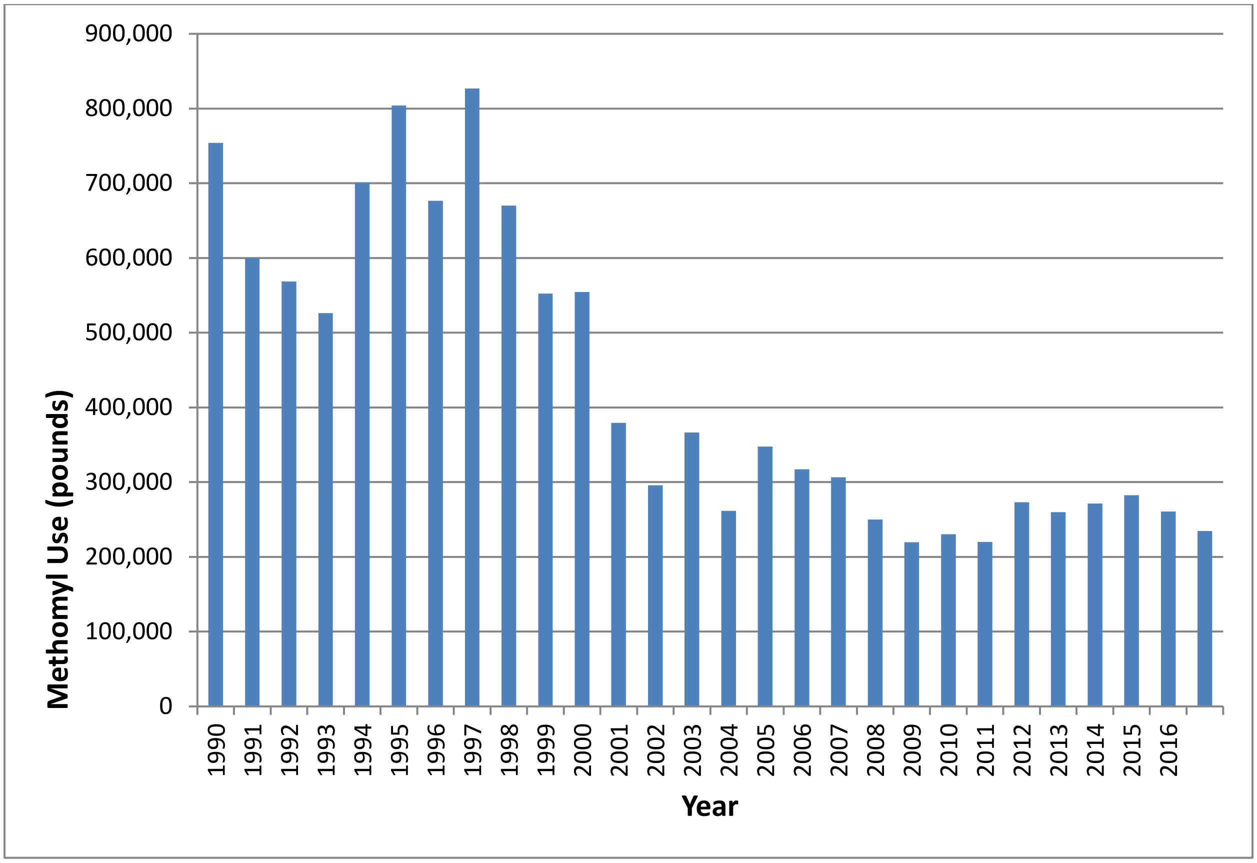
Table 2. Annual mass balance of methomyl additions and losses from the LEACHP model simulation following attainment of steady-state conditions.

	mg/m^2	
Addition by application to soil surface	1614.0	
Change in soil profile	1.2	
Loss by leaching	296.6	
Loss by volatilization	0.0	
Loss by transformation	1310.7	
Loss to soil surface in undissolved state	0.0	
Total loss	1607.3	
Mass balance error		5.5

Groundwater Monitoring of Methomyl

Data from DPR's Pesticide Use Reporting (PUR) database indicates that annual use of methomyl has declined from the 1990s from a high of about 827,000 lbs in 1997 to a low near 220,000 lbs in 2009 (Figure 1). Between 2004 and 2017, annual use of methomyl generally leveled off within a range of reported use with an average annual use of about 267,000 lbs per year. Based on its physical and chemical properties, methomyl is characterized as both mobile and moderately persistent in soil and is considered to have the potential to reach groundwater (Johnson, 1991). Consequently, methomyl is listed on the Groundwater Protection List (Title 3 CCR 6800[b]).

Figure 1. Annual reported methomyl use in California from 1990 to 2017.



The DPR's Well Inventory Database (WIDB) contains reported concentrations of methomyl from laboratory-analyzed groundwater samples collected by various local, state, and federal agencies from the mid-1980s through 2018. In total, the WIDB contains results of laboratory measurements for methomyl in 18,827 groundwater samples collected between 1986 to 2018 from 7,528 unique water wells in the state. Only two detections of methomyl in groundwater samples have ever been reported to DPR. However, DPR was not able to confirm those detections when its staff resampled the associated wells and submitted the samples for analysis to qualified laboratories. As such, despite being considered to have the potential to reach groundwater, methomyl has not been verifiably detected to date in any groundwater samples collected from water wells in the state. A review by DPR of laboratory analysis data for groundwater samples collected outside of California in other states did not find any verifiable detections of methomyl in groundwater in those states.

Conclusions

Under a worst-case scenario, the deterministic modeling analysis estimated a negligibly small well water concentration of 3.76×10^{-18} ug/L for the insecticidal active ingredient methomyl. The modeling scenario simulated two applications per year of methomyl, with each application at the maximum label rate for each year over a 30-year simulation period. The estimated well water concentration of methomyl was multiple orders of magnitude lower than DPR’s current pesticide reporting limit in groundwater of 0.05 ug/L. The negligibly small estimated well water concentration was corroborated by the lack of an actual confirmed detection of methomyl in more than 18,000 analyzed groundwater samples from approximately 7,500 unique wells as collected by various local, state, and federal agencies in California since the mid-1980s. In addition, no verifiable detections of methomyl in groundwater in other states outside of California were found by DPR through a survey of national databases. Based on computer modeling conducted in this evaluation, it is highly unlikely that methomyl residues will impact groundwater in California as a result of agricultural use at levels even remotely approaching current analytical method detection levels.

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