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

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Summary

This evaluation used a deterministic modeling approach for carbaryl that consisted of chemical-specific parameter selection based on a worst-case scenario of application and irrigation rates. The modeling scenario simulated applications at maximum label rates on an annual basis over a 5-year period. The results of the model determined that carbaryl had no transport below the root zone and does not have a significant potential to contaminate groundwater in California. These modeling results are supported by extensive groundwater monitoring conducted throughout California by multiple agencies where carbaryl has not been positively detected in over 21,000 analyses from more than 9,000 unique wells. Based on modeling results and monitoring data, carbaryl is not likely to impact groundwater as a result of its legal agricultural use.

Introduction

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

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 predict pesticide movement in leaching vulnerable soils and residue concentrations in well water. It 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. Agricultural use pesticides, including carbaryl, are evaluated based on their physical/chemical properties and use patterns and to determine if 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's upper vadose 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 in the 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-type modeling approaches were initially considered in order to estimate potential concentrations of carbaryl in domestic drinking water wells. However, the physical/chemical properties of carbaryl indicated that it was not conducive to mobility or persistence 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-type simulation to evaluate the extent of carbaryl's fate and movement in soil and potential to threaten groundwater. With this approach the LEACHP model was configured to simulate an idealistic, worst-case modeling scenario by selecting physical/chemical parameter-values for carbaryl 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 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 carbaryl consisted of chemical-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 of air and water. For each active ingredient DPR typically receives several TFD and soil adsorption studies from which dissipation half-life and Koc values are calculated, thereby providing some indication in the variability of these parameters. To determine the correct physical/chemical properties of carbaryl to use in the model, multiple studies were evaluated. Data from DPR's Pesticide Chemistry Database was compared to data from the Pesticide Properties DataBase (PPDB) maintained by the Agriculture and Environment Research Unit at the University of Hertfordshire, UK (Lewis et. al., 2016). DPR's Pesticide Chemistry Database values represented the lowest soil adsorption coefficient (Koc) and longest terrestrial field dissipation (TFD) half-life and were used to model a worst-case scenario. These parameter values and others utilized for the deterministic modeling in this current evaluation are given in Table 1.

The LEACHP simulation period for standard evaluations is five years whereby applications of the active ingredient are made annually at maximum label rates to the soil surface. Simulations for this length of time typically result in near steady-state conditions where the annual rate of chemical application and the sum of the dissipation losses approach equilibrium. At this stage of the simulation, annual loading and distribution of residues in the soil profile and residue movement below the 3.0-m deep LEACHP modeling profile are essentially stable. The empirical-based modeling phase utilizes this stabilized annual mass of residue movement below the LEACHP profile to estimate residue concentrations in well water.

Table 1. Carbaryl-specific LEACHP model input data. Where multiple values were available those values identified by '*' were selected.		
Modeling parameter	Value	Source
Active ingredient maximum annual application rate (mg/m^2)	2241[z]	Bayer Sevin SL Carbaryl Insecticide
Koc (cm^3/g)	162* 231 390 628	DPR pesticide chemistry database
TFD dissipation half-life (day)	12* 7 16 (typical) No field study	DPR pesticide chemistry database PPDB, University of Hertfordshire, UK
Aqueous solubility (mg/L)	113* 9.1	DPR pesticide chemistry database PPDB, University of Hertfordshire, UK
Vapor density (mg/L)	1.29E-5	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 diff. coeff. enhancement to account for atmos. pressure fluctuations (mm^2/day)	1.400E+05[y]	Spurlock (2000)

[z]Equivalent to max applications of 20 lbs a.i./acre/season, representing maximum label rate for citrus fruits.
[y]Universal values utilized for most non-volatile pesticides.

Modeling Results

Carbaryl residues failed to move below the LEACHP-simulated 3-meter deep soil profile when the model was run for the 5-year period that resulted in near steady-state conditions (Table 2). This rendered the empirical modeling procedure that would normally be coupled to the LEACHP model to simulate residue movement in the deep vadose zone redundant. Carbaryl's low aqueous solubility and short TFD half-life led to its rapid stabilization within the model. The model output shows that the majority of carbaryl mass was lost through transformation, most likely due to its short TFD half-life of ~12 days.

The model was also run using a 10-year simulation period to evaluate if the longer time period had any impact on the movement of carbaryl through the root zone. While this extended time period did result in 0.1 mg/m^2 of carbaryl leaching past the root zone, this mass was well below the mass balance error of 5.2 mg/m^2 so it was not used in this evaluation. It is worth noting that although carbaryl did not leach past the root zone in the modeling results, placement of carbaryl on the Groundwater Protection List (Title 3 CCR 6800[b]) is defined by the guidelines outlined by Dias (2013) and is independent of the results of the GWPP's deterministic modeling approach.

Table 2. Annual mass balance of carbaryl additions and losses from the LEACHP model simulated 5-year run following attainment of near steady-state conditions.

	mg/m^2	
Addition by application to soil surface	2241	
Loss by leaching	0.0	
Loss by volatilization	20.0	
Loss by transformation	2216.4	
Total loss	2236.4	
Mass balance error		5.2

<u>Groundwater Monitoring of Carbaryl</u>

DPR's pesticide use reports indicated that statewide use of carbaryl in California decreased from approximately 954,000 lbs in 1990 to 221,000 lbs in 2016. Carbaryl is used on a variety of crop types, with the top crop being citrus (Table 3).

Numerous agencies have sampled groundwater for carbaryl in California from 1987 to 2017. According to DPR's well inventory database, over 21,000 groundwater samples have been analyzed for carbaryl from 9,186 unique wells and have resulted in five detections reported to DPR (Table 4). Of those reported detections, three of the wells were resampled by DPR, the samples were submitted for analysis to qualified laboratories, and carbaryl was not detected. For the other two reported detections, one was determined to be a point source and the other was well below DPR's normal reporting limit and did not require follow-up (Table 5). While there have been reported detections of carbaryl in groundwater outside of California, many of these reported detections are currently under evaluation for quality control purposes and are have not been verified. The GWPP has determined that these reported detections should not be used in the evaluation of the potential for carbaryl to contaminate groundwater in California.

Table 3. Sites with the highest total use of carbaryl from 1990 to 2016.

Crop Type	Carbaryl Use (lbs)
Orange	2,823,240
Landscape Maintenance	745,869
Tomatoes	599,742
Olive	521,830
Peach	444,999

Table 4. Well analysis for carbaryl 1987-2017.

Sampling Agency	Number of Samples Analyzed	Reported Detections of Carbaryl
CALIF. DEPARTMENT OF PESTICIDE REGULATION	195	0
CALIF. DEPT. OF PUBLIC HEALTH	15,525	3
CALIF. DEPT. OF WATER RESOURCES (DWR)	233	0
CALIF. REGIONAL WQCB NO. 2 SAN FRANCISCO BAY	9	0
CALIF. REGIONAL WQCB NO. 3 CENTRAL COAST REGION	12	1
CALIF. REGIONAL WQCB NO. 5 CENTRAL VALLEY REGION	4	0
CALIF. STATE WATER RESOURCES CONTROL BOARD	2,659	1
CALIF. STATE WATER RESOURCES CONTROL BOARD DRINKING WATER PROGRAM (PREV CDPH 5060)	2,322	0
SANTA BARBARA COUNTY	4	0
SANTA CLARA COUNTY	84	0
STOCKTON-E. SAN JOAQUIN WATER CONSERVATION DISTRICT	29	0
U S DEPT. OF AGRICULTURE	6	0
U S ENVIRONMENTAL PROTECTION AGENCY	6	0
U S GEOLOGICAL SURVEY	195	0
YUBA COUNTY	26	0
Grand Total	**21,309**	**5**

Table 5. DPR response to reported carbaryl detections.

Agency	County	DPR Follow Up	Result/Reason
Cal. Dept. of Public Health	Napa	Yes, Z study Z089	No Detection by DPR
Cal. Dept. of Public Health	Ventura	Yes, Z study Z290	No Detection by DPR
Cal. Dept. of Public Health	Solano	Yes, Z study Z289	No Detection by DPR
Cal. Water Resources	Butte	Yes, N memo 103	Below Reporting Limit
Cal. Water Quality Control Board	Monterey	No	Point Source: This detection was determined to be from a pesticide spill or direct contamination of a well.

Conclusions

Computer modeling of carbaryl under a worst-case scenario, which simulated the unlikely convergence of several chemical-, environmental-, and management-related factors conducive to offsite movement of residues, predicted that carbaryl would not leach past the root zone and would therefore not be transported to groundwater. The modeling scenario simulated applications at maximum label rates on an annual basis over a 5-year period. Based on this computer modeling, it is very unlikely that carbaryl residues will impact groundwater in California as a result of agricultural use. This conclusion is supported by the extensive groundwater monitoring that has been conducted by DPR and other agencies that has not positively detected carbaryl in over 21,000 groundwater samples.

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