Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, California 95812

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

Rick Bergin
Groundwater Protection Program

April 3, 2019

Summary

In this evaluation, a deterministic modeling analysis predicted, under a worst-case scenario conducive to offsite movement of pesticide residues, that well water concentrations of chlorothalonil are potentially negligible at a concentration of 3.05E-15 ppb. This conclusion is supported by extensive groundwater monitoring conducted by several agencies where chlorothalonil was not positively detected in 4,880 wells sampled throughout California. In addition, no verifiable detections of chlorothalonil in groundwater in other states outside of California were found by DPR through a survey of national databases. Based on modeling results and monitoring data, chlorothalonil is unlikely to impact California's groundwater as a result of its legal agricultural use.

Introduction

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

The GWPP utilizes modeling and groundwater monitoring data for evaluating the potential of pesticide active ingredients to contaminate California groundwater under agricultural use conditions. Applications of the GWPP's model include investigating the potential of new pesticide active ingredients to contaminate groundwater, reevaluating pesticides with existing California registrations, identifying mitigation practices to reduce pesticide movement to groundwater, prioritizing pesticides for groundwater monitoring, and managing water inputs 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. Active ingredients of agricultural use pesticides, including chlorothalonil, 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 CCR 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 Procedure Overview

The GWPP modeled chlorothalonil movement to groundwater in two phases as developed by Troiano and Clayton (2009). The first phase consisted of the LEACHP model simulating chlorothalonil’s movement through the upper vadose zone in a soil considered vulnerable to leaching. The LEACHP model simulated 5 years of annual applications of chlorothalonil at maximum label rates. The final year of the model simulation resulted in near steady-state conditions where the annual rate of chlorothalonil application and the sum of the dissipation losses approach equilibrium. The second phase was a less complex, empirical-based model that simulated chlorothalonil’s fate and movement through the lower vadose and saturated zones. This empirical-based model used the stable annual mass of residue movement below the 3 meter LEACHP modeling profile to estimate chlorothalonil residue concentrations in well water.

LEACHP Model Methodology

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 describes the water regime and the chemistry and transport of solutes in unsaturated soils. 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, an area that is considered vulnerable to the leaching of pesticide residues to groundwater. Troiano et al. (1993) characterized the high leaching potential of this soil in a field study that determined the effect of irrigation applications and methods 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).

Water inputs used in 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. Water demand for the simulated grape crop was calculated from the long-term mean daily reference evapotranspiration (ETo) and crop coefficients, the latter of which for grapes ranged from 0 to 0.85 depending on the stage of canopy development. Water applications were made at 160% of this 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 (CATI, 1988; Snyder et al., 1986). A 6 month irrigation period was simulated from mid-April to mid-October. Irrigation events were at fixed-depth increments of 100 mm with the frequency of application determined by crop water demand and irrigation efficiency. Rainfall events occurred during the non-irrigation season from November through April when the long-term mean daily precipitation accumulated to 12 mm since the previous water input. Mean long-term daily temperature, precipitation, and ETo values were obtained from the California Irrigation Management Information System weather station #80 at California State University, Fresno and calculated over a consecutive 20-year period (CIMIS, 2019).

Empirical-Based Model Methodology

Transport time for residues from the base of the 3 meter LEACHP profile to the water table is considered equivalent to that of percolating drainage water by assuming the residues are non-interactive with the soil media. This assumption is based on very low levels of organic carbon in the subsurface and the profile being largely composed of sand (Spurlock, 2000). Residue transport time through the deep vadose zone was estimated by separate LEACHP simulations of bromide, which is often used as a tracer for the movement of water through soil. Travel time to a groundwater depth of 20 m in the study area was estimated at 4 years and was determined by tracking the bromide center of mass.

Elapsed time between residue entry into the water table and subsequent sampling at a domestic well is known as the groundwater recharge age. The median recharge age for the study area was 6 years and was estimated from chlorofluorocarbon dating analysis of well water sampled from 18 domestic wells located also within the study area (Spurlock et al., 2000).

Simulating the transport of residues from entry into the aquifer to a drinking water well requires parameterization of the annual groundwater recharge depth and transport time to a well. Annual groundwater recharge depth in the study area was considered equivalent to the annual cumulative depth of drainage water from the LEACHP outputs. Since irrigation inputs were constant across years, and the rainfall and evapotranspiration values were input as weekly means calculated from the previous 20 years of climate data, the estimated annual groundwater recharge depth of 0.5 m was assumed stable. For each model run the annual cumulative mass of chlorothalonil entering the saturated zone was subsequently dissolved into this annual depth of recharge water to provide an estimated groundwater concentration calculated as follows:

Eq 1. $$\textit{Well Water Concentration}\ (mg/m^3\ or\ \mu g/L) = \frac{R \times 0.5^{(Nt+Ns)}}{D_w}$$

where:

R = annual cumulative total pesticide loss below LEACHP root zone (mg/m^2)

N_t = number of dissipation half-lives chemical experienced during transport in the deep vadose zone

N_s = number of dissipation half-lives chemical experienced in the saturated zone

D_w = depth of annual groundwater recharge (m)

Chlorothalonil Parameterization

The physical/chemical properties of chlorothalonil indicate that it is not especially mobile (low water solubility) or persistent (short degradation half-life) in the soil environment, especially when compared to the properties of pesticides that have been found in California groundwater as a result of agricultural use such as those listed in Title 3 CCR 6800(a) (Troiano and Clayton, 2009). Examination of the Pesticide Properties DataBase (PPDB) maintained by the Agriculture and Environment Research Unit at the University of Hertfordshire, UK (Lewis et. al., 2016) indicate that the chlorothalonil values in DPR’s pesticide chemistry database are conservative for leaching when compared to other sources, i.e., low soil adsorption (Koc) and long terrestrial field dissipation (TFD) half-lives. Consequently, a single deterministic-type simulation was used to evaluate the extent of chlorothalonil’s fate and movement in soil and its 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 chlorothalonil 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. Three different maximum label rates were chosen for modeling because chlorothalonil is labeled for use on a wide variety of crops including row crops, tree crops, and turf (Table 1). The application rates and other parameter values utilized in this evaluation are specified in Table 2, with the LEACHP model input file included in Appendix 1. In the empirical-based model, the longest TFD half-life (69 days) was used to age chlorothalonil residues from the bottom of the LEACHP soil profile to a drinking water well according to Eq. 1.

Table 1. Top ten chlorothalonil uses in 2016 by pounds of active ingredient applied in California. (CDPR, 2019a)

Site	Lbs applied	Site	Lbs applied
Almond	401,530	Celery	53,923
Processing Tomatoes	220,714	Potato	42,646
Landscape Maintenance	92,308	Tomato	35,489
Dry Onion	83,093	N-Outdoor Flowers	15,290
Prune	69,390	Carrot	12,793

Table 2. Chlorothalonil LEACHP model input data.

Modeling Parameter	Value	Source
Active ingredient maximum annual application rate (mg/m^2)	2,018 2,690 8,182	Equus 720 SST (celery) Bravo WeatherStik (mango) Daconil WeatherStik (golf green)
Koc (cm^3/g)	4,085 794 625 500[a] 300-6,154	DPR pesticide chemistry database PPDB
TFD half-life (day)	51 69[a] 7-28	DPR pesticide chemistry database PPDB
Aqueous solubility (mg/L)	1.2[a] 0.81	DPR pesticide chemistry database PPDB
Vapor density (mg/L)	2.86E-05	DPR pesticide chemistry database
Molecular diffusion coefficient in water (mm^2/day)	120[b]	Spurlock (2000)
Molecular diffusion coefficient in air (mm^2/day)	4.300E+05[b]	Spurlock (2000)
Air diff. coeff. enhancement to account for atmos. pressure fluctuations (mm^2/day)	1.400E+05[b]	Spurlock (2000)

a Value used in modeling if multiple values available.
b Universal values utilized for most non-volatile pesticides.

Modeling Results

The results of the modeling scenarios are presented in Table 3. Less than 1% of applied chlorothalonil leached below the modeled soil profile in each application scenario resulting in an estimated well water concentration of 3.05E-15 ppb. At higher application rates, like in the golf green scenario, the majority of the residues accumulated on the surface due to chlorothalonil's low water solubility. Water inputs were not sufficient to fully dissolve the chemical applied to the soil surface despite simulations of winter rainfall and high irrigation applications at 160% of plant demand. Estimated well concentrations are negligible due to chlorothalonil's rapid degradation rate. The amount of chlorothalonil leached and the resultant well concentrations are magnitudes lower than the modeled concentrations of known groundwater contaminates listed in

Title 3 CCR 6800(a) (Spurlock, 2000). It is worth noting that despite the negligibly small simulated concentration of chlorothalonil in well water by the model, placement of chlorothalonil 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 3. Final annual mass balance of chlorothalonil and estimated well concentrations in three different LEACHP scenarios following attainment of steady-state conditions. All values are in mg/m^2 unless otherwise noted.

	Celery	Mango	Golf Greens
Addition to soil surface	2,017.5	2,690	8,182.2
Loss by leaching	**10.3**	**12.8**	**12.8**
Loss by volatilization	585.5	881.2	881.2
Loss by transformation	1,412.3	1,768.4	1,768.4
Loss by undissolved on surface	***3.7***	***19.1***	***5,506.7***
Total loss	2,011.8	2,681.5	8,169.1
Mass balance error	5.8	8.6	13.2
Estimated well concentration	2.45E-15 ppb	3.05E-15 ppb	3.05E-15 ppb

Groundwater Monitoring of Chlorothalonil in California

In the early 1980s, DPR established the Well Inventory Database (WIDB) under authority granted in FAC section 13152(c) and began collecting groundwater sampling data from public agencies. The database currently contains over 2.5 million records, including monitoring data from over 26,000 public and private wells sampled for over 370 different pesticides and pesticide degradates. According to the WIDB, chlorothalonil has been sampled in groundwater from 1984 to 2017 in 4,880 unique wells by nine different agencies (Table 4). In 2010 and 2011, DPR monitored for chlorothalonil in high use areas and did not detect the chemical in any of the 60 sampled wells. Several other agencies have also sampled for chlorothalonil in California and similarly failed to find any legitimate detections of the pesticide in groundwater. The California Department of Public Health reported a trace detection in 2011 that was below the reporting limit for that analysis. DPR investigated pesticide use around the well and determined it was located in a township with no reported chlorothalonil use (Nordmark, 2013). The other reported detection was by the California Regional WQCB NO.1 in 1986 that was determined to be a point source contamination from an improperly constructed well (CDPR, 2019b). 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 chlorothalonil in groundwater in those states.

Table 4. Monitoring results for chlorothalonil in California groundwater. (CDPR, 2019b)

Agency	Number of wells sampled	Number of wells reported with detections	All sample reporting limit range (ug/L)	Detection concentration / reporting limit (ug/L)	Detection notes
Calif. Dept. of Public Health	4323	1	0.01 - 5	0.02 / 5	Trace detection with no reported use
Calif. State Water Resources Control Board	495	0	0.1 - 5	--	
Calif. Dept. of Water Resources	120	0	0.05 - 50	--	
U.S. Geological Survey	77	0	0.002 – 0.05	--	
Calif. Dept. Pesticide Regulation	60	0	0.05	--	
U.S. Dept. of Agriculture	8	0	0.1	--	
U.S. Environmental Protection Agency	6	0	0.12	--	
Calif. Regional WQCB NO. 1	2	1	0.1	1.1 / 0.1	Point source
Yolo County	1	0	5	--	

Conclusions

The deterministic modeling analysis predicted under a worst-case scenario, which simulated the unlikely convergence of several chemical- and environmental-related factors conducive to offsite movement of pesticide residues, that well water concentrations of chlorothalonil are potentially negligible. At higher application rates, chlorothalonil residues remained undissolved on the soil surface with minimal residues leaching and resulting in an estimated well water concentration of 3.05E-15 ppb. Chlorothalonil is typically a foliar applied, non-systemic fungicide and the conservative modeling scenario assumes full application of the chemical directly to the soil surface. Under actual-use conditions only a fraction of the applied chlorothalonil would be expected to contact the soil surface, thereby resulting in a lower chance of accumulating undissolved residues on the soil surface.

Based on computer modeling conducted in this evaluation it is unlikely that chlorothalonil residues will impact groundwater in California as a result of legal agricultural use. This conclusion is supported by extensive groundwater monitoring conducted by several agencies where chlorothalonil was not positively detected in 4,880 wells sampled throughout California. In addition, no verifiable detections of chlorothalonil in groundwater in other states outside of California were found by DPR through a survey of national databases. These monitoring studies support the modeling analysis results which estimated that concentrations of chlorothalonil in well water would be below DPR’s reporting limit and the reporting limits of other agencies that have previously sampled for the pesticide in California.

References

CATI. 1988. Irrigation systems and water application efficiencies. CATI Center for Irrigation Technology, publication 880104. California State University, Fresno, California.

CDPR. 2019a. Pesticide Use Database. Available at https://www.cdpr.ca.gov/docs/pur/purmain.htm (verified March 29, 2019). California Department of Pesticide Regulation, Sacramento, California.

CDPR. 2019b. Well Inventory Database. California Department of Pesticide Regulation, Sacramento, California.

CIMIS. 2019. California Irrigation Management Information System. Available at https://cimis.water.ca.gov (verified March 29, 2019). California Department of Water Resources, Sacramento, California.

Dias, J. 2013. Memorandum to D. Duncan, Branch Chief. Guidelines for identifying pesticides to be added to and removed from the Groundwater Protection List: Title 3, California Code of Regulations Section 6800(B). Available at https://www.cdpr.ca.gov/docs/emon/grndwtr/polprocd/gwp_cacode_6800b.pdf (verified April 24, 2019). California Department of Pesticide Regulation, Sacramento, California.

Hutson, J.L. and R.J. Wagenet. 1992. LEACHM: Leaching Estimation and Chemistry Model: a process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone. Continuum Vol. 2, Version 3. Water Resources Inst., Cornell University, Ithaca, New York.

Lewis, K.A., J. Tzilivakis, D. Warner and A. Green. 2016. An international database for pesticide risk assessments and management. Human and Ecological Risk Assessment: An International Journal, 22(4), 1050-1064.

Nordmark, C. 2013. Memorandum to L. Quagliaroli. N102. Four-section surveys not necessary for reports of pesticide detections in California ground water by the California Department of Public Health. California Department of Pesticide Regulation, Sacramento, California.

Snyder, R.L., B.R. Hanson and R. Coppock. 1986. How farmers irrigate in California. Univ. of Calif. Division of Ag. And Nat. Res., Leaflet 21414. Oakland, California.

Spurlock, F. 2000. EH 00-01: Effect of irrigation scheduling on movement of pesticides to ground water in coarse soils: Monte Carlo analysis of simulation modeling. Available at http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps.htm (verified March 29, 2019). California Department of Pesticide Regulation, Environmental Monitoring Branch, Sacramento, California.

Spurlock, F., K. Burow and N. Dubrovsky. 2000. Chlorofluorocarbon dating of herbicide-containing well waters in Fresno and Tulare Counties, California. Journal of Environmental Quality, 29:474-483.

Troiano, J. and M. Clayton. 2009. Memorandum to J. Sanders, Branch Chief. Modification of the probabilistic modeling approach to predict well water concentrations used for assessing the risk of ground water contamination by pesticides. Available at <http://www.cdpr.ca.gov/docs/emon/pubs/analysmemos.htm (verified March 29, 2019). California Department of Pesticide Regulation, Environmental Monitoring Branch, Sacramento, California.

Troiano, J., C. Garretson, C. Krauter, J. Brownell and J. Hutson. 1993. Influence of amount and method of irrigation water application on leaching of atrazine. J. Enviorn. Quality 22:290-298.