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Comparison of USEPA and DPR Modeling Approaches and Validation Procedures to Predict Drinking Water Concentrations of Pesticide Residues for Use in Human Health Risk Assessments.

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September 26, 2017

EXECUTIVE SUMMARY

Data used for assessing health risks of pesticide residues in environmental samples should be based on the known range in concentrations that results from agricultural use and climatic conditions that reflect California conditions. If these data are not available then expected ranges in concentration generated from validated models are used in human risk assessments. The accuracy of a model is determined by comparing data collected in the field to model predicted values.

To address the need for well water environmental sample data, the Ground Water Protection Program (GWPP) in the Environmental Monitoring Branch (EM), Department of Pesticide Regulation (DPR), California Environmental Protection Agency, monitors domestic well water for the presence of pesticide residues. Sampling is conducted in areas of high pesticide use and high geographical vulnerability for contamination of ground water by surface-applied chemicals. The Well Inventory Database (WIDB), maintained by GWPP staff, contains results from EM's well water sampling investigations and also data for pesticide residues from other state, local, and federal agencies sampling studies.

In California the first step in modeling drinking water concentrations for human health risk assessments is to determine the presence of sampling data in the WIDB for a chemical of concern. If present and if representative of sampling conducted in areas of high use and high vulnerability, then the range in concentrations for this data should represent the expected range in concentrations that are relevant for a California-based health risk assessment. If representative

data are lacking, then modeling approaches to predict movement of residues to well water would provide estimates for predicated concentrations.

Although the US Environmental Protection Agency (USEPA) has developed an approach to modeling concentrations in well water, the choice of their model and its assumptions related to environmental fate do not represent California conditions. Their model predictions result in unrealistically high, estimated well water concentrations. Alternatively, GWPP staff has developed a modeling approach that produces estimated concentrations of residues in ground water that closely match the distribution of residues measured in domestic drinking water wells that have been sampled in areas of high pesticide use and high geographic vulnerability in California.

This memo presents data for propyzamide as evidence that the GWPP modeling approach provides greater accuracy for California assessments. The USEPA modeling approach estimated a concentration of 21.0 ug/L propyzamide in well water as a result from use at the recommended highest label rate. In contrast, the maximum estimated concentration in well water using the GWPP modeling approach was 0.00273 ug/L. The GWPP estimate indicates a very low potential for residues to be detectable in well water. Results from well sampling reported in the WIDB verify the low potential for detection of propyzamide in well water: No propyzamide residues have been detected from sampling conducted within California where GWPP has monitored 162 wells in areas of high use and high geographic vulnerability with a reporting limit of 0.05 ug/L. Monitoring conducted by the United States Geological Survey (USGS) in California verifies this conclusion where no propyzamide residues were reported in 1,893 sampled wells at a reporting limit of 0.004 ug/L.

This memo recommends a procedure for HHA to use in their health risk assessments. Working with GWPP, the first step is to determine if the targeted chemical in ground water has sampling results in California using the WIDB. If the representative data are not present, GWPP staff would determine maximum concentrations expected in ground water resulting from California use conditions using its more accurate ground water modeling approach.

INTRODUCTION

The Department of Pesticide Regulation's (DPR) Human Health Assessment (HHA) Branch proposes using US Environmental Protection Agency (USEPA) modeling estimates for concentrations of propyzamide pesticide residues in well water when they assess potential health effects from use in California. In response to data gaps that occur during the registration process, the USEPA has developed modeling approaches to predict pesticide residue concentration in streams and ground water. Historically, the model preferred by USEPA to estimate water and pesticide movement through soil is the PRZM model, which stands for Pesticide Root Zone Model (Carsel et al, 2003; Suarez, 2005). The model has been adapted to predict the environmental fate for various aspects of decision-making during the registration process of pesticide products. For ground water, the model has been modified to provide predictions of residue concentration in well water resulting from agricultural use.

DPR's Ground Water Protection Program (GWPP) has also developed a modeling approach to similarly address data gaps, but a different model is used to predict soil movement of residues. GWPP staff chose to use the LEACHP model, which stands for Leaching Estimation And Chemistry Pesticide (LEACHP) (Hutson, 2003). GWPP staff chose the LEACHP model over USEPA's PRZM model because it incorporated more sophisticated modeling algorithms that provide greater accuracy in estimates of soil water movement and evaporative water loss, processes that are especially important when modeling water and residue movement in irrigated agriculture.

In addition to model results, the GWPP program, according to a legal mandate of the Pesticide Contamination Prevention Act (Connelly, 1986), has developed expertise in conducting well monitoring studies to determine if currently used pesticide products have contaminated California's ground water. GWPP maintains an extensive record of well monitoring data in the Well Inventory Database (WIDB). Data also are collected for monitoring of pesticide residues in well water from other local, state, and federal agencies.

GWPP staff recommends that HHA use well monitoring data collected in the WIDB and/or GWPP modeling data in its health estimates made for use of agricultural pesticide products in California. This report provides supporting evidence for this recommendation by:

1. Discussing why the model of soil and residue movement used by DPR (LEACHP model) results in more accurate predictions under California agricultural conditions than the model used by USEPA (PRZM model).

2. Comparing USEPA and DPR approaches to predict concentrations in drinking water wells concentrations and the procedures used to validate each approach.

3. Describing how the environmental well monitoring data generated by the GWPP could be used in a tiered approach to determine appropriate estimates to use in health risk assessments.

4. Using well monitoring data for propyzamide as an example to compare predicted concentrations in drinking water wells between the USEPA and DPR modeling approaches.

Finally, this memo recommends a sequential process for using GWPP's well monitoring data and its modeling approach.

1. Comparison of Modeled Water Movement between PRZM and LEACHP

Both the PRZM and LEACHP models are one-dimensional models that incorporate environmental chemistry and fate data to estimate residue movement down through a soil profile. They differ in the approach used to model soil water movement through the profile, which in turn affects the estimated temporal movement of pesticide residues. The PRZM model runs on a daily time step where drainage to field capacity for each soil layer occurs within one day. The soil column is modeled as layers called horizons where each horizon can be assigned a specific depth. This method for modeling water movement is termed a tipping bucket approach. The soil

water holding capacity of each horizon is specified. Water is added to the soil column and, if the amount is greater than the water holding capacity specified in the first horizon, then the excess water is moved to the next depth. This process is continued down the entire soil column and the process repeated for each successive application of water.

The tipping bucket approach is viewed as a simple method to model soil water movement because it simulates only advective, downward movement of water and does not account for diffusive movement due to soil water gradients, or upward movement of water in response to evaporation or evapotranspiration losses **(**Scanlon et al., 2002**)**. More complex models allow for upward movement of water as affected by evaporation and local gradients in water content between soil layers. LEACHP provides for a choice between a similar tipping bucket approach and a more dynamic method that incorporates the Richard's equation. The Richard's equation simulates dynamic, transient vertical water flow where soil water movement is a product of a hydraulic gradient and a water content-dependent hydraulic conductivity (Hutson, 2003). In contrast to PRZM, water flow in LEACHP can move upward in response to established soil water gradients. The time step for LEACHP is set to 0.1 fractions of a day or less.

As part of an investigation to determine effects of model structure on predicted values, Troiano and Clayton (2007) compared results between PRZM (version 3.12.1, August 2003) and LEACHP models for movement of bromide ions. Bromide ions make ideal tracers for the movement of water in the soil profile because they are dissolved in soil water solution and they are not reactive to soil components (Bowman, 1984). Since the PRZM model version has been upgraded to PRZM5, discussion with one of the USEPA developers of the PRZM approach indicated that the two versions are conceptually the same with respect to estimating water and residue movement through soil (personal communication, Dirk Young, June 29, 2017). Changes were made primarily to remove routines that were not functioning properly (Young and Fry, 2016).

Field data used for the comparison of the two models were generated from a previous study of irrigation effects on movement of atrazine and bromide through soil (Troiano et al., 1993). That study was conducted to measure effects of irrigation method and amount of water applied on the soil movement of atrazine and bromide and it was conducted on the campus of the California State University, Fresno, with the cooperation of irrigation scientists located on the campus. The soil chosen for the study was considered extremely vulnerable to movement of solutes: The sand content was at 85% or greater from the surface down to the 10 foot depth and organic carbon content was very low at 0.7% in the first 6-inch soil segment, dropping to 0.1% at the 12- to 15-inch soil segment and remaining low throughout the rest of the soil profile. Atrazine was applied at a rate of 3.4 lbs/acre and bromide at 70 lbs/acre. Subsequent measure of the distribution of bromide in the soil reflected actual water movement through the soil profile. Data for climatic conditions were available from a nearby weather station. Basin, furrow, macro-sprinkler, and drip irrigation systems were set up to measure potential differences in solute movement through the soil profile between these types of water application. Water was applied at three different amounts to compare the effect of increasing amounts of percolating water in each irrigation method on subsequent movement of the solutes through the soil.

Figures 1A and 1B compare the modeled results for the distribution of bromide in soil for the macro-sprinkler irrigation treatment where water was applied at the medium (middle) rate of water percolation. Soil samples were obtained in 6-inch segments down to the 10-foot depth of soil. The distribution of bromide in the soil column reflects the processes used in each model to estimate actual soil water movement. The figures compare results from each of the models at 21, 28, and 35 days after chemical application to the soil, and then at 49 days when model results are also compared to the measured soil distribution of bromide. Soil distribution of bromide for the PRZM model (open circles in Figures 1A and 1B) illustrates the accelerated downward movement produced by the tipping bucket approach where by day 28 the distribution indicates movement of bromide below the 10-foot depth (Figure 1A). In contrast at day 28 LEACHP results (solid triangles in Figures 1A and 1B) indicated that the bromide mass was maintained above that depth. For the comparison to field data (solid squares in Figure 1B) at day 49, the LEACHP bromide distribution closely matched the measured soil distribution, providing proof that the more complex modeling of water movement and evaporation results in more accurate estimation of soil water movement than the tipping bucket approach used in PRZM. LEACHP maintained a discrete bulge that slowly flattened out over time, whereas PRZM rapidly distributed the mass throughout the soil profile, resulting in accelerated estimation of movement of mass below 10 feet. Use of the tipping bucket approach in PRZM to model soil water movement is one of the reasons the model overestimates the mass moving to ground water aquifers, as discussed in Section 2 below.

2. Comparison of USEPA and DPR Approach to Modeling Well Water Concentration

In both the USEPA and GWPP modeling approaches residues moved below the crop root zone travel through an unsaturated zone of soil named the vadose zone that extends down to the saturated zone of an aquifer (Figures 2 and 3). The residues entering a ground water aquifer then move within the saturated zone until the water is extracted by pumping through a wellhead. Owing to movement through these zones, it usually takes a number of years after pesticide application for residue extraction from the ground water aquifer. The USEPA and GWPP approaches, however, differ in their methods used to estimate travel time through the vadose zone and saturated ground water. The PRZM model was developed for estimating pesticide degradation and soil concentration within the crop root zone. In order to produce estimated concentrations in ground water, the model was expanded to consider potential degradation in the subsurface soil and in saturated ground water. This revision was termed PRZM-GW (Barrett et al., 2015). The processes of degradation in these subsurface areas are not well known so assigning values for dissipation rates in the vadose zone and saturated ground water aquifer is problematic. For the PRZM-GW approach, the hydrolysis rate is the theoretical dissipation rate to be applied in the subsurface areas. Data for hydrolysis half-life values, though, are rare because USEPA guidance for conducting the study indicates that the study should span only 30 days. Many pesticide residues do not exhibit degradation within the 30-day time span so they are determined to be stable. Consequently, many PRZM-GW model runs result in no further degradation of residues once they move past the crop root zone estimated as the 1-meter depth of soil. For example, PRZM-GW predictions for only 12 of 66 pesticide chemicals had a hydrolysis rate that indicated dissipation: The hydrolysis rate of the other 48 chemicals was set at 0 (Barret et al., Appendix B, Table B.2).

Mechanistically, the theoretical structure of the PRZM model was modified to produce ground water estimates within a single run (Barrett et al, 2015). Eight designated soil horizons in the PRZM model normally represent the soil texture down to the 1-meter depth. The 8 horizons were modified to represent the vadose zone and saturated aquifer, where horizons 1 through 6 represented the soil down to the 1-meter depth, horizon 7 represented fate in the vadose zone, and horizon 8 the fate of the residues in the saturated aquifer. Guidance for this approach and values to use in the PRZM model are presented in Table 1 (reprinted from Barret et al., 2015). The accuracy of PRZM-GW estimates of concentrations for pesticide chemicals in ground water was tested by comparing PRZM-estimated values to those measured in the field generated by the USGS national well sampling program titled the National Water-Quality Assessment Program (NAWQA). Data from this well sampling program dates back to 1992. The highest concentration measured for a chemical in this program was compared to the estimated concentration produced from PRZM-GW model runs. A statement in the Summary on page 60 of the report describes the validation study and indicates that 'Using conservative input parameters, PRZM conservatively estimates (>100x) pesticide concentrations for most chemicals.' (Baris et al., 2012).

The concept for the GWPP modeling approach is similar to the USEPA approach where residue movement is partitioned into the same 3 phases: the crop root-zone, vadose zone, and saturated ground water (Figure 3). In contrast to the USEPA approach, DPR staff provided estimates for potential dissipation in the vadose zone and ground water aquifer. A recent presentation at a USEPA Environmental Modeling Public Meeting summarized studies comparing degradation rates between surface and subsurface soil (Washington, 2017). Estimates of half-life degradation rates for the subsurface were longer than those measured in surface soil, but they were fast enough to indicate that degradation rates in the subsurface should be included when modeling movement. For the GWPP approach, estimated residence times within the vadose zone and ground water aquifer were determined from an age-dating study of ground water sampled from domestic drinking water wells (Spurlock et al., 2000). The domestic wells were located in areas where ground water was known to be contaminated with pesticide residues in Fresno and Tulare Counties in California and where soils were coarse-textured. These areas matched the scenario that is used in the LEACHP model to estimate soil movement of chemical residues through the first 10 feet of soil. Well water concentrations are estimated as follows:

1. The mass of residue that is moved below the 10-foot (3-meter) soil depth is dissolved in 0.5 meters of water which is the estimated amount of annual ground water recharge. Multiple years are run for an annual application scenario and the mass is determined when a steady state is observed for mass moving past the 10-foot depth.
2. The residues are aged for a total of 10 years representing the total residence time in the vadose zone and ground water aquifer prior to extraction from a well.
3. The longest half-life reported from terrestrial field dissipation studies is used as the aging factor.

A further addition to the GWPP's approach is the use of Monte Carlo simulation to produce a distribution for estimated concentrations of residues in well water. The two most variable physical/chemistry parameters input into modeling are measures of sorption of residues to soil and half-life values determined from terrestrial dissipation studies. These data are required to be reported to USEPA prior to registration of a pesticide product. Other inputs into the model are

water solubility, Henry's constant, and vapor pressure, but these values have very little variation when reported. In order to provide a measure of the effect of variability in soil sorption and terrestrial field dissipation half-life values, the GWPP approach is run 1,000 times with 1,000 different combinations of these two parameters. The pairs are formed from the range of reported values for soil sorption and terrestrial field dissipation. The result is a distribution of estimated concentrations and not just a single predicted value. Data from well sampling of pesticide residues (atrazine, simazine, diuron, bromacil, and norflurazon) known to contaminate ground water were used to validate the approach. Figure 4 compares the distribution of concentrations measured in domestic drinking well waters for known ground water contaminants and the distribution predicted from the GWPP's modelling approach (Troiano and Clayton, 2009). The agreement was good where the estimated well concentration at the median and 75th percentile values were essentially the same. There were a few high values measured in wells, which skewed the distribution for data from well samples where the maximum value was at 2.2 ug/L compared to the modeled distribution maximum at 1.0 ug/L. If a conservative approach to modeling is required then an uncertainty factor of 10 could be applied to the maximum modeled concentration, which would then include the highest observed value in the well sampling data set.

In summary, the DPR approach to estimate concentrations of pesticide residues in well water results in a much closer approximation to measured environmental samples than the USEPA method. The USEPA acknowledges that their approach generally produces estimates that are at least 100 times greater than concentrations actually measured in drinking water well samples. The differences in the approaches are due to:

- Soil water routines used in the PRZM model overestimate water and residue movement through the soil profile, whereas the LEACHP model accurately estimates water and residue movement that is especially important for modeling fate of pesticide residues in irrigated agriculture.

- The USEPA approach generally assumes no degradation of residues once they are moved below the crop root zone, whereas the DPR approach incorporates data from studies of travel time to wells and where residues are dissipated based on the longest reported terrestrial field dissipation value.

- The GWPP approach has been validated with monitoring data collected in California in areas where leaching through coarse sandy soils is the known pathway to ground water.

- The GWPP approach uses dissipation half-lives determined from terrestrial field dissipation studies to provide degradation values, whereas the USEPA approach uses laboratory-derived aerobic half-life values in their model. Laboratory-derived aerobic half-life values do not represent all potential pathways of degradation that residues are exposed to in agricultural applications. The GWPP approach uses half-life values derived from terrestrial field dissipation studies because they integrate all processes of degradation that a pesticide residue is exposed to after application.

For these reasons, the GWPP's approach should be used for estimating concentrations of pesticide residue in wells that result from use of pesticide products under climatic and

agricultural conditions in California.

3. Use of Tiered Decision-Making Approach in relation to DPRs Well Sampling Data

As indicated in USEPA's Guidelines for Exposure Assessment (USEPA, 1992), data for concentrations in environmental media of interest is preferred for use in projecting potential health effects. In the absence of actual measurements conducted on environmental media, predicted concentrations from modeling approaches are substituted. Therefore, the first question to pose is whether or not information is available regarding measured concentrations of a targeted pesticide residue in environmental samples. In the absence of monitoring data, modeling data would be the only available information on which to base an assessment. Modeling data also could be used as additional evidence to provide expected concentrations if the monitoring data do not represent the desired range in scenarios.

In the tiered decision-making approach, GWPP staff recommends first using actual field data of concentrations of pesticide residues in drinking water wells in health risk assessments. In general, studies conducted by DPR's GWPP yield high quality field data. For example, targeted well monitoring studies conducted by EM staff should represent expected environmental concentrations encountered in California. Highest concentrations of pesticide residues in drinking water wells would be expected in areas of highest use that also occurs in areas where ground water is vulnerable. During development of a monitoring study for targeted pesticide residues, data from the Pesticide Use Report database are analyzed to identify geographic areas of highest use. The monitoring studies target sampling of wells identified as domestic drinking water wells, which are wells typically used by single families located in rural areas of the state. Wells are expensive to drill so these wells are typically situated in shallow ground water aquifers throughout the state. These shallow aquifers are the first ground water encountered by pesticide residues as they move through the soil profile. Consequently, the location of domestic wells in rural agricultural areas and their location in shallow ground water aquifers confer a high degree of susceptibility with respect to measuring the presence of pesticide residues in their water. In addition, EM staff has identified areas of the state that are vulnerable to contamination of pesticides based on soil condition and depth to ground water data bases (Troiano et al., 1999; Troiano et al., 2000). This data is then overlain upon the pesticide use data, identifying the most likely areas of the state where residues of that specific pesticide chemical would be found in a well monitoring study. The sampling of the vulnerable domestic drinking water wells then provides a high degree of confidence that residues will be detected in the ground water aquifer, if they had actually migrated from sites of application.

In many cases, new active ingredients lack well monitoring data, so EM staff use the modeling approach to estimate potential concentrations in well water upon use in California. Some estimates have resulted in concern that a pesticide chemical could contaminate ground water so registrants have been requested to conduct additional terrestrial field dissipation studies within California.

4. Propyzamide: Comparison of Predicted Well Water Values to Well Monitoring Data

Propyzamide was first registered for use with the USEPA in 1972 (USEPA, 1994). In California, the first registration is indicated as Kerb in 1987, but use may have been established in California before that date. The label has a wide range of crop uses including alfalfa, apple, artichoke, cherry, clover, endive, grapes, legumes, lettuce, nectarine, ornamental conifers ornamental herbaceous plants, ornamental turf, peach , pear, plum small fruits, trefoil and uncultivated agricultural or non-agricultural areas (Available at: http://apps.cdpr.ca.gov/cgi-bin/label/labrep.pl).

Results from the GWPP's targeted well monitoring studies in combination with estimated ground water concentrations using the GWPP's modeling approach for propyzamide indicate that USEPA's approach greatly overestimates ground water concentrations, and, subsequently, does not represent actual fate under California climatic and use conditions. The PRZM-GW approach was used in a recent USEPA review of proposed expansion of propyzamide use on leaf lettuce. An estimated ground water concentration of 21 ug/L was cited as the result of application patterns to artichokes (USEPA 2015). The model reflected potential use in the Wisconsin sands scenario.

EM staff has conducted targeted sampling for propyzamide in areas of high use in California with two studies conducted in 1995 and in 2011 (DPR, 1996; DPR in press). In total, DPR sampled 162 wells with no detection of propyzamide at a reporting limit of 0.05 ug/L. The wells sampled were primarily single family domestic wells located in areas of highest propyzamide use. Additional well monitoring data was available from USGS studies conducted for the California State Water Resources Control Board. Again, there were no detections reported for 1,893 wells sampled at a reporting limit of 0.004 ug/L. For comparison, the GWPP ground water modeling approach for a worst-case scenario estimated a concentration at 0.00273 ug/L. This value was obtained using the longest reported terrestrial field dissipation half-life at 53.7 days and the lowest Koc value (soil sorption) of 556 cm^3/g (Clayton, 2017). This value is substantially below DPR's reporting limit of 0.05 ug/L, confirming that propyzamide has a low potential to move to ground water. Also note that this value is 4 orders of magnitude lower than the estimated concentration from the USEPA approach.

Since the USEPA approach is meant to reflect nationwide use of a pesticide it might be possible that propyzamide would be detected from use in other states. Data from the aforementioned NAWQA program had been downloaded in February, 2015, for use in a project to determine chemical properties of residues detected in ground water. Data for propyzamide from that data set were investigated where sampling occurred from 1992 to 2012. During review of the well sampling data, it became apparent that additional quality control data were required to determine veracity of results. EM staff made an additional request to USGS staff from which QA/QC laboratory blank data was also obtained. Results from the laboratory blank samples are especially interesting because a blank accompanies each injection of a well sample for subsequent chemical analysis. The chemical analyses were conducted at the USGS National Water Quality Laboratory located in Denver, CO. Table 2 summarizes a comparison of results reported for environmental well samples and for laboratory blank samples. Although there were 6 reported detections out of 11,950 well water samples, there were also 4 detections reported in the laboratory blank samples. Furthermore, 3 of the 4 values measured in the laboratory blank samples were higher than the 6 values reported in well samples. Non-parametric statistical tests

indicated that the distributions between well water and laboratory blank samples were similar, providing evidence that the data reported for the well water samples most likely reflected variance derived in the laboratory and did not reflect presence in well water. One other detection has been reported in South Carolina of propyzamide in well water at 1.3 ug/L where the source was from a different USGS sampling program with the acronym NWIS. GWPP staff contacted the author of the reported detection and the detection was determined to be a transcription error that was supposed to be an entry for an alkalinity value (Personal Communication with Celeste Journey, USGS, June 17, 2017). It should be noted that the USEPA assessment for propyzamide indicated that there was a reported value from the NAWQA program at 0.82 ug/L measured in Benton County, Arkansas, in April, 1994. No detection of propyzamide was noted in the NAWQA data set that was downloaded in February, 2015, in Benton County (7 total records) nor was any detection noted in any other sampling conducted in Arkansas (58 total records in Arkansas). The record, though, is recoverable from the new site where NAWQA data is available at the National Water Quality Monitoring Council site at: https://www.waterqualitydata.us/portal/. Follow-up discussion with staff from Arkansas indicated that for this sample the original bottle broke, so the value was determined from a back-up sample and that it should be viewed as acceptable (Personal Communication with James Kingsbury, USGS, July 19, 2017). This appears to be the only valid reported detection of propyzamide, nationwide.

The results from the nationwide well sampling data, where only 1 potential detection had been reported, provide additional evidence that the estimates of well water concentrations produced by the USEPA PRZM-GW are not substantiated and that this modeling approach greatly overestimates the potential for propyzamide to move to ground water.

5. RECOMMENDATIONS

GWPP staff in the EM branch has been conducting well monitoring studies to determine the presence of pesticide residues in well water since the 1980s. The data have been documented in publications and stored in the WIDB maintained by the EM Branch. By law, other California agencies conducting sampling must report their results for pesticide-related chemicals to DPR, whereupon GWPP staff review analytical chemistry data, conduct follow-up well water sampling if warranted, and the data is then added to the WIDB. Since data in the WIDB may be from various agencies, GWPP staff recommends the following process to ensure the best available data are used in health risk assessments.

- For pesticides with registered agricultural uses:
    1. Determine if well monitoring data for the targeted pesticide are available in the following order of preference:
        1.1. Potential detection in California as measured in well monitoring studies conducted by the GWPP staff: Assures that areas of highest use and vulnerability were sampled.
        1.2. Potential detection in California obtained from studies submitted by other agencies: GWPP staff would compare location of sampled wells to pesticide use patterns and location of geographical known vulnerable areas

to verify potential for movement to and detection in ground water.

1.3. Potential detection reported from studies conducted in other states: Data for quality assurance and quality control for the chemical analyses would be required to determine the validity of detections.

2. If well monitoring data do not exist, request GWPP staff to conduct a modeling exercise to determine estimated concentrations in ground water based on submitted physical/chemical data for the targeted pesticide chemical. For risk assessment purposes, a 10-fold uncertainty factor could be applied to the maximum predicted value to provide a conservative estimate.

3. If modeled results appear equivocal then a request could be made to the EM GWPP to conduct a targeted well monitoring study.

- For pesticides with no registered agricultural use:
    1. Determine if well monitoring data for the targeted pesticide are available for studies conducted in other states.

    2. And/or if there are no monitoring data, request EM GWPP staff to conduct a modeling exercise to determine estimated concentrations in ground water based on submitted physical/chemical data for the targeted pesticide chemical. For risk assessment purposes, a 10-fold uncertainty factor could be applied to the maximum predicted value to provide a conservative estimate.

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Table 1. Degradation Reduction Factors and Discretizations for Layers and Nodes in PRZM Standard Groundwater Scenarios. Reprinted from Appendix I, USEPA, 2012.

Layer	Multiplication Factor for Aerobic Degradation Rate	Depth (cm)	Δ x	Nodes
1	1.0	0 to 10	1	1 to 10
2	0.94	10 to 20	5	11 to 12
3	0.78	20 to 40	2	13
4	0.55	40 to 60	2	14
5	0.33	60 to 80	2	15
6	0.11	80 to 100	2	16
7	0	100 to 900	5	17 to x
8	0	900 to 1000	5	x+1 to x+2

Table 2. Propyzamide: Comparison of NAWQA well sampling data to field and laboratory blank data with respect to the number of samples taken, the number of detections, and the range in measured values.

Propyzamide (82676)				
	Well Samples		QA/QC Blank Samples	
Statistic	All	Depth > 50 Feet	Field	Laboratory
Dectected/Total (#)	6	5	1	4
Total Samples (#)	11950	6855	919	9195
Freq (%)	0.05	0.07	0.11	0.04
Values for Reported Detections				
	0.013	0.013	0.004	0.103
	0.0077	0.0077		0.042
	0.0062	0.0062		0.0305
	0.0056	0.0198		0.0016
	0.00198	0.00122		
	0.00122			

Figure 1A. Comparison of the modeled movement of bromide ion between LEACHM and PRZM models for 21 and 28 days after application to bare soil and with irrigation simulated for macrosprinklers at a the medium percolation rate of water application. Solid black triangles are data generated from the LECHM model and open green circles are data generated from the PRZM model. Depth refers to the distance below the surface.

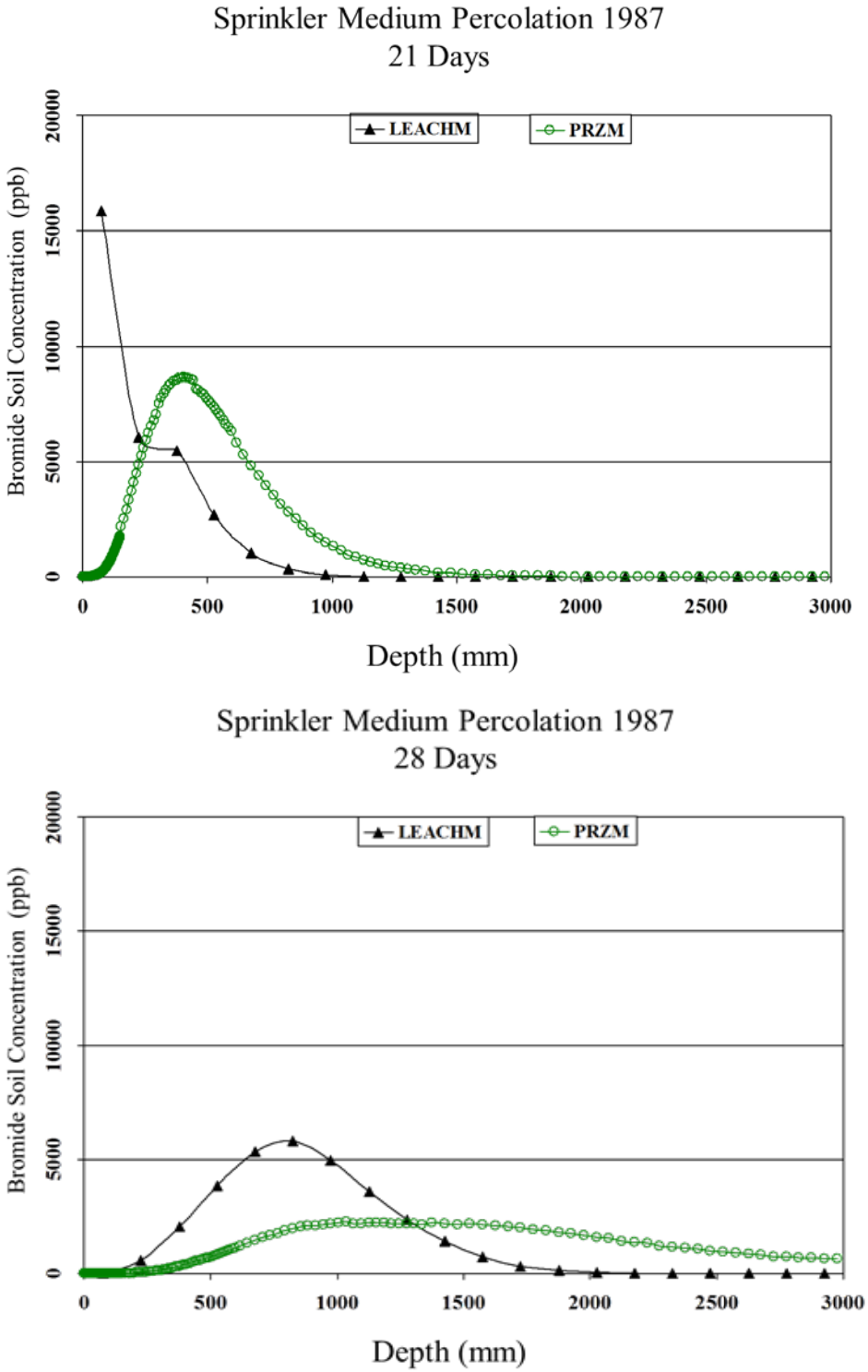

Figure 1B. Comparison of the modeled movement of bromide ion between LEACHM and PRZM models for 35 and 49 days after application to bare soil and with irrigation simulated for macrosprinklers at a the medium percolation rate of water application. The graph at 49 days compares the modeled distributions to concentrations measured in soil cores. Solid black triangles are data generated from the LECHM model, open green circles are data generated from the PRZM model, and blue squares for day 49 is concentrations measured in soil cores. Depth refers to the distance below the surface.

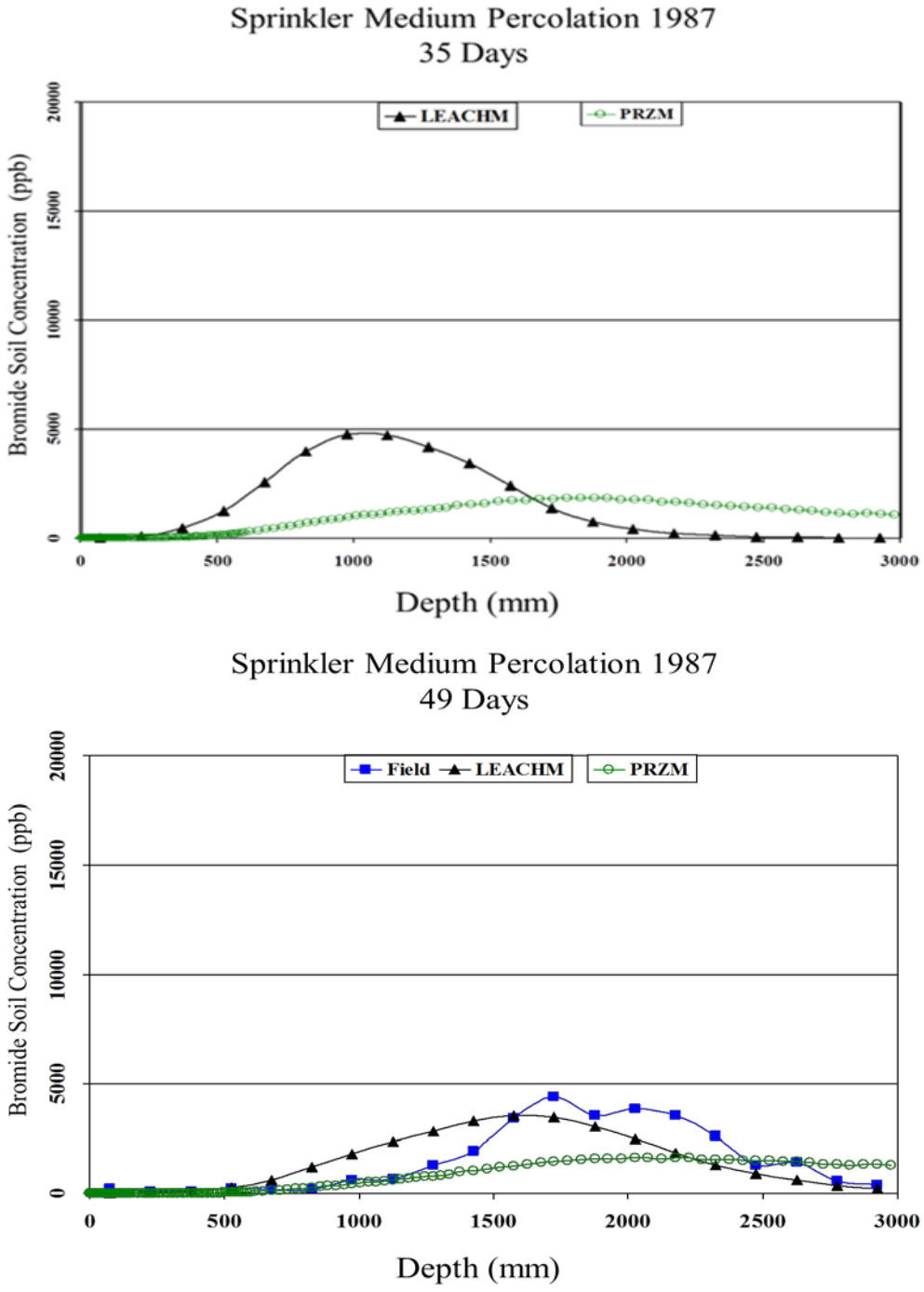

Figure 2. USEPA conceptual model for estimating concentrations of pesticide chemicals in ground water. Graphic reprinted from Barret et al., 2015.

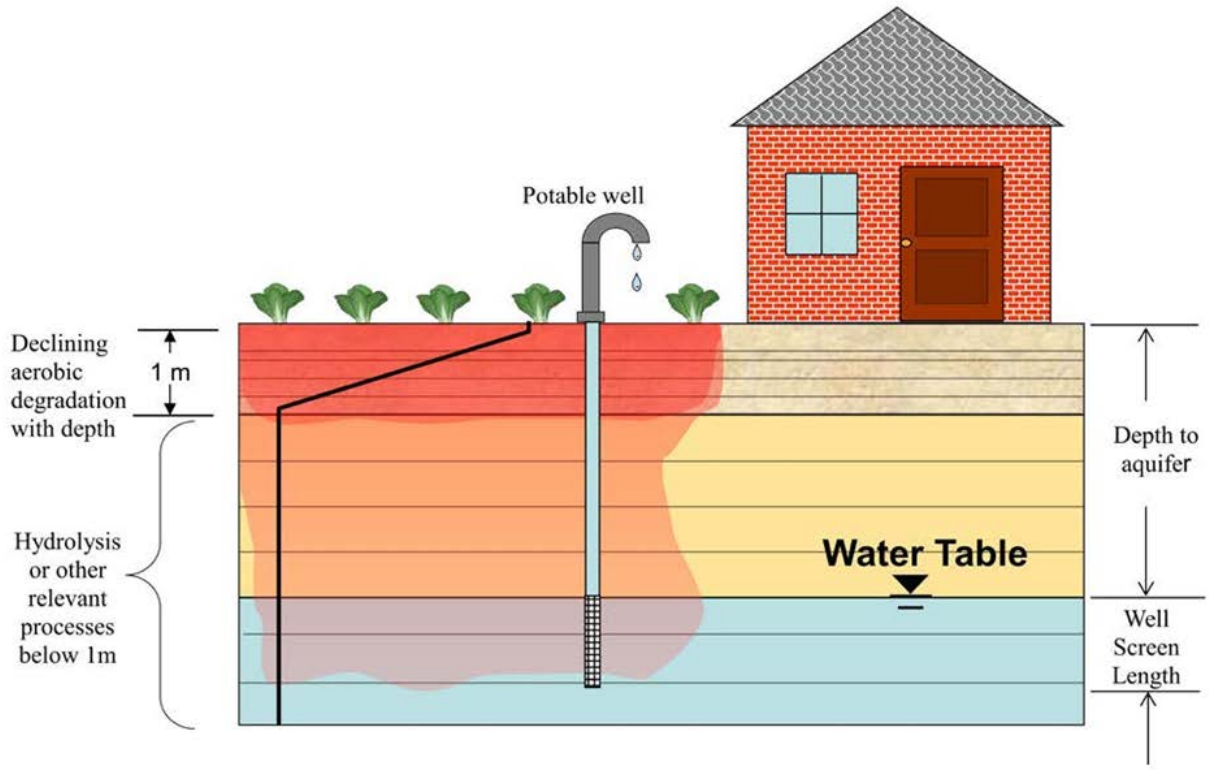

Figure 3. Conceptual model used by DPR to estimate concentration of pesticide residues in drinking water wells. Reprinted from Troiano and Clayton, 2009.

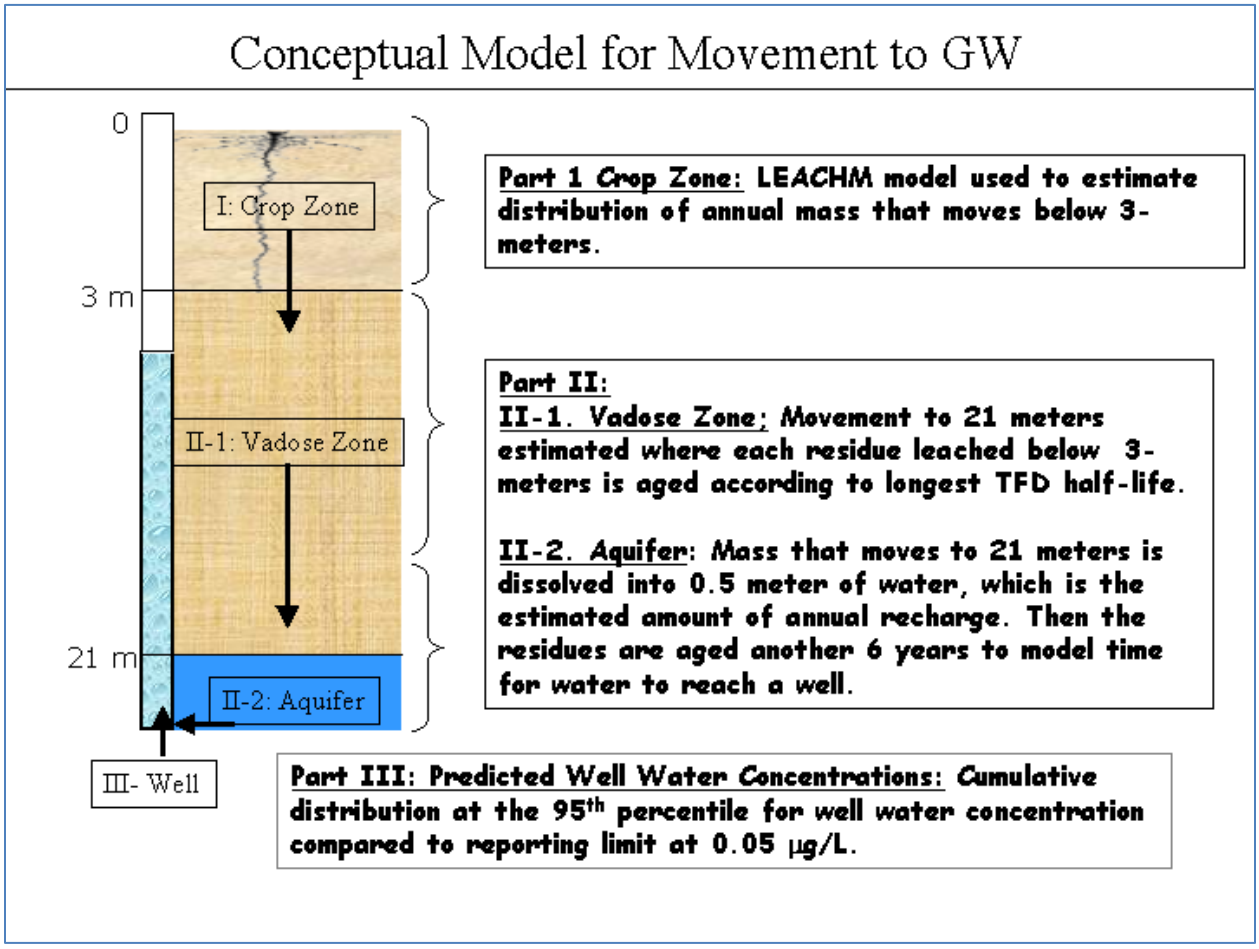

Figure 4. Comparison of distribution of well water concentrations for A. Observed Data from wells sampled in leaching GWPAs in Fresno County and B. Predicted data from modeling procedure at 160% irrigation efficiency. Reprinted from Troiano and Clayton, 2014.