Department of Pesticide Regulation

Mary-Ann Warmerdam
Director

Arnold Schwarzenegger
Governor

M E M O R A N D U M

TO: John Sanders, Ph.D.
Branch Chief
Environmental Monitoring Branch

FROM: John Troiano
Research Scientist III
Environmental Monitoring Branch
916-324-4115

Murray Clayton
Staff Environmental Scientist
Environmental Monitoring Branch
916-324-4095

DATE: May 7, 2009

SUBJECT: Modification of the probabilistic modeling approach to predict well water concentrations used for assessing the risk of ground water contamination by pesticides.

Background

When a pesticide is submitted to the Department of Pesticide Regulation (DPR) for registration, the Registration Branch can request the Environmental Monitoring Branch (EM) to evaluate the potential of the active ingredient(s) in that pesticide to contaminate ground water. Such evaluations are typically conducted based on concerns about the physical-chemical properties of active ingredients not contained in currently registered pesticides ("new active ingredients") or new use patterns of active ingredients contained in currently registered pesticides ("old active ingredients").

Registration evaluation by EM staff of a chemical's potential to move to ground water was originally based on a procedure prescribed in the Pesticide Contamination Prevention Act (PCPA) of 1985. The PCPA required DPR to establish threshold values for six physical-chemical properties that characterize environmental fate: water solubility, organic carbon normalized soil adsorption coefficient (Koc), hydrolysis half-life, aerobic and anaerobic soil metabolism half-lives, and field dissipation half-life. The threshold values were identified as specific numerical values (SNVs) and they are used to determine whether or not a pesticide active ingredient has the potential to pollute ground water and thus be placed on the Groundwater Protection List in section 6800(b) of Title 3 of the California Code of Regulations. The PCPA requires DPR to monitor ground water for pesticides on this list to determine if they have migrated to ground water. The methodology derived by Wilkerson and Kim (1986) to establish SNVs was based on comparing distributions of environmental fate variables between two groups of pesticides: those that were sampled and found in ground water due to agricultural use and classified as contaminants, and those that were

sampled and not found in ground water and classified as non-contaminants. The SNVs were revised by Johnson in 1988, 1989, and 1991 (Johnson, 1988, 1989, and 1991).

Two potential limitations with the SNV process are:

1. It is a univariate-based approach because the tests were derived separately for each environmental variable, ignoring potential relationships between variables.
2. Information on variability of environmental fate characteristics for individual active ingredients is not included. When multiple data existed for each variable, the mean was obtained and used to represent the environmental fate of each pesticide. Since the profile for each pesticide was set in a deterministic manner, information on the variance for each variable was not included.

A modeling process was developed to address these limitations (Troiano and Clayton, 2004). The first limitation was addressed by using a modeling approach where multiple physical/chemical properties of the pesticide are simultaneously evaluated. Owing to previous calibration studies, the LEACHM model was used to simulate potential movement through soil (Hutson and Wagenet, 1992; Spurlock, 2000). Although modeling provides a method to determine the joint effects of environmental fate variables, the prevalent modeling methodology was to use a deterministic approach where, similar to the SNV process, a single set of input variables was used to represent the environmental fate of an active ingredient.

Subsequently, the second limitation was addressed by using a probabilistic approach to predicting residue movement through soil. Advances in computer technology have allowed development of computationally intensive probabilistic modeling techniques where a distribution of outcomes is estimated. A distribution of the modeling output is generated from repetitious model simulations, each representing a different combination of input values. The potential combinations and number of computer simulations can be extremely large when the input variables themselves are described by distributions. In this case, sets of input values for each parameter are derived through random sampling of input distributions. The outcomes from the repetitive model simulations provide a distribution that, when expressed as a cumulative function, can be used to provide a range in expectations of the outcome or, when described by a mean and variance, can be used in a statistical test. Troiano and Clayton's (2004) initial determination of potential leaching was formulated as a comparison of the distribution of the amount leached below 3-meters between the known ground water contaminants and the active ingredient under review.

This memo updates the approach of Troiano and Clayton (2004) to provide a more robust measure of potential leaching. One potential problem with the test specified by Troiano and Clayton is that a new active ingredient may be applied at a lower rate than the known active ingredients. Based on amount applied, the resulting distribution would indicate less total mass leached below the 3-meter depth and a lower potential to move to ground water. If the new

active ingredient's dissipation half-live is longer than any of the known ground water contaminants, then the conclusion of lower contamination potential would be offset by consideration of the time it takes residues to move from below 3-meters to well water: longer dissipation rate for the active ingredient under review would mean greater conservation of mass during the travel time for recharge water and residues to move below the 3-meter depth to a well. An active ingredient with a lower application rate but with a longer dissipation half-life could result in well water concentrations that would be equal to or higher than those projected for the known ground water contaminants. The approach has been modified to include a module for the travel time of water and residues to move from below the 3-meter depth to ground water and then eventually to a well (Figure1). This addition incorporates the effect of relative differences in dissipation values as reflected in Terrestrial Field Dissipation (TFD) studies. Also, the determination of potential for contamination is now based on an empirical analysis of the distribution of predicted well water concentrations.

Basis for Determination of Leaching Potential Using Probabilistic Based Modeling

Studies conducted by EM have enabled development of a probabilistic modeling approach to determine the leaching potential of pesticides. The LEACHP model, a module of the Leaching Estimation and Chemistry Model (Hutson and Wagenet, 1992) had been used by EM in a probabilistic Monte Carlo study that investigated the effects of irrigation management on leaching of known California groundwater contaminants: atrazine, bromacil, diuron, hexazinone, norflurazon, and simazine (Spurlock, 2000). The study objective was to produce a distribution of ground water contaminant concentrations for different irrigation management strategies. Soil data for the modeling scenario were obtained from a field study that determined the effect of method and amount of irrigation water application on atrazine movement in a coarse, loamy-sand soil in Fresno County (Troiano et al., 1993). This site was vulnerable to leaching of pesticides because the soil was coarse-textured, freely draining, and low in organic carbon content. The irrigation study of Troiano et al. (1993) measured water and pesticide movement at different amounts of water applications. These data were used as the calibration data set in the Spurlock (2000) study.

For the Monte Carlo study, Spurlock (2000) compiled TFD half-life and organic carbon normalized soil adsorption coefficient (Koc) values for six ground water contaminants (Table 1). The combined data consisted of 52 TFD half-life and 56 Koc values, resulting in approximately 3000 uniquely paired values for testing into the model. Since the study involved comparing a number of different irrigation scenarios, computing time was minimized by a smaller subset of paired samples that provided similar results to using all potential paired values. One conclusion was that reduction in the amount of water that percolates during the growing season is effective in restricting pesticide movement. Consequently, efficient management of irrigation was identified as a method to reduce concentrations in ground water to levels below the current DPR reporting limit of 0.05 μg/L (0.05 ppb). Reducing the amount of water that percolates from irrigation requires increased management because crop water

demand or soil water depletion must be monitored, and these results related to the frequency and volume of irrigations.

Procedure for a Probabilistic Approach to Determining Leaching Potential of Pesticides

This revision builds upon the method described by Troiano and Clayton (2004) to predict the leaching potential for products with new active ingredients or new proposed products for already registered active ingredients. The revised approach is parsed into three parts (Figure 1). In the first part, the distribution of the annual amount of pesticide leached below 3-meters is developed from random sampling of Koc and TFD input distributions. The second part accounts for aging of residues as they move with percolating water to the ground water aquifer and eventually to a well. Lastly, in the third part, the cumulative distribution of the predicted well concentrations at the 95th percentile is compared to the current reporting limit of 0.05 µg/L for detection of pesticides and their breakdown products in California's well water.

Part 1- Development of distribution for amount leached below 3-meters: In order to encompass the variability in reported TFD and Koc values, the LEACHM model is run 1000 times with randomly selected paired Koc and TFD values. The input data for the known ground water contaminants are the same 56 Koc values and 52 TFD half-life values that were collated by Spurlock (2000). One thousand paired values are generated from random sampling from a gamma distribution fit to each variable.

In contrast to the grouping of the known ground water contaminants used by Spurlock (2000), data for individual pesticides are sparse and in most cases insufficient in number to test for a specific distribution. When data are sparse, Dubus et al. (2002) recommended use of an empirical triangular distribution. The triangular distribution is characterized by the minimum, maximum, and modal values. When a mode cannot be determined then the median value is used as a substitute. For example, if the bare minimum of 3-dissipation values are available for a TFD study with 50-, 75-, 150-day half-lives, then 50 is the minimum, 150 is the maximum and 75 is the median value. As for the known ground water contaminants, one thousand paired random samples of Koc and TFD values are based on sampling from a triangular distribution fit to each variable. In the SAS statistical package, the following syntax in Eq. 1 produces a random sample from a triangular distribution:

Eq. 1 TFD=(Maximum-Minimum)*rantri(seed,(Median-Minimum)/(Maximum-Minimum))+Minimum

For the 3 TFD half-life values given above and for 3 Koc values at 300, 600, and 750 cm^3/g, the following syntax produces 1000 random pairs of TFD and Koc values and outputs the values to an external data set using the SAS statistical package:

```
data a;
do i=1 to 1000;
```

```
 TFD=(150-50)*rantri(0,(75-50)/(150-50))+50;
 Koc=(750-300)*rantri(0,(600-300)/(750-300))+300;
 output;
end;
proc print;
data _null_;set a;
filename it 'd:\Jtroiano\chemicals\reptfdkocrand.dat';
file it noprint;
put TFD Koc;
run;quit;
```

In the example, the do loop results in 1000 pairs of Koc and TFD values and the language starting at 'data _null_;set a;' identifies an output path and file name to which the paired data are stored.

The scenario used for the LEACHP simulations is for a grape crop with water applications at 160% or 125% of crop need. An inefficient irrigation management practice is represented by the addition of water at 160% of crop water requirements. An efficient irrigation management practice is represented by addition of water at 125% of crop need. The active ingredient-specific variables of application rate, vapor pressure, and water solubility are fixed for each simulation. An example of an input file for each irrigation management practice is given in Appendix I. The LEACHM model simulation for each paired TFD and Koc value is run for a 5-year period with the maximum rate of application applied each year. Running the model for multiple years results in a constant annual flux of amount of test substance leached below 3-meters.

Part 2 – Estimation of Well Water Concentration: In the second part, residues are aged according to an estimate for the amount of time it takes for water to migrate from the 3-meter depth to wells. For water applications at 160% of plant demand, the estimated time interval is 10 years. The 10 years was developed as the summation of the number of years for water to recharge an aquifer located 21.3-meters below the soil surface, indicated as II-1 in Figure 1, and the time for subsequent movement to a well, indicated as II-2 in Figure 1. These estimates are 4 and 6 years, respectively, and are based on LEACHP simulations of a conservative tracer for the movement of water, and on results from a chlorofluorocarbon dating study for the age of ground water in domestic wells located in the lower Jan Joaquin Valley (Spurlock et al., 2000). The amount of water that annually recharges ground water is approximately 0.5 meters in depth (Spurlock, 2000). Following the conceptual model, estimated pesticide concentration in well water is determined in a two step process where the first step is the dissolution of the amount of chemical leached annually that is obtained from the 5^{th} simulated-year of modeling into the amount of water that annually recharges ground water. In the second step, residue mass is decreased due to dissipation processes according to the appropriate aging parameters.

Dissipation half-lives are known to be longer in the vadose zone because there is a lack of

microorganisms and nutrients to support robust degradation, and lower temperatures also slow down chemical processes such as hydrolysis. Since direct measurements of breakdown rates of pesticide active ingredients in the vadose zone soil are lacking, the longest reported TFD half-life value is used to age the residues. For the known ground water contaminants, the longest half-life was approximately 365 days (Table 1).
Estimated travel times to a well are 10 and 13 years for the 160 and 125% irrigation water management treatments, respectively. The concentration of residue in well water from each LEACHP simulation is determined according to Eq. 2.

Eq 2. $$Well\ water\ concentration\ (\mu g / L) = \frac{M_L * 0.5^N}{D}$$

where:

M_L = annual mass of product leached below root zone as determined by LEACHP (mg/m^2);
N = number of product dissipation half-lives during transport in the vadose zone and during aging and in the aquifer until arrival at a well;
D = depth of annual ground water recharge (0.5 m).

The value for N will be the number of half-lives for a product simulated under either the inefficient irrigation regime where total transport time is 10 years or under the efficient irrigation regime where the total transport time is 13 years. In either instance, the total transport time, which is given in days, is divided by the product's longest TFD half-life value, which is also given in days, to yield the number of half-lives predicted during transport from the 3-meter soil depth to a well. For the known ground water contaminants, the longest reported TFD value provided an estimate of 365 days. Each of the residues produced in Part 1 are separately aged based on the 365-day value. For 160% and 125% irrigation water management treatments, this results in each of the 1000 simulations conducted in Part 1 aged for 10 and 13 half-lives, respectively.

Part 3 – Comparison of Cumulative Well Water Concentrations: The result from Part 2 is 1000 estimates for residue concentration in well water. In Part 3, the cumulative frequency distribution of these values is determined. Procedures in SAS, such as Proc Univariate, produce simple statistics for variables: cumulative distribution is one statistic produced. For a new active ingredient or for a new proposed use of an already registered active ingredient, the inefficient irrigation scenario is first simulated. If the value at the 95th percentile is below DPR's current reporting limit of 0.05 µg/L, then potential for contamination is determined as low and no further modeling is required. If the 95th percentile value exceeds the reporting limit, the pesticide is determined to have a high potential to contaminate ground water. The modeling is conducted again at the efficient irrigation management practice at 125% of crop

need to determine if application of the mitigation measure decreases the threat for ground water contamination at the 95th percentile to below 0.05 μg/L.

Calibration of the Approach

The approach was calibrated by comparing the distribution of predicted well concentrations of the known ground water contaminants to the distribution of actual well water concentrations that have been measured in domestic wells sampled in Fresno County (Figure2). The predicted concentrations were from the 160% inefficient irrigation management practice. The observed data were obtained from the Well Inventory Data Base where wells were sampled in leaching ground water protection areas (GWPAs) in Fresno County (Nordmark et al., 2008). A GWPA is a section of land designated as vulnerable to contamination. GWPAs designated as leaching are predominantly coarse-textured soils with depth to ground water at approximately 21.3-meters or less. The location of this subset of wells has the highest degree of similarity to modeled soil conditions and recharge processes. For wells with multiple concentrations, the maximum concentration in a well was obtained for atrazine, bromacil, diuron, norflurazon, or simazine: hexazinone was not detected in these wells.

There were 178 maximum concentration values that were derived from 111 sampled wells. The number of maximum concentrations is greater than the number of wells because multiple pesticide active ingredients were measured in well water. Agreement was good for the distribution of well water concentrations between observed and predicted values (Figure 2). Well water concentration at the 50th percentile (median) for observed data was 0.21 μg/L compared to 0.18 μg/L for the predicted distribution. Agreement was very good at the 75th percentile where the observed value was 0.32 μg/L for observed data compared to 0.30 μg/L for the predicted distribution. At the 95th percentile the observed value was 0.83 μg/L compared to 0.47 μg/L for the predicted distribution, indicating a tendency for the model approach to under predict the higher concentrations. The predicted value for the modeled data at the 95th percentile was an order of magnitude higher than the 0.05 μg/L reporting limit, capturing the high potential for this group of pesticides to move to ground water.

Summary

The probabilistic approach described by Troiano and Clayton (2004) was based on providing a distribution of the amount of pesticide leached below the 3-meter-deep root zone of a simulated crop. This revision extends the prediction to well water concentrations by including an estimate of the dissolution and eventual degradation of residues in ground water that eventually recharges a well. This extension was added to account for active ingredients that may have longer soil half-lives but that have lower application rates than the known ground water contaminants. The distribution leached below 3-meters for a pesticide product with a low application rate could

indicate a low risk to contaminate groundwater when compared to the distribution for known ground water contaminants. But once leached below the root zone, greater stability in the vadose zone or in ground water due to longer half-life could result in well water concentrations that are equivalent to the known contaminants.

The revised procedure is split into three parts:
Part 1 – As indicated in the previous memo by Troiano and Clayton (2004), the LEACHM model is run multiple times at randomly paired TFD and Koc values to produce a distribution of the annual amount of pesticide leached below the 3-meter depth. For sparse TFD half-life and Koc data, random sampling for model input values is conducted from a fit of a triangular distribution to the available data. The output distribution is determined from 1,000 model simulations.

Part 2 – The amount of pesticide leached below 3-meters is diluted into the amount of water that annually recharges ground water, which is approximately 0.5 m in depth. This initial concentration is aged by applying an estimate of the number of half-lives the residue would be exposed to during recharge to a well. The total recharge time is 10 years for the 160% irrigation water management treatment and 13 years for the 125% irrigation water management treatment. The longest TFD half-life value is used as an estimate for the degradation rate below the 3-meter depth. For example, at the 160% irrigation treatment, a TFD half-life value of 365 days means that each of the 1000 estimates of residue concentration from LEACHM is aged for 10 years thereby experiencing a total dissipation of 10 half-lives before arriving at a well. At a TFD half-life value of 700 days, residues aged for 10 years would be subjected to only 5.2 half-lives.

Part 3 - The cumulative distribution for the predicted 1000 well water concentrations is constructed. If the value at the 95^{th} percentile is greater than or equal to 0.05 μg/L, then the active ingredient is determined to have a high potential to contaminate ground water; otherwise, it is determined to have a low potential to be detected in ground water.

There are some situations that might require a different approach. For example, the modeling approach does not include anaerobic conditions, so special cropping scenarios such as rice culture will not be adequately modeled. Evaluations for products that are not yet adequately modeled should continue using the SNV procedure to compare physical-chemical properties and they should rely upon field-derived measures of offsite-movement.

References

Dubus, I.G., C.D. Brown, S. Beulke, and N.L. Turner. 2002. Uncertainty and Probabilistic Approaches to Pesticide Fate Modelling. Cranfield Centre for EcoChemistry research report for DEFRA PL0548, Cranfield University, Silsoe, UK, 138 pp.

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, NY.

Johnson, B. 1988. Setting revised specific numerical values. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA. Report EH 88-12. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh8811.pdf (vaerified 02 Mar 2009).

Johnson, B. 1989. Setting revised specific numerical values. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA. Report EH 89-13. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh8913.pdf (verified 02 Mar 2009).

Johnson. B. 1991. Setting Revised Specific Numerical Values. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA. Report EH 91-06. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh9106.pdf (verified Mar 17 2009).

Nordmark, C., J. Dias, M. Clayton, J. Troiano, and M. Pepple. 2008 Update of the Well Inventory Database. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA. Report EH 08-01. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh0801.pdf (verified 02 Mar 2009).

Spurlock, F. 2000. Effect of irrigation scheduling on movement of pesticides to ground water in coarse soils: Monte Carlo analysis and simulation modeling. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA. Report EH 00-01. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh0001.pdf (verified 02 Mar 2009).

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. 2004. Probabilistic Modeling For Risk Assessment of Ground Water Contamination by Pesticides. Analysis Memo, Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prob_mod_policy.pdf (verified 02 Mar 2009).

Troiano, J., C. Garrestson, C. Krauter, J. Brownell and J. Huston. 1993. Influence of amount and method of irrigation water application on leaching of atrazine. Journal of Environmental Quality, 22:290-298. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapref/atrzne.pdf (verified 02 Mar 2009).

Wilkerson, M.R. and K.D. Kim. 1986. The pesticide contamination prevention act: setting specific numerical values. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA. Report EH 86-02. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh8602.pdf (verified 02 Mar 2009).

Table 1. Appendix 2 reprinted from Spurlock (2000) that contains the TFD half-life and Koc values used as the basis for Monte Carlo sampling.

Appendix 2 - Input data for 6800(a) pesticides

Field dissipation half-life (days)- USDA-ARS, 1999; Kollman and Segawa, 1995

atrazine	bromacil	diuron	hexazinone	norflurazon	simazine
173	207	90	105	163	26
61	227	102	60	33	87
48	165	134	90	180	125
64	350	100	79	304	369
18	61	127	75		55
74	120		75		186
119	350		120		44
70	175		154		119
102	155		123		33
	168				89
	124				84
	137				9
					144

K_{OC} - USDA-ARS, 1999

148	12	453	41	490	138
288	33	418	37	430	230
214	2.3	560	41	370	112
149	14	476	300	120	160
163			34		155
111			74		124
170			54		115
163			38		114
160					144
127					114
107					103
174					
88					
38					
72					
157					
102					
90					
57					
120					
139					
155					
87					
39					
70					

Figure 1. Conceptual model for predicting the concentration of pesticide residues in well water.

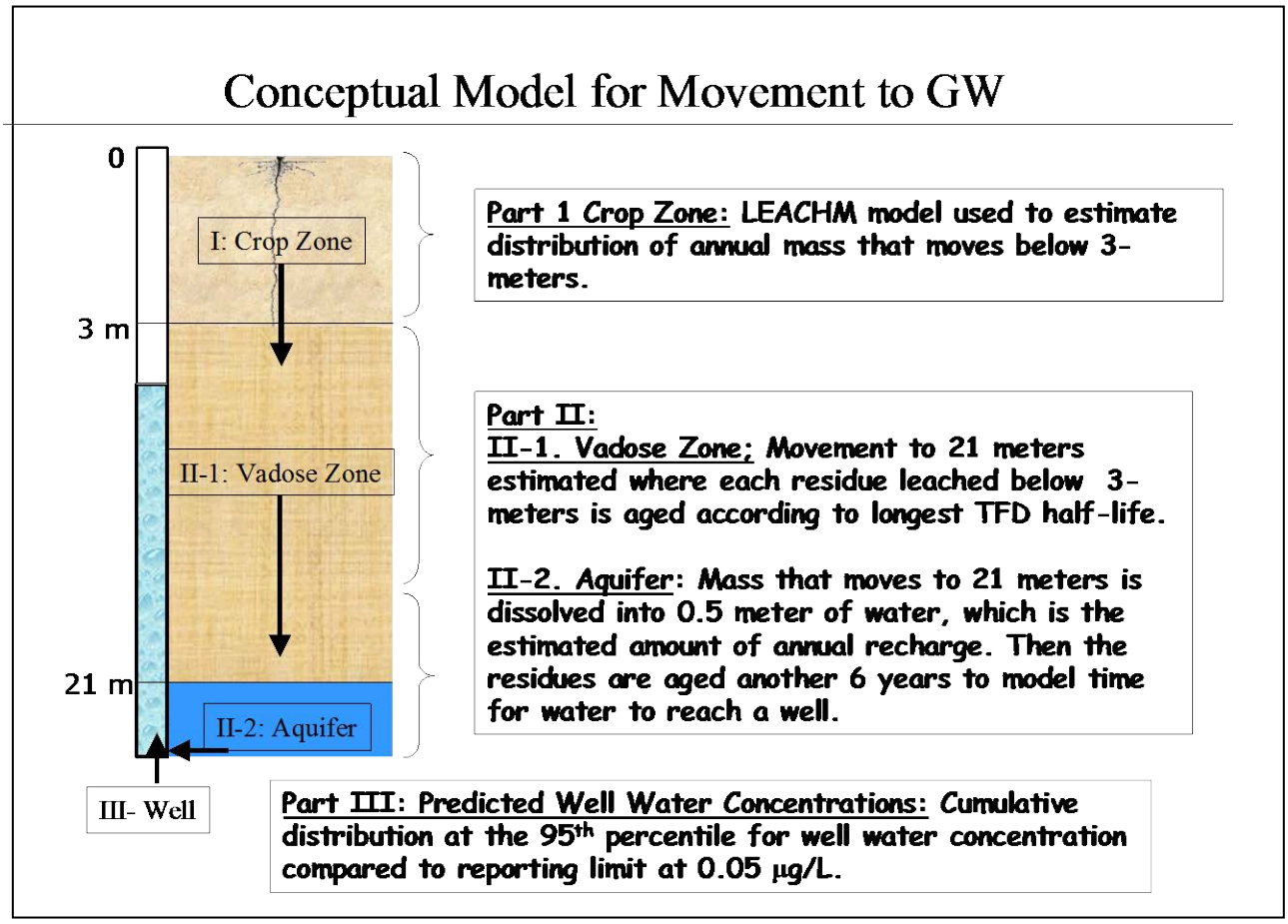
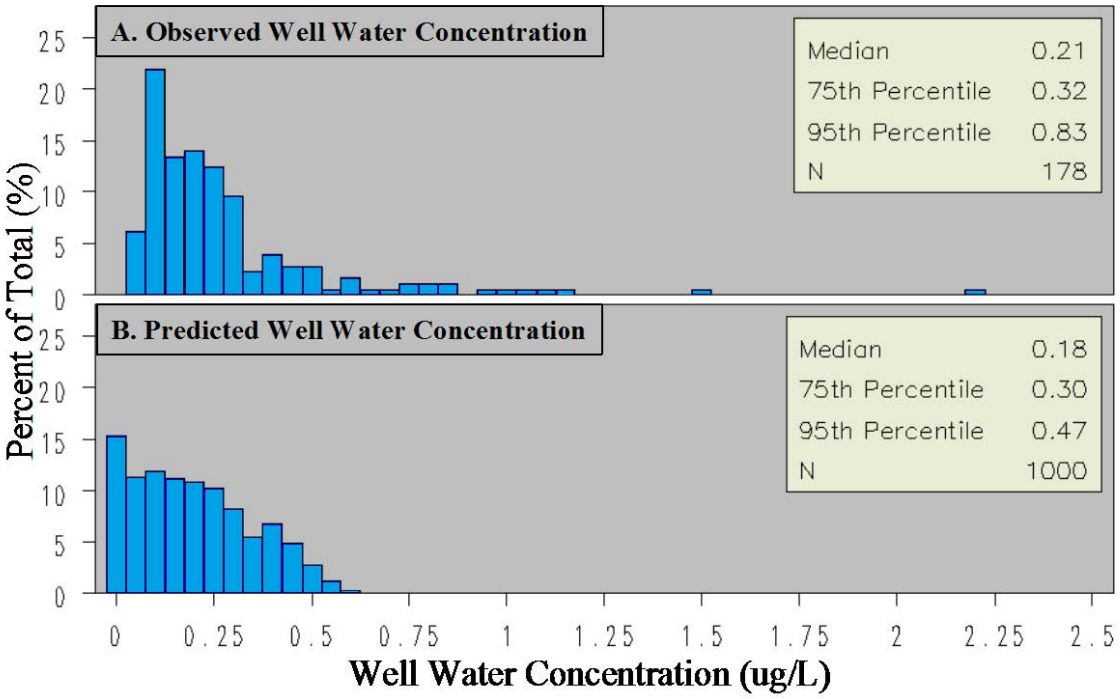


Figure 2. Comparison of distribution of well water concentrations for A. Observed Data from wells sampled in leaching GWPAs in Fresno County and B. Predicted data from modeling procedure at 160% irrigation efficiency.



APPENDIX I

The input files for 160% irrigation efficiency (pages 14-29) and 125% irrigation efficiency (pages 30-45) are available upon request at GWPP@cdpr.ca.gov