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SUBJECT: Probabilistic modeling for risk assessment of ground water contamination by pesticides.

Background

During registration of an active ingredient, the Environmental Monitoring Branch (EM) receives requests from the Pesticide Registration Branch to evaluate the potential for groundwater contamination by the pesticide. Such evaluations are typically conducted based on concerns about the physical-chemical properties of new active ingredients or new use patterns of older active ingredients.

Previous evaluations by EM staff were primarily based on procedures prescribed in the Pesticide Contamination Prevention Act (PCPA) of 1985. The PCPA required the California Department of Pesticide Regulation (DPR) to establish thresholds 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 methodology derived by Wilkerson and Kim (1986) was based on comparing distributions of environmental fate variables between two groups of pesticides: those that were ground water contaminants and those that were classified as non-contaminants. If a significant difference was found between the distributions, then a cut-off value for inclusion in the contaminant group was determined as the estimated 90th percentile of the respective environmental fate variable for the contaminant group. This procedure has been named the Specific Numerical Values (SNV) procedure; the SNVs were revised by Johnson in 1988 and lastly in 1989 (Johnson, 1988 and 1989). The purpose of the SNV process was to provide a method to determine whether or not pesticides were potential ground water contaminants. If environmental fate variables indicated a potential to move offsite and if specific use conditions were met, then the active ingredient was placed on the 6800(b) list and DPR was required to provide ground water monitoring.

Two potential limitations with the SNV process are:

1. It is a univariate approach. 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.

One approach to address the first limitation is to use a model for pesticide fate. Since models simultaneously simulate different environmental fate processes, they provide a method to determine the joint effect of physical-chemical properties on potential for offsite movement and subsequently can produce estimates for contamination potential. Although use of modeling determines the joint effects of environmental fate variables, the prevalent modeling methodology is to use a deterministic approach where, similar to the SNV process, a single set of input variables is used to represent the environmental fate of an active ingredient.

An approach to address the second limitation is to use probabilistic methods. 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.

Basis for Determination of Leaching Potential Using Probabilistic Based Modeling

Studies conducted by the Environmental Monitoring Branch 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) has been used by EM in a probabilistic Monte Carlo study that investigated the effects of irrigation management on leaching of known California groundwater contaminants: namely atrazine, bromacil, diuron, hexazinone, norflurazon, and simazine (Spurlock, 2000). The objective of that study was to produce a distribution of ground water contaminant concentrations for different irrigation management strategies and to base comparisons on those distributions. 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 to calibrate the leaching model in the Monte Carlo study.

In conducting the Monte Carlo study, field dissipation half-life and organic carbon normalized soil adsorption coefficient (Koc) were compiled for the six ground water contaminants. The combined data from all contaminants consisted of 52 field dissipation half-lives and 56 Koc values, producing over 2900 potential paired values for substitution into the model. Because the study involved comparing a number of different irrigation scenarios, computing time was minimized by randomly choosing a smaller but representative subset of paired environmental fate values for each scenario. One conclusion was that reductions in the amount of water that percolates during the growing season is effective in restricting pesticide movement, consequently, irrigation management was identified as a method to reduce concentrations in ground water to levels below the current DPR reporting limit of 0.05 $\mu g \cdot L^{-1}$ (0.05 ppb). Reducing the amount of percolating water during 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

The probabilistic approach is based on the procedure developed by Spurlock (2000). In Spurlock's study, data for Koc and terrestrial field dissipation were collected for 5 pesticides, resulting in 56 values for Koc and 52 values for terrestrial field dissipation half-life. In contrast to Spurlock's study, data for individual pesticides are sparse. A recent evaluation of employing Monte Carlo methods to determine pesticide fate has recommended use of statistical distributions for input variables, such as normal or lognormal functions, when there are sufficient data (Dubus et. al., 2002). In most cases, data will be insufficient to test for the specific distributions. When data are sparse, use of an empirical triangular distribution is recommended. Thus, the set of data for Koc and terrestrial field dissipation half-life to be input into the modeling will be based on sampling from a triangular distribution. In addition, the output distributions of the known leachers generated by Spurlock (2000) will be redefined with the input data set based on sampling from a statistical distribution that best fits the distribution for Koc and terrestrial field dissipation half-life data sets. The data set from the resulting benchmark distribution will be used for comparison of leaching potential of candidate pesticides.

The following procedure will be used to determine the leaching potential of a candidate pesticide.

1. Data for terrestrial field dissipation half-life and Koc physical-chemical properties will be collected for a candidate pesticide.
2. An output distribution of estimated residue concentrations for the candidate pesticide below 10 feet will be produced from repetitive simulations using the previously calibrated LEACHP model. In anticipation of a sparse data set for Koc and terrestrial field dissipation half-life, an empirical triangular frequency distribution will be constructed. Parameterization of the distribution will utilize the median of the data set for the peak while the upper and lower bounds will reflect those values derived from percentiles (%) given by 100*(2N-1)/(2N) and 100/(2N), respectively, where N is the number of values in the data set. Sampling for input values from a subsequent cumulative probability distribution will utilize Latin Hypercube methodology, as discussed by Dubus *et al* (2002).
3. The output distribution for the candidate pesticide will be compared to the redefined distribution for known ground water contaminants, as based on the data sets collated by Spurlock (2000). Distributions from two irrigation conditions will be developed and compared as follows:
    a. <u>Over-Watered Condition</u>: First, a distribution of the candidate pesticide will be generated using test parameters that mimic an over-watered condition where a large portion of the applied water is lost to deep percolation. This was referenced as 160% irrigation efficiency in Spurlock (2000). This output distribution will be used to reflect the potential for the candidate pesticide to leach under California agronomic conditions where irrigation is not managed.
    b. <u>Managed Irrigation Condition</u>: Secondly, the candidate pesticide distribution will be generated using test parameters that mimic controlled irrigation where the amount of percolating water is reduced. This was referenced as 133% irrigation efficiency in Spurlock (2000). Since that study, a better understanding of the appropriate method to input crop evapotranspiration has been determined through discussion with one of the developers of the model (John Hutson, personal communication). The target irrigation efficiency has been revised down to 125% based on updated modeling results. This output distribution will be used to determine whether or not a high potential to leach can be mitigated using efficient irrigation management practices.
4. When there is no overlap of distributions between the candidate and the benchmark distributions, the conclusions are straightforward. Under the over-watered condition of 3a, no overlap between the candidate and benchmark distributions would indicate that the candidate pesticide possesses either a lesser or greater potential to leach compared to current ground water contaminants. Furthermore, if the candidate pesticide's distribution from the managed irrigation condition of 3b exceeds the distribution for current ground

water contaminants, this result would indicate that efficient irrigation might not adequately mitigate the potential for contamination.

5. When there is overlap of distributions, a statistical test will be required to determine if the candidate pesticide's distribution is significantly different from the benchmark distributions. The appropriate test will be based on whether or not the distributions conform to t-test assumptions. When they are not normally distributed or when the variances are not homogeneous then a nonparametric test such as a Wilcoxon Rank Sum test will be used to determine similarity of the candidate and benchmark distributions. Otherwise, a standard t-test will be used. Significant differences will be determined at a 95% probability level.
6. When application rates are lower than the range for the current ground water contaminants, then the distribution for proportion of chemical leached would be compared in addition to concentration. This distribution of proportion should be considered for rates lower than 1 lb/acre.

In contrast to the SNV approach, which relies upon a test of five determinate variables, this approach uses only two variables, Koc and terrestrial field dissipation half-life but it incorporates information on the variability associated with these variables. Reasons for varying these two variables instead of all five from the SNV process are:

1. Values for water solubility and hydrolysis half-life usually exhibit much smaller variability so varying their values would have a small effect on the outcome of the model. Water solubility and hydrolysis half-lives are two variables from the SNV process that are used for the LEACHM modeling procedure. In many cases there may be only one submitted value for these variables. When there is more than one submitted value, they are usually very similar and the coefficients of variation are small. Owing to the small range in variability, the means, when they exist, should be entered for water solubility and hydrolysis half-life.
2. Other investigators have developed modeling approaches using only data for soil adsorption and half-life. A ground water screening model developed by US E.P.A. staff denoted SCIGROW employs data for Koc and aerobic soil half-life (U.S. EPA, 2001). Another screening model developed by Gustafson (1989) denoted the GUS index is based on only soil adsorption and field half-life data. This indicates that there is general consensus that soil adsorption and half-life data are key determinants to describe mobility and persistence of pesticide active ingredients.

Summary

In order to estimate the potential of a pesticide to leach to groundwater, DPR will utilize probabilistic modeling approaches, such as Monte Carlo procedures, as opposed to deterministic approaches for two reasons. First, in contrast to deterministic approaches, which normally use a single set of estimates, probabilistic modeling includes information on variability that is observed in multiple measurements of environmental variables. Second, a distribution of outcomes is produced which enables estimations of risk assessment across a continuous scale of scenarios and which can also be the basis for statistical testing.

The procedure to compare leaching potential of a candidate pesticide is based on a Monte Carlo approach developed by Spurlock (2000). That study produced distributions of concentrations of known groundwater contaminants under varied irrigation management treatments applied to a coarse soil located in Fresno County. These distributions will be recomputed and the updated distributions will serve as benchmarks against which distributions derived from the candidate pesticide will be compared.

There are some situations that might require a different approach. For example, the LEACHP model does not include anaerobic conditions, so special cropping scenarios such as rice culture may require using the SNV procedure.

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