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Study #287: Investigation into the Revision of the Special Numerical Procedure to Determine Leacher vs Non-Leacher Status Based on Physical/Chemical Properties of Pesticide Active Ingredients.

I. Introduction

Detections of pesticide residues in ground water in the late 1970's resulted in the enactment of the Pesticide Contamination Prevention Act (PCPA) in 1986. As indicated by its name, the goal of the legislation was to protect California's ground water resources from further contamination. One preventative part of the legislation mandated the Department of Pesticide Regulation, which at the time was a branch in the California Department of Food and Agriculture, to provide a list of pesticide active ingredients registered in California that have chemical properties similar to those found in ground water throughout the US. That list of potential leachers was then enacted into regulation and known as the 6800(b) list in reference to the part of the CA Food and Agricultural Code of regulations in which it resides. The list is updated as new pesticide active ingredients are registered in California and identified as potential leachers. The Environmental Monitoring Branch's Ground Water Protection Program prioritizes pesticides on the 6800(b) for well sampling studies based on additional data for pesticide use, agricultural use practices, and on further modeling of potential fate after application. An example is the 2012 protocol for sampling potential presence of linuron, mefenoxam, methomyl , and propyzamide in drinking water wells (Garretson, 2012).

The PCPA prescribed a statistical approach to determine cut off values for physical and chemical properties that were identified as important determinants for potential offsite movement of a chemical. The identification of important chemical properties was developed from early observations contained in a 1983 USEPA report authored by Cohen et al. (1984) where they listed water solubility, soil adsorption adjusted to organic carbon content of soil (Koc), Henry's law constant, speciation, hydrolysis half-life, photolysis half-life, and soil half-life as important chemical characteristics. They also provided values that they thought identified a pesticide active ingredient as a potential leacher. The values were their best guess as they were not derived through a statistical procedure. In order to provide a more rigorous determination of the cut-off values, the PCPA prescribed an approach where cut-off values were to be developed for each of the chemical properties listed. The properties were grouped into mobility and persistence categories and if one cut-off value was exceeded from each category then the pesticide was determined as a potential leacher. The pesticide undergoes further investigation as to use patterns before placement on the 6800(b) list.

The approach to determining cut-off values for each chemical property was initiated by Wilkerson and Kim (1986). First, two lists were developed. One for pesticides that had been sampled for and found in well water denoted as ‘Leachers’, and a second for pesticides that had been sampled for but not found in well water denoted as ‘Non-Leachers’. Independent outside review of reports for the detections and chemical methodology was provided by University of California professors with expertise in Environmental Toxicology. Next, data for the listed chemical properties was collected and also subjected to review. The last step was to conduct a T-test to determine if a difference could be detected in the mean values of the groups based on the distribution of values between the Leacher and Non-leacher group. If a significant difference was observed then the cut off value was determined as the value of the 10^{th} or 90^{th} percentile of the cumulative distribution for the ‘Leacher’ group. The lower or upper percentile value was used depending on the chemical property. If no difference was observed between the two distributions, then the value was determined from the combined distribution of ‘Leacher’ and ‘Non-Leacher’ values. The values were labelled as Specific Numeric Values (SNVs).

The current cut-off values are based on a report authored in 1991 (Johnson, 1991). Since that time there has been a large addition of well monitoring studies to measure pesticide residues in well water. For example, with respect to well monitoring, the USGS has been monitoring the quality of ground water through sampling of drinking water wells in a program entitled National Water-Quality Assessment Program (NAWQA http://water.usgs.gov/nawqa/). In an initial report of the results of that study, Kolpin et al. (1998) identified 30 pesticide active ingredients in well water samples that were not identified as Leachers on the 1991 list used in the statistical analysis for SNVs.

There have also been improvements in chemical analytical methodology that provide information for modifying the lists. An example is the report of chlorthal-dimethyl as a leacher on the 1991 list. The early analytical methods were not capable of differentiating between the parent and the breakdown product TPA. Initial detections from Oregon were indicated as parent but later there was indication that those detections were actually the breakdown product. The propensity for TPA to move to ground water rather than the parent appeared confirmed according to results of a national well sampling program conducted by the USEPA between 1988 and 1990. The most widely detected chemical was TPA while the parent was not reported (USEPA, 1992). The parent has an extremely high inherent soil sorption whereas TPA is only slightly bound.

The products of this protocol will be an update of the knowledge base for pesticide active ingredients that have been found in ground water. In addition other statistical methods, such as multivariate discrimination methods, will be tested as providing an effective approach to identify pesticides with the potential to move to ground water. The previous methodology is denoted as a univariate approach where separate chemical properties are compared. However, properties such as water solubility and soil sorption are related so it may be more appropriate to conduct statistical analysis on the combined data for each pesticide. This approach is denoted as a multivariate statistical analysis.

II. Objective

Three objectives of this protocol are:

1. Update the lists for pesticides found in ground water (Leachers) and for those that were sampled for but not detected (Non-Leachers).
2. Evaluate potential for additional chemical properties as indicators of potential offsite movement of a chemical.
3. Investigate the use of multivariate statistical methods for discriminating between the Leacher and Non-Leacher list with respect to physical/chemical properties.

III. Personnel

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IV. Study Plan

Pesticide Well Sampling Data Collection and Review

The number of studies conducted to measure pesticide residues in well water have increased greatly since the 1991 SNV analysis (Johnson, 1991). Sampling conducted for the DPR Ground Water Protection Program, alone, has identified detections from 3 additional parent active ingredients as originating from nonpoint source agricultural applications. The well sampling program is targeted to vulnerable areas of high pesticide use so active ingredients that have not been detected will provide additions to the Non-Leacher list.

The USGS is also a large provider of well sampling data in California and nationwide. The NAWQA program is a nationwide assessment of ground water quality. In California the State Water Resources Control Board under the mandate of AB599 has contracted with the USGS to provide well sampling data to determine the condition of ground water aquifers statewide. Much of that data has already been entered into the EM's Well Inventory Database. Additional sources for statewide and federal well sampling data will be identified and the data retrieved.

Ancillary data on laboratory quality control, pesticide use, and/or cropping patterns are important in determining whether or not detections are laboratory false positives or whether they were caused by nonpoint source agricultural applications. The laboratory and well sampling procedures incorporated into EM's protocols provide the required information to assure that the detection was not a false positive and that its source was from nonpoint source agricultural applications. Data collected from other agencies will require identification of other sources of ancillary data. For example, the number of field blanks included in the design of USGS well sampling studies is around 10% of the total samples. In contrast, the EM protocol specifies that a field blank sample of water is to accompany each well water sample when new active ingredients are investigated. In the presence of detection, the field blank is also analyzed to provide additional information on potential contamination at the site or on laboratory methodology. The USGS field blanks are pre-determined so the data they provide cannot be linked back to a specific detection at a well site. Reports of results for chemical analysis conducted on wells for USGS studies are not first screened by the quality control data. Quality control data is reviewed by staff other than those conducting the well sampling and results are contained in separate reports. The reported well sampling results by Kolpin et al. (1998) contain detections of a number of active ingredients not on the current Leacher list. Analysis of the accompanying quality control data indicated that the results for some must be considered suspect. In another separate report that analyzed the quality control data, the authors specifically state that contamination was a consideration in the well water analyses reported for fenuron, benfluralin, proamide, cis-permethrin, triallate, chlorpyrifos, trifluralin, propanil, DDE, bromacil, dacthal, diazinon, and diuron (Martin et al., 1999). Consequently, the potential additional 30 active ingredients reported by Kolpin et al. (1998) in ground water must be compared to the quality control data and those that are consistent with suspected contamination regarded as false positives with inclusion then onto the Non-Leacher list.

Consequently data reported to EM from the USGS or other federal and state agencies will require further comparison to available laboratory quality control data. For data reported for well sampling conducted in California, pesticide use data can be retrieved with the level of use compared for the section of land containing the detection. Estimates of use can also be accumulated on larger spatial scales, for example for the 8 sections surrounding the section with the reported detection in well water. If the pattern indicates general lack of pesticide use or extremely low use in the surrounding area then a potential agricultural source for the detection would be in question. Determining the veracity of data collected from other states would be more problematic. Initially, laboratory quality assurance data will be required to determine if the detections are valid. If detections appear valid, then additional data on well construction, location in the landscape, pesticide use, and/or cropping patterns will provide further proof for non-point applications as the source of detection. It is possible that pesticides considered as a Non-Leacher in California might be detected in other states due to differences in agricultural use setting, such as cropping patterns, or to local aquifer vulnerability where use in California would be in less susceptible areas compared to other areas of the US. One decision to be determined in this study is whether to limit the list to detections in California whereby the process would reflect California pesticide use and agricultural cropping conditions.

Physical/Chemical Data Collection and Review

Once the list for Leachers and Non-Leachers is updated then the physical/chemical properties of each pesticide will be reviewed and updated. EM's Pesticide Chemistry Database will be the main source for data. This database focuses on pesticides registered in California. Detections for some pesticides may occur in other states and that pesticide may not be registered in California. Other sources of information will be

- Contact US EPA staff for available information
- USDA Pesticide Properties Database

- FOOTPRINT database which was developed in Europe
- Contact Registrant

Other physical/chemical properties will be reviewed for addition as discriminating between the lists. For example, volatilization may be a property that could provide additional information with discriminatory effect.

Statistical Analysis

In a previous test of the univariate method that was developed according to the PCPA approach, application of the SNVs to the original lists indicated a large potential misclassification error rate. For example, 14 of 27 (52%) pesticides on the original list identfied as Non-Leachers were miss-classified as Leachers when subject to the SNV test (Johnson, 1991). In multivariate techniques all of the pesticide properties are included in a single analysis to determine if there is potential discrimination between the lists. If there is a significant difference between groups, a discriminatory algorithm is produced where coefficients for each property are developed. One potential method is Canonical Discriminant Analysis where a multivariate analysis of variance is conducted to test for potential differences between the lists. Coefficients for each of the chemical properties are produced that can be applied to the raw data, producing an index for each pesticide. This one index value would then represent the information from all pesticide properties and it would provide a single test for inclusion on the Leacher list. For example, further tests could be conducted on the distribution of the indexes produced for the two lists where, similar to the previous procedure for SNVs, the distribution of the Leacher indexes might be used to formulate a cut-off value for comparison to a single index value. In addition, the coefficients also provide information on the importance of a physical/chemical factor as a discriminating factor. It may be possible that a physical/chemical factor could be dropped from the analysis with little to no effect on the outcome. The final product will be a recommendation on the most efficient process by which to identify pesticide active ingredients as potential leachers.

V. Time Table

Fall/winter 2013 – Review and revise lists of Leachers and Non-Leachers
Winter 2013-2014/spring 2014 – Review and revise physical/chemical properties
Spring 2014 – Investigate statistical methodology to discriminate between the lists
Summer 2014 – Report or journal manuscript prepared.

VI. References

Cohen, S.Z., S.M. Creeger, R.F. Carsel, and C.G. enfield. 1984. Potential for pesticide contamination of ground water resulting from agricultural use. In (R.F. Krueger and J.N. Seiber, eds): Treatment and Disposal of Pesticide Wastes. American Chemical Society Symposium Series 269. Pp 297-325.

Garretson, C. 2012. Protocol for Ground Water Protection List Monitoring for Linuron, Mefenoxam, Methomyl, and Propyzamide. Environmental Monitoring Branch, Department of Pesticide Regulation, CALEPA, Sacramento, CA. EH 91-06. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/protocol/studygw11protocol.pdf

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

Kolpin, D.W., J.E. Barbash, and R.J. Gilliom. 1998. Occurrence of pesticides in shallow groundwater of the United States: initial results from the National Water-Quality Assessment Program. Environ. Sci. Technol. 1998 32:558-566.

Martin, J.D., R.J. Gilliom, and T.L. Schertz. 1999. Summar and Evaluation of Pesticides in Field Blanks collected for the National Water-Quality Assessment Program. U.S. Geological Survey, Denver, Co. Open-File Report 98-412.

USEPA. 1992. Another Look: National Survey of Pesticides in Drinking Water Wells. Phase 2 Report. USEPA, Washington D.C., USA. 570/9-91-020, January 1992.

Wilkerson, M. R. and K. D. Kim. 1986. The pesticide contamination prevention act: setting specific numerical values. Environmental Monitoring Branch, Department of Pesticide Regulation, CALEPA, Sacramento, CA. EH 91-06. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh8602.pdf