# Background Document for FIFRA Scientific Advisory Panel

# "The N-methyl Carbamate Cumulative Risk Assessment: Drinking Water Exposure Assessment for Ground Water"

Session 3
February 17, 2005
National Airport Holiday Inn
Arlington , VA

Prepared by:
Office of Pesticide Programs
US Environmental Protection Agency

## Table of Contents

## I. Background and Purpose

The Food Quality Protection Act (FQPA) of 1996 requires the Agency to assess the risks from different pesticides having a common mechanism of action, focusing on the likelihood that a person will be concurrently exposed to multiple pesticides from multiple sources (food, drinking water, and residential uses). In response to this mandate, the Environmental Protection Agency (EPA) has developed methods for estimating tiered screening-level concentrations of pesticides in drinking water from surface and ground water sources. These methods and models have been peer-reviewed on numerous occasions by the FIFRA SAP (FIFRA SAP, 1997, 1998, 1999, 2000; USEPA, 1999, 2000, 2001).

In addition to developing methods for estimating single pesticide residues in water, the Agency has developed methods for estimating multiple pesticide residues in surface-water sources of drinking water for the organophosphate (OP) pesticide cumulative risk assessment (FIFRA SAP, 2002; USEPA 2002). Because the carbamates have similar uses, hazard endpoints, and exposure requirements as the organophosphate pesticides, the Agency will use the same methods used in the OP cumulative assessment for estimating surface water exposure in the carbamate drinking water assessment. Section 5 of the case study, which will be presented in Session 4 of this SAP, describes how those methods are being applied specifically to the N-methyl carbamates included in this cumulative assessment group.

The carbamate cumulative risk assessment will also assess the potential impacts of residues in ground water since monitoring studies have shown that these chemicals are likely to reach ground water sources of drinking water. In its ground water assessment, EPA evaluated three ground water models to estimate carbamate concentrations.

As a preliminary screen for pesticide levels in ground water sources of drinking water in individual pesticide risk assessments, EPA uses the SCI-GROW (Screening Concentrations In GROund Water) model. (A description of this model is available at the following Web site: http://www.epa.gov/oppefed1/models/water/index.htm ). Because SCI-GROW is based on ground water monitoring studies in which pesticides were applied at maximum allowed rates and frequency to vulnerable sites (i.e., shallow aquifers, sandy, permeable soils, and substantial rainfall and/or irrigation to maximize leaching), pesticide concentrations estimated by SCI-GROW are expected to represent high-end exposure values. This screening model provides a single estimated concentration that can be used for both short-term and longer-term exposures, and as such is not designed to provide the kind of exposure estimates needed for a cumulative risk assessment.

EPA has not yet developed a more refined ground water model for estimating pesticide exposures in ground water sources of drinking water. However, USGS

has recently evaluated the capabilities of a number of existing leaching (vadose zone) models (Nolan et al, 2004). Based upon the results of USGS's evaluation, EPA considered three models – LEACHP, RZWQM, and PRZM – for predicting ground water concentrations of carbamate pesticides. In addition to USGS's evaluation, EPA considered the data requirements of these models and an earlier evaluation of the leaching portion of the PRZM model by the FIFRA Environmental Model Validation Task Force (Jones and Russell, 2001; Russell and Jones, 2002) in determining a modeling approach to estimate drinking water exposures from carbamate pesticide residues in ground water.

This document is meant to provide the members of the FIFRA Scientific Advisory Panel (SAP) and the public with the following information:

- an evaluation of existing ground water / leaching models for use in estimating residues in ground water sources of drinking water for the N-methyl carbamate group of pesticides;

- a description of the conceptual model OPP proposes to use in applying these ground water models to estimating drinking water exposure from the N-methyl carbamate cumulative assessment group.

## II. Tier 2 Ground Water Model Evaluation

### A. Introduction

The Environmental Fate and Effects Division (EFED) of EPA's Office of Pesticide Programs (OPP) currently uses an empirically-based screening model, SCI-GROW (Screening Concentrations In GROund Water), to estimate groundwater concentrations of pesticides. As mentioned previously, SCI-GROW provides high-end concentrations on a national basis, and as such does not take into account region-specific transport characteristics or crop and pesticide management practices. Instead SCI-GROW estimates are based on the pesticide's partitioning coefficient, the pesticide's laboratory soil half life, and the pesticide application rate for a single season. More information and background on SCI-GROW can be found on OPP's water models Web site: (http://www.epa.gov/oppefed1/models/water/scigrow_description.htm ).

For the carbamate cumulative assessment OPP investigated the use of more refined models that consider more mechanistic transport processes and region-specific characterization. These models can produce the temporal estimates needed for FQPA aggregate and cumulative exposure assessments.

As part of this investigation, EPA reviewed an evaluation of seven vadose-zone models, which was conducted by the United State Geological Survey (USGS) (Nolan et al, 2004). After reviewing USGS's comparison of these models, EPA selected three models (RZWQM, LEACHP, and PRZM) that could be potentially usable in OPP's pesticide risk assessment and that warrant further investigation. OPP deemed the other four models (HYDRUS2D, VS2DT, GLEAMS, CALF) as less usable for reasons related to proprietary issues, cost, lack of support, or lack of difference from the other three.

The first model, which was chosen for further investigation, was PRZM (Pesticide Root Zone Model). Although OPP has not used this model routinely to estimate leaching, it has used it for surface runoff estimations for more than a decade. PRZM was also chosen because its hydrological submodel is very simple (as discussed in detail later), and thus can be used to evaluate the need for more complex hydrological models such as those contained in RZWQM and LEACHP. It should be noted that OPP frequently uses PRZM in combination with EXAMS for its tier 2 assessments for surface water sources of drinking water. These two models have been the subject of a number of FIFRA SAP reviews (1997, 1998, 1999, 2002). This evaluation, though, considers the hydrology component of PRZM in the context of leaching, not runoff.

A second model considered was RZWQM (Root Zone Water Quality Model), a model that has been used for over a decade by the Agricultural Research Service (ARS) of the United States Department of Agriculture (USDA). This model includes a more advanced hydrology than PRZM and offers crop and pesticide management options that are not available in the simpler PRZM model (as discussed later).

The last model that EPA considered was LEACHP (Leaching Estimation and Chemistry-Pesticides), a model used by the State of California and by Canada in pesticide regulatory work. In determining which model to use, Health Canada's Pest Management Regulatory Agency (PMRA) evaluated several vadoze zone models (PRZM, MACRO, LEACHP, PESTAN) and concluded that only LEACHP met their requirements (PMRA, 2004). In terms of complexity, LEACHP lies between PRZM and RZWQM, having more advanced hydrology than PRZM and less sophisticated crop management practices than RZWQM. Because of resource limitations, LEACHP was explored only qualitatively in this evaluation, but will be investigated more fully in the future.

## B. Comparison of Model Processes

All three models (PRZM, RZWQM, and LEACHP) are one-dimensional vertical transport models. Thus, horizontal heterogeneities are not explicitly considered, but are implied in the selection of bulk field properties. Although these models are not expected to precisely predict subsurface concentrations, they should be able to capture the most salient processes. For example, the model should be able to differentiate between an aquifer confined by a meter thick clay layer and one that is overlain only by sand. It would also be desirable for a model to account for mitigating management practices (a feature present in the models being evaluated but not in SCI-GROW).

The most salient differences among the models are in their treatment of hydrology, management practices, and pesticide transport. PRZM is the simplest in all three aspects, and RZWQM is the most complex. LEACHP is very similar to RZWQM, but has simpler management practices, crop growth, and rain-event infiltration routines. Another important difference among the models is their ease of use and documentation. Details of these differences are discussed in the following sections.

### 1. Hydrology

The driving process behind all leaching models is the mechanism of vertical water transport. Of the three models selected for further evaluation, two are mechanistically based (LEACHP and RZWQM);

PRZM is empirically based. LEACHP and RZWQM use Richard's equation to address redistribution coupled with an infiltration model to address rain events. PRZM infiltration is based on the empirical curve number method and the concept of freely draining soils.

All models have evapotranspiration routines that simulate water depletion.

***PRZM Hydrology:***

In regards to hydrology, PRZM is the simplest of the three models. It is primarily nonmechanistic and is essentially controlled by three concepts. The first concept is that precipitation partitions into runoff and infiltration according to the curve number relationship (NRCS, 2003). The second one is that all soil horizons drain to field capacity in 24 hours. The third is that all rainfall occurs as a 24-hour average event. These three assumptions are advantageous in that they allow for simplified numerical routines that result in potentially faster run times than more complicated models. However, as discussed below, these simplifications may also cause conceptual difficulties.

The most influencing concept in PRZM hydrology is that infiltration is driven by the curve number because this number alone controls the amount of infiltration. The curve number is a rough estimator of watershed-scale runoff and, by implication, infiltration (Ponce and Hawkins, 1996). Although the curve number is reportedly the most sensitive parameter in PRZM (Carbone et al, 2002), the selection of potential curve numbers is limited as illustrated in the NRCS tables (NRCS, 2003) for appropriate curve numbers. For example, for row crops and a hydrologic group B soil, there is either a curve number of 81 for "poor" hydrologic conditions or 78 for "good" hydrologic conditions. Although there is a vast infiltration response difference between these curve numbers, the difference is well within the natural event-to-event variability within even a single field (FIFRA SAP, 2004). Such tabulated values do not account for any specialized management practices, crop stages, or soil physics such as macropores, and to date no definitive curve number tables have been produced to account for infiltration differences caused by such phenomena. On the other hand, more mechanistic infiltration models (e.g., Green-Apt as used by RZWQM) have not been a dramatic improvement over the curve number method, at least in terms of runoff generation and large spatial scales (Wilcox et al, 1990).

The second influential concept is that field capacity controls drainage. Once the infiltration amount is determined by the curve number method, the infiltrating water passes into the soil profile and fills up any part of the profile to the field capacity, starting at the top of the profile. The amount of water exceeding field capacity in any compartment passes freely down through the profile. The only avenue for water depletion below field capacity is through evapotranspiration.

In PRZM, evapotranspiration occurs in the soil profile only to the depth of the root zone, which causes the soil below the root zone to be at field capacity throughout the PRZM simulation. As a result, any water leaching through the root zone freely passes through the remaining profile. This happens regardless of the hydraulic conductivity of any horizon. Conceptually transport-wise, this is the same as a saturated constant flow column, albeit with “saturation” being field capacity. Because water content can never be above field capacity in PRZM, velocities are higher and mixing is lower than they are for a corresponding system that allows variable water content.

Another conceptual difficulty with PRZM is that field water capacity is difficult to determine and is not constant (Romano and Santini, 2002). For example, impeding horizons or shallow water tables can substantially decrease drainage of overriding layers. Being primarily a parameter used by farmers for root zone water management, the use of field capacity in layered soils or for profiles of substantial depth may not accurately reflect vertical hydrological processes. Furthermore, *field capacity* is typically defined as the percentage of water remaining in the soil two or three days after the soil has been saturated and free drainage has practically ceased (Romano and Santini, 2002). PRZM’s assumption of drainage to field capacity after one day is inconsistent with this definition.

The third influencing concept is that rain events occur over a 24-hour period and rainfall intensity is not considered. This requirement for PRZM is necessary because the curve number method is not a continuous event model but instead is based only on rain event depth. Because PRZM does not consider rainfall intensity, PRZM treats a 1-inch rainfall over 20 minutes the same as it would a 1-inch rainfall over 24 hours. Runoff and infiltration would obviously be quite different for these two cases, but the practical differences in considering intensity are unknown with regard to estimating pesticide fluxes in the subsurface over the long term.

Despite these conceptual difficulties, the PRZM hydrologic concept may work sufficiently well for freely draining soils (i.e., those profiles in which hydraulic conductivity is either constant or increases with depth). On the other hand, the concept may not work as well for soil profiles that contain a layer of low hydraulic conductivity in which a layer would not allow higher layers to freely drain to field capacity. Additionally, PRZM may not be sufficiently conservative for soils containing macropores.

***RZWQM Hydrology:***

RZWQM simulates water infiltration during a rain event by the Green-Apt approach, and redistribution of water between events is modeled according to Richard's equation. This more mechanistic approach accounts for rainfall intensity and the different hydraulic conductivities of subsurface layers, features that are not available in PRZM. RZWQM also has the ability to simulate macropore flow, surface storage, fluctuating water tables, and tile drainage.

Macropore simulation in particular may be an important asset, as macropores have been shown to be important means of subsurface transport (Ahuja et al, 1995; Barbash and Resek, 1996; Christiansend et al, 2004; Kay et al, 2005; Malone et al, 2001).

Because of its Green-Apt approach to infiltration, RZWQM (unlike PRZM) can consider rainfall intensity. Breakpoint rainfall data can either be input from a known site or it can be generated with the built-in CLIGEN weather generator, which can produce weather simulations from its data base for nearly any area of the United States.

The additional complexity of RZWQM involves the cost of obtaining additional parameters, some of which are not readily available. In order to assist users, RZWQM developers have provided numerous correlations so that only a few are required to run the model. For example, the model can be run by providing only the soil texture, in which case all other parameters (e.g., $K_{sat}$, porosity, etc.) are calculated from correlations. Obviously, the more parameters that can be supplied, the better the output will be. If only soil texture is known, then the RZWQM output would not likely be much better than the simpler PRZM model.

***LEACHP Hydrology:***

Infiltration quantities in LEACHP can be controlled by the curve number method and by both the hydraulic characteristics of the soil

and the rain event. The redistribution of water in the soil profile is modeled with the Richard's equation in LEACHP. OPP has not explored the difference between this method and that of RZWQM, but will pursue this when resources permit.

## 2. Management Practices

Agricultural management practices, such as tillage and pesticide application methods, may influence pesticide leaching behavior. The three models differ considerably with regard to management practices, ranging from nearly nonexistent in LEACHP to quite sophisticated in RZWQM. Highlights of these differences are reviewed below.

***PRZM Management Practices:***

In PRZM, management practices that influence vertical transport are essentially manifested through curve number changes. The current version of PRZM allows for two curve numbers: one during the cropping period and one for non-cropped periods. However, future versions are anticipated to incorporate up to 30 curve numbers in order to simulate various cropping practices. PRZM allows the user to determine the curve number most suitable for the management practice, and to date there is no comprehensive data that suggests what an appropriate curve number would be for a specific management practice; curve number selection in this case is left to best professional judgment.

Irrigation in PRZM has several stated options, but can be classified as either above canopy, below canopy, or furrow. The only difference in PRZM between above-canopy and below-canopy irrigation is that the pesticide is washed off foliage in above-canopy but not in below-canopy irrigation. Because furrow irrigation in PRZM is more complex than any other routine in PRZM, it has not been tested for functionality and is not recommended for use by OPP. Flood irrigation, although an option in PRZM, is essentially below-canopy irrigation with runoff prohibited.

Pesticide applications in PRZM are handled either as above-canopy or directly to the soil in various vertical distributions. When a pesticide is applied to the soil in PRZM (either directly or through foliar washoff), spatial discretization appears to affect the mass balance of pesticide applied to the soil. At this time, EPA presumes there is an error in the program code and notes that spatial discretizations of 3 cm and 2.5 cm may cause mass losses of up to

25 percent. Until EPA can understand the cause of this problem, the Agency recommends discretizations that evenly divide into the incorporation depth at least to the point of maximum pesticide incorporation.

***RZWQM Management Practices:***

RZWQM management practices are incorporated into the model in various ways that can influence hydrology and transport. Practices may include tillage, tile drainage, irrigation, manure and pesticide applications.

Tillage is notable among the management practice options in that it is comprehensive (See Table 1). Each of these tillage practices affects soil properties in a different way as described in Ahuja et al (2000). Within the model's program, the various tillage practices affect infiltration, bulk density, macroporosity, and incorporation of surface applied materials (pesticides, manure). Furthermore, the tillage zone is reconsolidated over time as a function of rainfall.

Irrigation in RZWQM can occur at fixed intervals, specified dates, or according to root zone demand. Sprinkler, drip, furrow, or flood is available. RZWQM treats sprinkler irrigation as a rain event, and treats drip irrigation as a rain event with an intensity rate that is less than Ks. The handling of flood and furrow irrigation is not specified in the RZWQM documentation.

**Table 1. List of Available Tillage Practices in RZWQM**

| | |
|---|---|
| 1. moldboard plow | 16. roller package |
| 2. chisel plow, straight | 17. row planter w/ smooth coulter |
| 3. chisel plow, twisted | 18. row planter w/ fluted coulter |
| 4. field cultivator | 19. row planter w/ sweeps |
| 5. tandem disk | 20. lister planter |
| 6. offset disk | 21. drill |
| 7. one-way disk | 22. drill w/ chain drag |
| 8. paraplow | 23. row cultivator w/ sweeps |
| 9. spike tooth harrow | 24. row cultivator w/ spider wheels |
| 10. spring tooth harrow | 25. rod weeder |
| 11. rotary hoe | 26. rolling cultivator |
| 12. bedder ridg | 27. NH3 applicator |
| 13. V-blade sweep | 28. ridge-till cultivator |
| 14. subsoiler | 29. ridge -till planter |
| 15. rototiller | |

***LEACHP Management Practices:***

LEACHP management practice capabilities are much less than those found in either PRZM or RZWQM. Crop growth routines are similar to those in PRZM where crops are characterized by percent canopy cover and root depth over time. In the near future, the Agency will further explore ways in which management practices can be used in LEACHP.

### 3. Pesticide Processes

Basic pesticide processes are similar in all three models — that is, all consider sorption and first-order degradation. However the models differ substantially in the level of sophistication of additional process options.

***PRZM Pesticide Processes:***

PRZM uses a linear sorption isotherm, and first-order degradation that can be attributed to the sorbed and/or the aqueous phase. A more complicated "bi-phasic" degradation routine is available in PRZM, but this routine is known to be conceptually problematic in the way that pesticide mass is tracked over time. For this reason, the Agency does not support its functionality. Both degradation and sorption parameters can vary by horizon. Sorption is addressed by a linear equilibrium isotherm. Temperature routines in PRZM, which simulate heat transfer through the subsurface, are not working at this time; thus temperature effects on degradation cannot be simulated.

***RZWQM Pesticide Processes:***

RZWQM incorporates the ability to use both linear and nonlinear (Freundlich) isotherms, as well as dissociation chemistry. The model uses time steps shorter than one day in its nonlinear sorption routines. In addition, RZWQM has capabilities for considering sorption mass transfer (or kinetic) limitations, as well as irreversible binding, although EPA is not likely to obtain the necessary input parameters from pesticide registration data submissions. RZWQM routines can be very complex, including degradation variations with moisture, microbial population accounting, and heat transfer routines. RZWQM provides default correlations among the parameters if such complexity is desired. Most likely, however, EPA will only be able supply rudimentary chemical properties so that the processes modeled in RZWQM will be similar to those in PRZM with the exception of temperature simulation. RZWQM, on the

other hand, provides more options than PRZM when chemical data are available.

***LEACHP Pesticide Processes:***

At this time, EPA knows little about the mechanisms within LEACHP other than that LEACHP has the capability to simulate nonlinear Freundlich or Langmuir isotherms and temperature-dependent first-order degradation. The Agency will pursue a more thorough investigation when resources permit.

## 4. Ease of Use

RZWQM has a graphical user interface that facilitates scenario development. While RZWQM potentially can accept a large amount of input parameters to characterize a site, it can also operate with a minimum because of its built-in correlations among the minimum parameters and unknown parameters. As an extreme example, if only the soil texture is known, RZWQM will estimate all other relevant soil properties (e.g., bulk density, hydraulic conductivity etc.). RZWQM includes a weather generator (CLIGEN) and a fairly comprehensive soils database from STATSGO. However, primarily because of EPA's lack of experience with RZWQM, data entry difficulties have been reported from internal evaluations of the model. To resolve these issues, EPA will meet with ARS in the near future.

PRZM requires that strictly formatted input text files be created. However, EPA has created a program (PE4) that greatly simplifies scenario input file development. Historical weather information must also be in formatted text files, and EPA already has a fairly comprehensive set of these files (typically 30 years is available). One advantage of PRZM is that the Agency has a long history of use, and for a large part understands the nature of the program in estimating runoff; however, EPA has much less experience with the vertical transport component of PRZM.

RZWQM is fairly well documented in a book (Ahuja et al, 2000) and in an online context-sensitive help program. The output is presented in both graphical and tabular form. PRZM documentation is still being revised, and many of PRZM's modifications in the last several years have not been reported. At present, examination of the PRZM Fortan 77 code is required in order to understand the way that PRZM works. Examination of the RZWQM code may also be required in the future as EPA becomes more familiar with the program.

## C. Model Assessments by Users Outside of EPA

### 1. Industry Evaluation of PRZM

Russell and Jones (2002) showed that PRZM tends to underpredict pesticide leaching when PRZM is parameterized according to field-specific pesticide properties; however, the authors concluded that PRZM performs adequately. These studies were analyzed at about 2-meter depths, which is somewhat greater than the root zone for which PRZM would be expected to perform best. Russell and Jones (2002) suggested that PRZM perform well if the peak concentration of the data is within a factor of 3 of the peak concentration of the predicted PRZM concentration, without regard to the time of occurrence of the peaks. In other words, a simulated peak could occur a year after the data peak, and the model would still be judged as adequate by Russell and Jones as long as the simulation was within a factor of 3 of the data.

Graphs of the Russell and Jones' (2002) PRZM predictions and data are shown in Figures 1 and 2 in order to give a more balanced representation of the model's adequacy. Figure 1 shows the PRZM simulation and 6-ft lysimeter data for bromide at a site in California. PRZM substantially underpredicts the transport behavior of both the peak measured value and the average value of lysimeters at same 6 ft depth across the site. Figure 2 shows a similar plot for bromide in North Carolina. In this simulation, PRZM captures the peak lysimeter data quite accurately and overpredicts the average. Figure 3 shows another simulation and data set from Georgia. In this figure, PRZM simulates a well defined peak, while the data show a lower peak and significant concentrations that linger for longer than the duration of the study.

Although plots of pesticide concentrations have not yet been fully developed, summary results from Russell and Jones (2002) indicate that peaks are substantially underpredicted in most cases. The only data set that Russell and Jones (2002) used to test EPA's conservative parameter selection protocol was from one study. In this study, PRZM substantially overpredicted pesticide concentrations and thus the "conservative" parameterization also overpredicted concentrations. In most cases, the "conservative" inputs would have improved predictions, but would likely be underpredictions.

Recommendations from Jones and Russell (2002) suggest that PRZM would be inappropriate when soil temperature and soil moisture variations are important. They recommend that PRZM be improved with regard to crop uptake, sorption rate, preferential flow, crusting, and use of rainfall intensity. It should be noted that RZWQM already incorporates these recommended processes.

Registrant groups have also investigated the effect of spatial discretization on PRZM output (Jones and Russsell, 2001). Historically, PRZM has been used without entering a value for a dispersion coefficient; instead dispersion has been simulated by relying on numerical dispersion caused by the backward differencing of the velocity term in the PRZM code. The PRZM manual suggests discretization of 5 cm based on comparison with (uncited) data, whereas Boesten (2004) suggests using 2.5 cm to match dispersion in other European regulatory models. However, our investigations have shown that both values create potentially severe mass balance errors. We presume that these errors are caused by truncation of mass inputs, but this presumption has not been confirmed yet. Discretizations of 0.25, 0.5, 1, or 2 cm do not produce the mass balance errors. We also note that discetization in PRZM affects the available pesticide mass for erosion since the erosion depth of interaction only occurs in the first discretized compartment. Further study of these effects is required to fully understand the impact of PRZM discretization.

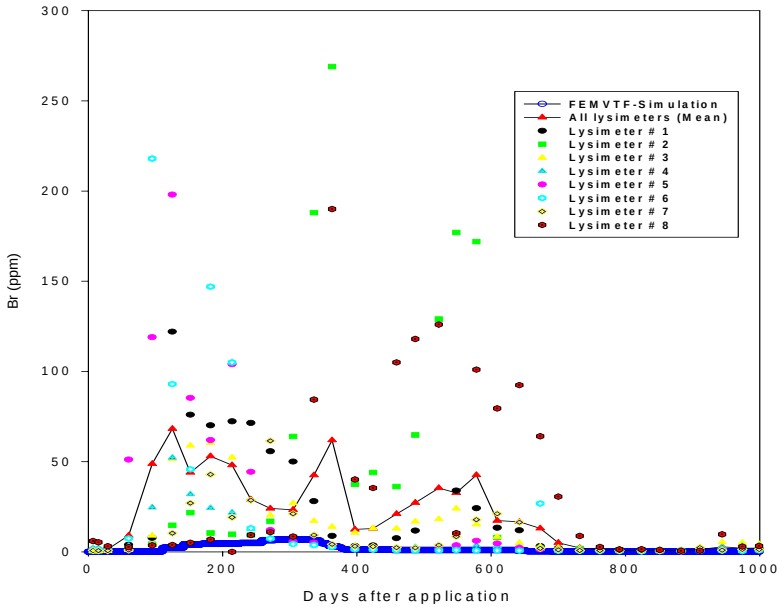


**Figure 1. Plot of bromide FEMVTF data and PRZM simulation for a groundwater site in California (CA1L in Russell and Jones, 2002)**

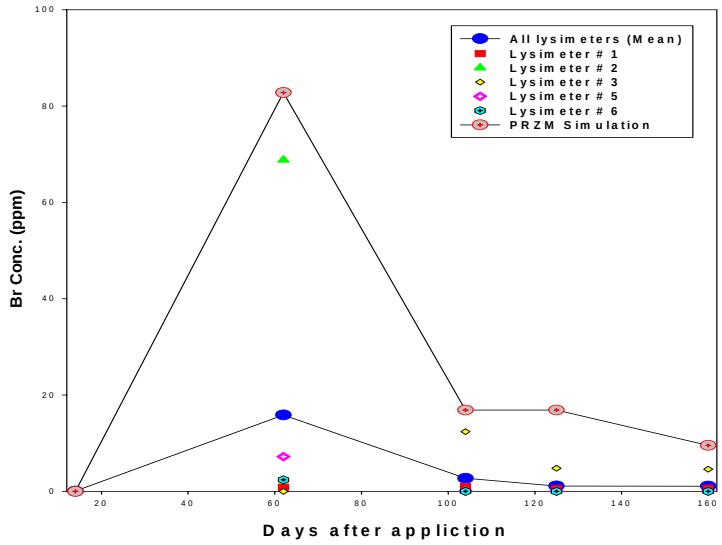


**Figure 2. Plot of bromide FEMVTF data and PRZM simulation for a groundwater site in North Carolina (NC4L in Russell and Jones, 2002)**

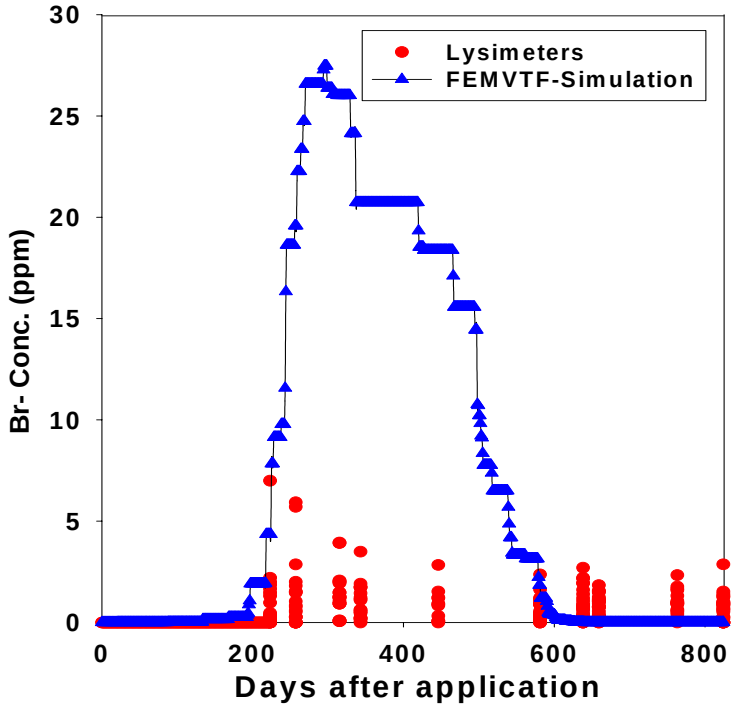


**Figure 3. Plot of bromide FEMVTF data and PRZM simulation for a groundwater site in Georgia (GA2L in Russell and Jones, 2002)**

### 2. USGS Comparison of Leaching Models

USGS compared the performance of seven leaching models on four study sites (Nolan et al, 2004). The USGS analysis suggests that RZWQM more closely simulates actual data than does PRZM. In several cases, PRZM underpredicted concentrations by an order of magnitude, while RZWQM predicted concentrations that were considerably closer. One of the more important aspects of the USGS study was the evaluation of the usability of the models. While RZWQM was highly regarded in terms of usability and documentation, PRZM was characterized as “not user friendly”, and the manual was characterized as being “of poor quality”.

## D. Comparison of RZWQM and PRZM on Hypothetical Sites

In order to test the comparative usability of PRZM and RZWQM, EPA ran simulations of several regions where carbamate cumulative scenarios may be developed. Sites were hypothetical in that no field data were available to test whether one model performed better than the other. The goal instead was to determine if any substantial difference may result from use of one model or the other. In this regard, only the hydrological transport components were tested here since these make up the most significant differences between the two models. Hydrological testing was accomplished by simulating the application of a non-sorbing and nondegrading compound to the soil.

One site was chosen in Maryland with a Fort Mott loamy sand (Hydrologic group A). The site is characterized by relatively freely draining surface horizons underlain by a horizon with substantially lower hydraulic conductivity. Relevant soil characteristics are given in Table 2. Weather for the site was generated from the CLIGEN weather generator for RZWQM, and the output was converted to daily values for use in PRZM. Output for this test (Figure 4) shows that PRZM transports the tracer much faster than RZWQM, primarily because PRZM is incapable of accounting for the transport-hindering middle horizon. PRZM output also includes more spikes than RZWQM because transport in PRZM can only occur on rain event days, whereas transport in RZWQM can occur during rain events as well as during redistribution periods. A check on mass balance showed that both models had excellent mass balances, with more than 99% of the applied mass accounted for in these simulations.

**Table 2. Soil Profile for Maryland soil.**

| Horizon | Thk | BD | porosity | Field Capacity | Wilting Point | Ksat (cm/hr) |
|---|---|---|---|---|---|---|
| 1 | 30 | 1.410 | 0.468 | 0.049 | 0.023 | 150 |
| 2 | 46 | 1.46 | 0.449 | 0.0610 | 0.393 | 150 |
| 3 | 61 | 1.48 | 0.442 | 0.111 | 0.615 | 2.03 |
| 4 | 91 | 1.55 | 0.415 | 0.1064 | 0.0467 | 75.1 |
| 5 | 137 | 1.53 | 0.423 | 0.0633 | 0.0245 | 150 |
| 6 | 277 | 1.59 | 0.40 | 0.0400 | 0.024 | 173 |

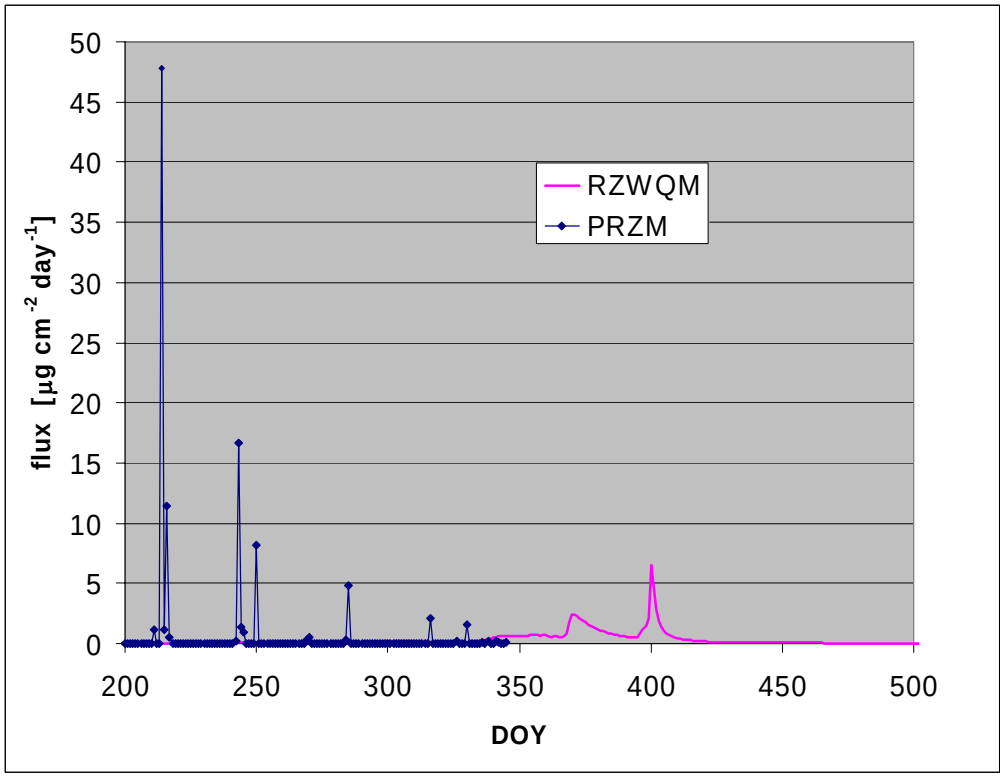


**Figure 4. Simulated flux of nonsorbing nondegrading tracer at 2 meter depth.**

A second investigation was conducted with a Greenville soil ( Hydrological Group B) for a hypothetical site in Sumter County Georgia. The profile of the site is given in Table 3. Weather was generated with CLIGEN as previously described. In order to emphasize the "free draining" concept in PRZM, an additional RZWQM run was conducted in which the low hydraulic conductivity layers below the subsurface were replaced with highly conductive layers, as shown in Table 4. In the output shown in Figure 5, PRZM predicts much earlier breakthrough than RZWQM with the original soil profile and again shows more spikes. RZWQM predicts

transport over a much longer period at lower flux levels. When the subsurface profile is switched to high conductivity layers, then RZWQM matches very closely to the PRZM profile. Thus RZWQM could be made to match the much simpler PRZM hydrology by any of the low conductivity layers.

**Table 3. Soil Profile for Georgia site.**

| Horizon | texture | Depth | Thk | BD | porosity | Field Capacity | Wilting Point | Ksat (cm/hr) | oc |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Sandy clay loam | 23 | 23 | 1.75 | 0.34 | 0.217 | 0.1255 | 0.23 | 1.15 |
| 2 | clay | 50 | 27 | 1.63 | 0.385 | 0.287 | 0.2029 | 0.2 | 0.34 |
| 3 | clay | 125 | 75 | 1.63 | 0.385 | 0.302 | 0.2187 | 0.2 | 0.17 |
| 4 | clay | 190 | 65 | 1.7 | 0.358 | 0.337 | 0.240 | 0.1 | 0.12 |
| 5 | clay | 225 | 35 | 1.66 | 0.374 | 0.335 | 0.2388 | 0.2 | 0.10 |

**Table 4. Profile Free draining**

| Horizon | | Depth | Thk | BD | porosity | Field Capacity | Wilting Point | Ksat (cm/hr) | oc |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Sandy clay loam | 23 | 23 | 1.75 | 0.34 | 0.217 | 0.1255 | 0.23 | 1.15 |
| 2 | -- | 50 | 27 | 1.63 | 0.385 | 0.287 | 0.2029 | 21 | 0.34 |
| 3 | -- | 125 | 75 | 1.63 | 0.385 | 0.302 | 0.2187 | 21 | 0.17 |
| 4 | -- | 190 | 65 | 1.7 | 0.358 | 0.337 | 0.240 | 21 | 0.12 |
| 5 | -- | 225 | 35 | 1.66 | 0.374 | 0.335 | 0.2388 | 21 | 0.10 |

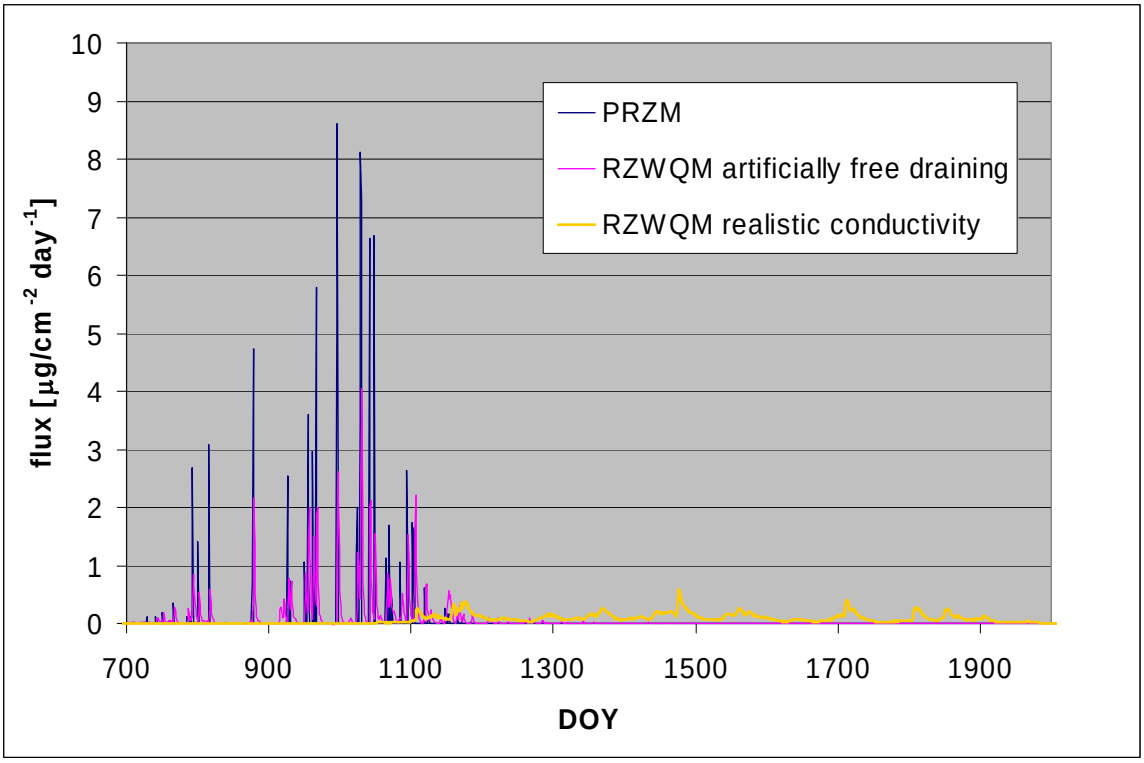


**Figure 5. Predicted flux by RZWQM and PRZM on Tifton Georgia site.**

## E. Proposal to Evaluate Models in the Preliminary Carbamate Cumulative Assessment

Because of the great variability in agricultural landscapes and geology, it is unlikely at this time that any model could accurately predict ground-water concentrations. In predictive modes, model accuracy would not likely be more than an order of magnitude accurate, and various model predictions would likely be both above and below actual ground water concentrations depending on the modeled site. It is important, however, to recognize the variability among the various models in order to understand the possible range of predicted concentrations. EPA thus proposes to use both RZWQM and PRZM over a trial period in order to address this concern and to become familiar with the nuances of both models. When resources permit, LEACHP will also be investigated. For the carbamate assessment, ground water concentrations from both models will be used in order to demonstrate conceptual model variability, and estimated concentrations will be compared against available monitoring data.

Initial scenarios will be developed for both models using the most descriptive inputs available. In this regard, USDA-ARS has been working with the Agency to help parameterize RZWQM, while the Agency is developing equivalent PRZM scenarios. Initial scenarios will be located in vulnerable areas as described in an earlier document. Depth to ground

water may be a critical parameter that needs to be carefully researched, and the Agency is investigating the Canadian and European approaches (PMRA, 2004; FOCUS, 2000). Additionally, the relevant output concentration that would be used in drinking water assessments needs further investigation. Initially, a temporally averaged flux concentration over a time period of several days may be an appropriate choice for a conservative estimate.

## III. Ground-Water Modeling in the Carbamate Drinking Water Exposure Assessment

In addition to the criteria EPA used to evaluate the suitability of the models for estimating pesticide concentrations in ground water (comparisons to monitoring, availability of inputs for the model, ease of use, maintenance, etc.), the models must also address the needs of the cumulative exposure assessment. Despite some differences in the nature of pesticide exposure in ground water as compared to surface water, the requirements of a ground water exposure assessment are similar:

- ❑ account for the potential for any or all of the carbamates included in the cumulative assessment group to occur in ground-water sources of drinking water;

- ❑ take into account those factors (crop uses, pest pressures, timing of application, etc.) that determine whether more than one carbamate pesticide can occur together in time and place;

- ❑ provide a time-series estimate of carbamate residues in ground water that can be incorporated with food and residential exposures in the cumulative exposure assessment.

This section describes the conceptual models on which EPA is basing its ground water exposure assessment and its estimate of co-occurrence. It also describes briefly the assumptions the Agency is using to identify vulnerable ground water exposure scenarios for the carbamate cumulative assessment.

### A. Conceptual Model for Ground Water Source of Drinking Water

The potential for pesticide movement to ground-water sources of drinking water depends on a variety of factors, including hydrologic properties of the overlying soil and vadose zone that affect downward movement of water and chemicals, travel time through the unsaturated zone to ground water, aquifer properties (conductivity, porosity, depth, type, location of recharge area), the leaching potential of the pesticide (persistence and mobility), and the type of well drawing water for drinking purposes (Focazzio et al, 2002). While these factors may vary geographically and cause certain wells in one region to be more vulnerable than those in another region, EPA is basing its ground water exposure assessment on private rural wells drawing its drinking water from a shallow, unconfined aquifer. In general, such drinking water sources tend to be more vulnerable and are more likely to provide health-protective estimates of drinking water exposure.

The estimated exposure in drinking water from these wells is based on the concentration estimated at the top of the aquifer (crossing the aquifer, or water table, plane) and is based on the assumption that the ground water near the top of the unconfined aquifer is most vulnerable to contamination. Several approaches for calculating estimated pesticide concentrations in ground water are used in regulatory contexts (PMRA, 2004). The depth-weighted average approach averages the estimated concentration of the pesticide at the aquifer plane over the top portion of the aquifer (the upper meter, for example). The flux-averaged concentration divides the mass of pesticide that passes the aquifer plane by the volume of water that passes the plane during the same period. EPA proposes using the flux-averaged approach, consistent with PMRA (2004) and the recommendations of FOCUS (2000).

The depth to the top of the unconfined aquifer is an important factor in determining the travel time and estimated concentrations of pesticides reaching ground water. For modeling purposes, the depth to which pesticide concentrations reaching ground water can be estimated depends on the capabilities of the models being used and the availability of data on the vadose zone properties. Given the evaluation of the three leaching models in the previous section, OPP plans to base its estimates on the flux reaching a depth of three (3) meters.

In order to estimate a time-series, EPA will average the flux concentrations over incremental time periods. While surface water exposure estimates modeled by PRZM/EXAMS are reported on daily time steps, a longer time period is likely to be more suitable for ground water exposures, which are less variable temporally. The Agency is evaluating the suitability of time increments ranging from several days to several weeks to produce a time series for use in the cumulative exposure assessment.

## B. Conceptual Model for Co-occurrence in Ground Water

The conceptual model the Agency uses for determining co-occurrence of N-methyl carbamate pesticides in surface water sources of drinking water is based on the amount and timing of pesticide use in the watershed that contributes to the surface water source. County- or multi-county level pesticide use information, based on agricultural chemical use surveys, serves as a surrogate for identifying the potential for co-occurring carbamate uses in the same location. Timing of the applications, along with pesticide persistence and transport characteristics, reflect the relative potential of multiple carbamates to occur together in time. The relative proportions of each carbamate used in the watershed area are based on the amount applied in a given year (a function of application rate and frequency and the crop area treated), pesticide fate and transport

properties that affect the amount of pesticide available at the surface for runoff, the runoff susceptibility of the soil, and the timing, amount, and frequency of rainfall.

While carbamate concentrations in ground water are affected by pesticide use, rainfall, and soil conditions, the response time between an application or leaching event and detection in ground water is not as rapid as it is for surface water. Carbamate concentrations in ground water are less likely to reflect same-season or same-year events. Pesticide fate properties and available monitoring data indicate that several of the N-methyl carbamates in the cumulative group are likely to persist in acidic ground waters. In addition, cumulative exposure in ground water is likely to reflect past as well as current uses.

Available monitoring data, primarily from the USGS NAWQA program, confirm that more than one carbamate in the cumulative action group may occur together in ground water (see the drinking water exposure section of the case study).

Given this information, the Agency believes that co-occurrence in ground water will result when more than one carbamate is used at different times on the same crop, on different crops in rotation on the same fields, or on different crops grown on adjacent fields. Because of lags in travel time and in reported persistence of some carbamate residues in ground water, EPA must consider historical usage in addition to current use on the surface above the aquifer recharge area. The Agency is considering three possible approaches:

- ❑ at one extreme, assume no background residues (drinking water exposures would reflect only what is estimated by modeling), i.e., all residues in GW are “fresh”;

- ❑ at the other extreme, assume a baseline background concentration (based on available monitoring), with model estimates as additions and no decline;

- ❑ in between, include the background levels with model estimates, but provide an estimate of decline in residues over time (estimate based on long-term trends in monitoring)

## C. Selection of Vulnerable Ground Water Scenarios

In both the organophosphate (OP) cumulative assessment and this carbamate cumulative assessment, EPA identified regional drinking water exposure sites for surface water sources of drinking water based on

cumulative pesticide use, location of drinking water intakes, and relative vulnerability of the surrounding watersheds to runoff. The process, which was deemed a valid approach by the FIFRA SAP (2002), identified those areas where high combined cumulative pesticide use coincided with drinking water sources that were particularly vulnerable to runoff. Assuming that the selection accounts for the key factors affecting drinking water vulnerability to pesticide contamination, this functioned as a regional screening assessment in that if the regional cumulative risk assessment finds that exposure in water is not a significant contributor to the overall exposure in that area, it will not be a significant contributor in other areas in the region.

The Agency used a similar approach for identifying the most vulnerable ground-water sources of drinking water. EPA used agricultural chemical usage surveys from two sources – USDA NASS and Doane's – to identify high carbamate usage areas (see Section 5 of the case study for details). The use data represents an average over a 5-year period (1998-2002). EPA adjusted the county-level estimates of pounds of each carbamate by their respective relative potency factors to reflect the areas of greatest use of the most potent of the carbamates.

The Agency used a spatial dataset that describes water use for all the counties in the continental US (USGS, 1998) to select those high use areas where the dominant source of drinking water was from either public supplies served by ground water, or domestic self-supplied drinking water (primarily private wells).

The final step in choosing a location is to assess the vulnerability of drinking water sources within the high usage area within the region. For ground water sources of drinking water, EPA compared relative ground water vulnerabilities of the high carbamate use areas based on a variety of sources, including Nolan et al (2002), USGS NAWQA reports, and USGS Ground Water Atlases.

## IV. References


Ahuja, L.R., K.E. Johnsen, and G.C. Heathman. 1995. Macropore transport of a surface-applied bromide tracer: model evaluation and refinement. *Soil Sci. Soc. Am. J*. 59:1234-1241.

Ahuja, L.R., Rojas, K.W., Hansen, J.D., Shaffer, M.J. and Ma, L. 2000. *Root Zone Water Quality Model,* Water Resources Publications, LLC. Highlands Ranch, CO.

Barbash, J.E., Resek, E.A., 1996. *Pesticides in Groundwater: Distribution, Trends, and Governing Factors*, Ann Arbor Press, Inc, Chelsea, Michigan.

Boesten, J.J. 2004. "Influence of Dispersion Length on Leaching Calculated with PEARL, PELMO, and PRZM for FOCUS Groundwater Scenarios". *Pest Management Science*, 60(10), 971-980.

Carbone, J.P., Havens, P.L., and Warren-Hicks, W. 2002. Validation of Pesticide Root Zone Model: Employing Uncertainty Analyis. *Environmental Toxicology and Chemistry*, 21(8), 1578-1590.

Carsel, R.J., Imhoff, P., Hummel, Cheplick, J., and Donigan, A. 1997. *PRZM 3.1 Users Manual*, National Exposure Research Lab, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia.

Christiansend, J.S., Thorsena, M., Clausena, T., Hansenb, S. and Refsgaardc, J.C. 2004. Modelling of Macropore Flow and Transport Processes at Catchment Scale, *Journal of Hydrology,* 299,136–158

FIFRA SAP. 1997. "Estimating drinking water exposure as a component of the dietary risk assessment." Report from Session 1 of the FIFRA Scientific Advisory Panel Meeting of December 10-11, 1997. FIFRA Scientific Advisory Panel, Office of Science Coordination and Policy, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency. Washington, DC. SAP Report available: http://www.epa.gov/scipoly/sap/1997/December/finaldec.pdf

FIFRA SAP. 1998. "Proposed methods for basin-scale estimation of pesticide concentrations in flowing water and reservoirs for tolerance reassessment." Report from Session 1 of the FIFRA Scientific Advisory Panel Meeting of July 29-30, 1998. FIFRA Scientific Advisory Panel, Office of Science Coordination and Policy, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency. Washington, DC. Background documents and SAP report available: http://www.epa.gov/scipoly/sap/1998/july/finaljul.htm

FIFRA SAP. 1999. "Proposed methods for determining watershed-derived percent crop areas and considerations for applying crop area adjustments to

surface water screening models." Report from Session III of the FIFRA Scientific Advisory Panel Meeting of May 25-27, 1999. FIFRA Scientific Advisory Panel, Office of Science Coordination and Policy, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency. Washington, DC. Background documents and SAP report available: http://www.epa.gov/scipoly/sap/1999/may/final.pdf

FIFRA SAP. 2000. "Progress report on estimating pesticide concentrations in drinking water and assessing water treatment effects on pesticide removal and transformation: a consultation." Report from Session VI of the FIFRA Scientific Advisory Panel Meeting of September 26-29, 2000. FIFRA Scientific Advisory Panel, Office of Science Coordination and Policy, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency. Washington, DC. Background documents and SAP Report 2001-02 available: http://www.epa.gov/scipoly/sap/2000/september/draftwaterdocfinal.pdf

FIFRA SAP. 2001. "Case Study of the Cumulative Risk of 24 Organophosphate Pesticides; Cumulative Risk Assessment Method for Dietary Food Exposure; Cumulative Risk Assessment for Residential Exposure; Cumulative Risk Assessment for Drinking Water; Integrated Cumulative Risk Assessment." Report from Session II of the FIFRA Scientific Advisory Panel Meeting of December 7-8, 2000. FIFRA Scientific Advisory Panel, Office of Science Coordination and Policy, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency. Washington, DC. SAP Report 2001-06. Available: http://www.epa.gov/scipoly/sap/2001/December/

FIFRA SAP. 2002. "Organophosphate Pesticides: Preliminary OP Cumulative Risk Assessment." Report from the FIFRA Scientific Advisory Panel Meeting of February 5-7, 2002. FIFRA Scientific Advisory Panel, Office of Science Coordination and Policy, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency. Washington, DC. SAP Report 2002-01. Available: http://www.epa.gov/scipoly/sap/2002/february/final.pdf

FIFRA SAP. 2004. A Discussion with the FIFRA Scientific Advisory Panel Regarding the Terrestrial and Aquatic Level II Refined Risk Assessment Models (Version 2.0). Environmental Protection Agency. Chapter 4, Section F. March 30 – April 2, 2004. Available: http://www.epa.gov/scipoly/sap/2004/index.htm

Focazio, M.J., T.E. Reilly, M.G. Rupert, and D.R. Helsel. 2002. Assessing ground-water vulnerability to contamination: providing scientifically defensible information for decision makers. US Geological Survey Survey Circular 1224. Available: http://water.usgs.gov/pubs/circ/2002/circ1224/

FOCUS. 2000. FOCUS ground water scenarios in the EU review of active substances. Report of the Groundwater Scenarios Workgroup of FOCUS (FOrum

for the Coordination of pesticide fate models and their USe). EC Document Reference Aanco/321/2000 rev.2, 202pp.

Jones, R.L. and Russell, M.H. 2001. FIFRA Environmental Model Validation Task Force, Final Report, The FIFRA Environmental Model Validation Task Force, American Crop Protection Association, 1156 Fifteenth Street, NW, Suite 400, Washington, DC 20005

Kay, P., Blackwell, P.A., Boxall, A.B.A. 2005. A lysimeter experiment to investigate the leaching of veterinary antibiotics through a clay soil and comparison with field data, *Environmental Pollution*, 134, 333-241.

Malone, R.W., Shipitalo, M.J., Ma, L., Ahuja, L. R., and Rojas, K. W. (2001) Macropore component assessment of the Root Zone Water Quality Model (RZWQM) using no-till soil blocks. Trans. ASAE. 44:843-852.

Nolan, B.T., Bayless, N.E., Green, C.T., Garg, S., Voss, F.D., Lampe, D.C., Barbash, J.E., Bekins, B.A. 2004. *Evaluation of Vadose-Zone Solute-Transport Models for USGS Agricultural Chemical Transport Studies and EPA's Office of Pesticide Programs*. Unpubished report, United State Geological Survey.

Nolan, B.T., K.J. Hitt, and B.C. Ruddy. 2002. Probability of nitrate contamination of recently recharged ground waters in the conterminous United States. Environ. Sci. Tech. 36:2138-2145.

NRCS. 2003. *National Engineering Handbook. Section 4: Hydrology*. National Soil Conservation Service, USDA, Washington DC.

PMRA, 2004. Estimating the Water Component of a Dietary Exposure Assessment. Science Policy Notice SPN2004-01. Pesticide Management Regulatory Agency, Health Canada. Ottawa, Ontario.

Ponce, V.M. and Hawkins, R.H. 1996. Runoff Curve Number: Has it Reached Maturity? *J. of Hydrologic Engineering*, 1(1), 11-19.

Romano, N. and Santini, A. 2002. Chapter 3.3.3 Field, in *Methods of Soil Analysis Part 4 Physical Methods*, ed J.H. Dane and G.C. Topp, Soil Science Society of America Inc, Madison WI

Russell, M.H. and Jones, R.L. 2002. Comparison of Pesticide Root Zone Model 3.12: Leaching Predictions with Field Model. *Environmental Toxicology and Chemistry*, 21(8) 1552-1557.

USEPA. 1999. Estimating the drinking water component of a dietary exposure assessment (revised). US Environmental Protection Agency, Office of Pesticide Programs science policy paper. Federal Register Notice Docket No. OPP-0577A.

Nov. 10, 1999. http://www.epa.gov/fedrgstr/EPA-PEST/1999/November/Day-10/6044.pdf

USEPA. 2000. Drinking water screening level assessment. US Environmental Protection Agency, Office of Pesticide Programs science policy paper. Federal Register Notice Docket No. OPP-00679. Oct. 11, 2000. http://www.epa.gov/oppfead1/trac/science/reservoir.pdf

USEPA. 2001. Water treatment effects on pesticide removal and transformation. US Environmental Protection Agency, Office of Pesticide Programs science policy paper. Federal Register Notice Docket No. OPP-00731. Nov. 21, 2001. http://www.epa.gov/oppfead1/trac/science/water_treatment.pdf

USEPA. 2002. Revised organophosphorus pesticide cumulative risk assessment. US Environmental Protection Agency, Office of Pesticide Programs. Washington, DC. June 10, 2002. http://www.epa.gov/pesticides/cumulative/rra_op

USGS. 1998. Water Use in the United States:U.S. Geological Survey, accessed August 4, 2003, at http://water.usgs.gov/lookup/getspatial?ofr99-78_cowu95

Wilcox, B.P., Rawls, W.J., Brakensiek, D.L., and Wright, R. 1990. Predicting Runoff from Rangeland Catchments, *Water Resources Research*, 26(10), 2401-2410.