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II. PRZM-EXAMS OVERVIEW

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OPP currently uses linked PRZM and EXAMS models for a refined (Tier 2) estimation of pesticide concentrations in surface waters for FQPA drinking water and aquatic exposure assessments.

The standard PRZM-EXAMS runoff modeling scenario is based on a 10 ha field draining into a 1 ha by 2 meter deep small water body. This scenario represents a watershed drainage area:water volume ratio of 5 m²/m³. Each PRZM modeling scenario represents a unique combination of climatic conditions (*e.g.*, rainfall), crop specific management practices, soil specific properties, site specific hydrology, and pesticide specific application and dissipation processes. Each PRZM simulation is conducted for multiple years to provide a probabilistic exposure characterization for a single site.

Daily edge-of-field loadings of pesticides dissolved in runoff waters and sorbed to entrained sediment, as predicted by PRZM, are discharged into a standard small water body simulated by the EXAMS model. The physicochemical properties of the small water body are characteristic of a farm pond in Georgia. Since EXAMS is a steady-state model, the farm-pond volume is maintained at a constant volume (20,000 L). Therefore, the small water body is a closed-system with no outflow. It is assumed the inflow from runoff is exactly balanced by evaporative losses. The EXAMS model accounts for volatilization, sorption, hydrolysis, biodegradation, and photolysis of the pesticide.

Multiple-year pesticide concentrations in the water column are extracted from the simulation as the annual daily peak, maximum annual 96-hour average, maximum annual 21-day average, maximum annual 60-day average, and annual average. The upper 10th percentile concentrations (except annual average) are used to compare against ecotoxicological and human health levels of concern (LOC).

The PRZM and EXAMS models are described below according to user's manuals and personal communications with model developers (Larry Burns, 6/98).

Pesticide Root Zone Model (PRZM), Version 3.12

Introduction

PRZM3.12 is a USEPA Model for predicting pesticide fate in the crop root and unsaturated Soil Zones. PRZM3.12 simulates the transport of field-applied pesticides in the crop root zone and the vadose zone taking into account the effects of agricultural management practices. The model provides a means to estimate of probable exposure concentrations by taking into account the variability and the uncertainties in system properties and processes.

PRZM3.12 links two models, PRZM and VADOFT, to predict pesticide transport and transformation down through the crop root zone, and vadose (unsaturated) zone to the water table. PRZM3.12 has the option to incorporate soil temperature simulation, volatilization and vapor phase transport in soils, irrigation simulation, and microbial transformation.

The overviews presented below are grouped into three sections: PRZM for simulating the root zone, VADOFT for simulating the vadose zone, and Monte Carlo pre- and post-processors for addressing the uncertainty natures of model parameters.

PRZM Overview

The Pesticide Root Zone Model (PRZM) is a one-dimensional, dynamic, compartmental model that can be used to simulate chemical movement in unsaturated soil systems within and immediately below the plant root zone. It has two major components: hydrology (including hydraulics) and chemical transport. The hydrologic component for calculating runoff and erosion is based on the Soil Conservation Service curve number technique and the Universal Soil Loss Equation. Evapotranspiration is estimated either directly from pan evaporation data, or based on an empirical formula. Total evapotranspiration is divided among evaporation from crop interception, evaporation from soil, and transpiration by the crop. Water movement is simulated by the use of generalized soil parameters, including field capacity, wilting point, and saturation water content. The chemical transport component can simulate pesticide application on the soil or on the plant foliage. With a newly added feature, biodegradation can also be considered in the root zone. Dissolved, adsorbed, and vapor-phase concentrations in the soil are estimated by simultaneously considering the processes of pesticide uptake by plants, surface runoff, erosion, decay, volatilization, foliar washoff, advection, dispersion, and retardation. Two options are available to solve the transport equations: (1) The original backwards-difference implicit scheme that may be affected by excessive numerical dispersion at high Peclet numbers, or (2) The method of characteristics algorithm that eliminates numerical dispersion while slightly increasing model execution time.

PRZM has the capability to simulate multiple zones. This allows PRZM and VADOFT to combine different root zone and vadose zone characteristics into a single simulation. Zones can be visualized as multiple land segments joined together in a horizontal manner. There are three reasons a choosing multiple zones:

- (1) to simulate heterogeneous PRZM root zones with a homogeneous vadose zone
- (2) to simulate a homogeneous root zone with heterogeneous vadose zones
- (3) to simulate multiple homogeneous root zones with multiple homogeneous vadose zones

PRZM3.12 can simulate as many as three chemicals simultaneously as separate compounds or as a parent-daughter relationship. The user can observe the effects of multiple chemicals without making additional runs or the ability to enter a mass transformation factor from a parent chemical to one or two daughter products.

Predictions are made on a daily basis. Output can be summarized for a daily, monthly, or annual period. Daily time series values of various fluxes or storages can be written to sequential files during program execution for subsequent analysis.

VADOFT Overview

VADOFT is a finite-element model incorporating Richard's equation for simulating water movement and solute transport in the vadose zone. It is the second part of the two-component PRZM3.12 model for predicting the movement of pesticides within and below the plant root zone and assessing subsequent groundwater contamination. The VADOFT code simulates one-dimensional, single-phase water and solute transport in unconfined, variably saturated porous media. Transport processes include hydrodynamic dispersion, advection, and linear equilibrium sorption. Pesticide degradation is described using a first-order decay model. The code predicts infiltration or recharge rate and solute mass flux entering the saturated zone.

The code, which employs the Galerkin finite-element technique to approximate the governing equations for flow and transport, allows for a wide range of nonlinear flow conditions. Boundary conditions of the variably saturated flow problems may be specified in terms of prescribed pressure head or prescribed volumetric water flux per unit area. Boundary conditions of the solute transport problem may be specified in terms of prescribed concentration or prescribed solute mass flux per unit area. All boundary conditions may be time dependent. An important feature of the algorithm is the use of constitutive relationships for soil water characteristic curves based on soil texture.

Monte Carlo Overview

MCARLO performs all the functions necessary to execute a Monte Carlo simulation. It reads special data for parameters to be varied (e.g., distribution types and moments) and output variables to be observed, generates random numbers, correlates them and performs transformations, exchanges these generated values for PRZM3.12 parameters, performs statistical analysis on the output variables, and writes out statistical summaries for the output variables.

The MCARLO module makes use of an input and output files. Many of the parameters entered in the MCARLO input file, previously once designated as constants, will be used in lieu of that same parameter value entered in the standard input file. A small number of input variables may be changed at random by invoking the Monte Carlo routines.

PRZM3.12 can be run in a Monte Carlo mode so that probabilistic estimates of pesticide loadings to the saturated zone from the source area can be made. The input preprocessor allows the user to select distributions for key parameters from a variety of distributions: The Johnson family (which includes the normal and log-normal); Uniform; Exponential; and Empirical. If the user selects distributions from the Johnson family, correlations between the input parameters may be specified. The Monte Carlo processor reads the standard deterministic input data sets for each model, then reads a Monte Carlo input file that specifies which parameters are to be allowed to vary, their distributions, and correlation matrix. The model then executes a pre specified number of runs.

The output processor is capable of preparing statistics of the specified output variables including mean/maximum values and quantiles of the output distribution. The output processor also can tabulate cumulative frequency histograms of the output variables and send them to a line printer for plotting.

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Exposure Analysis Modeling System (EXAMS), Version 2.97

Introduction

The Exposure Analysis Modeling System provides interactive computer software for formulating aquatic ecosystem models and rapidly evaluating the fate, transport, and exposure concentrations of organic chemicals-pesticides, industrial materials, and leachates from disposal sites. EXAMS contains an integrated Database Management System (DBMS) specifically designed for storage and management of project databases required by the software. User interaction is provided by a full-featured Command Line Interface (CLI, context-sensitive help menus, an on-line data directory and CLI users) guide, and plotting capabilities for review of output data. EXAMS provides 20 output tables which both document the input databases and provide integrated results summaries to aid in ecological risk assessment.

EXAMS' core is a set of process modules that link fundamental chemical properties to the limnological parameters that control the kinetics of fate and transport in aquatic systems. The chemical properties are measured by conventional laboratory methods, which are required under various regulatory authority. EXAMS' limnological data are composed of elements historically of interest to aquatic scientists world-wide, so generation of suitable environmental datasets can generally be accomplished with minimal project-specific field investigations.

EXAMS provides facilities for long-term (steady-state) analysis of chronic chemical discharges, initial-value approaches for study of short-term chemical releases, and full kinetic simulations that allow for monthly variation in mean climatological parameters and alteration of chemical loadings on daily time scales. EXAMS has been written in generalized (N-dimensional) form in its implementation of the algorithms representing spatial detail and chemical degradation pathways. EXAMS provides analyses of

- ! exposure: the expected environmental concentrations (EECs) resulting from a particular pattern of chemical loadings;
- ! fate: the distribution of the chemical in the system and the fraction of the loadings consumed by each transport and transformation process; and
- ! persistence: the time required for purification of the system (via export/transformation processes) should the chemical loadings cease.

Input and Output

Input parameters include

- ! A set of chemical loadings on each sector of the ecosystem.
- ! Molecular weight, solubility, and ionization constants of the compound.
- ! Sediment-sorption and biosorption parameters: K_p , K_{oc} or K_{ow} , biomasses, benthic water contents and bulk densities, suspended sediment concentrations, sediment organic carbon, and ion exchange capacities.
- ! Volatilization parameters: Henry's Law constant or vapor pressure data, wind speeds, and re-aeration rates.
- ! Photolysis parameters: reaction quantum yields, absorption spectra, stratospheric ozone, cloudiness, relative humidity, atmospheric dust content and air-mass type, scattering parameters, suspended sediments, chlorophyll, and dissolved organic carbon.
- ! Hydrolysis: second-order rate constants or Arrhenius functions for the relevant molecular species, pH, pOH, and temperatures.
- ! Oxidation: rate constants, temperatures, surface oxidant concentrations, dissolved organic carbon, and oxygen tension.
- ! Biotransformation: rate constants, temperatures, bacterial population densities.
- ! Parameters defining strength and direction of advective and dispersive transport pathways.
- ! System geometry and hydrology: volumes, areas, depths, rainfall, evaporation rates, entering stream and non-point-source flows and sediment loads, and ground-water flows.

Although EXAMS allows for the entry of extensive environmental data, the program can be run with a much reduced data set when the chemistry of a compound of interest precludes some of the transformation processes. For example, pH and pOH data can be omitted in the case of neutral organics that are not subject to acid or alkaline hydrolysis. EXAMS produces 20 output tables; these include an echo of the input data, and integrated analyses of the exposure, fate, and persistence of the chemical or chemicals under study. The program prints a summary report of the results obtained. Printer plots of longitudinal and vertical concentration profiles, as well as time-based graphics, can be used by the user.

System Resource Requirements

EXAMS has been implemented in FORTRAN90. The currently available MS-DOS version of EXAMS was compiled under Lahey FORTRAN90 v. 4.5b. The program requires available DOS memory of 407 Kbytes to load plus 32Kb for program operations; its size thus precludes co-residence with some PC "TSR" (terminate and stay resident) programs. EXAMS is overlaid to run in the DOS environment but, after reserving its 32 Kb for program operations, will establish memory caches in available extended memory space to minimize disk I/O overhead.

Applications and Validation

EXAMS can be used to assess the fate, exposure, and persistence of synthetic organic chemicals in aquatic ecosystems in which the chemical loadings can be time-averaged or event loaded, and chemical residuals are at trace levels. The program has been used, for example, by EPA to evaluate the behavior of relatively field-persistent herbicides and to evaluate dioxin contamination downstream from paper mills. EXAMS has been successfully used to model chemodynamics of organics in field situations (Games 1982, 1983, Plane et al. 1987, Pollard and Hern 1985, Reinert and Rodgers 1986, Reinert et al. 1987, Sanders and Seiber 1984, Schramm et al. 1988), for a general assessment of the behavior of phthalate esters in aquatic systems (Wolfe et al. 1980), and in microcosm studies (Staples et al. 1983). EXAMS has been implemented by numerous manufacturing firms for environmental evaluations of newly synthesized materials and has been used in an academic setting for both teaching and research.

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Documentation and Software Availability

The computer program for version 2.97.5 of the Exposure Analysis Modeling System II (EXAMS-II, v. 2.97) is available gratis from the U.S. Environmental Protection Agency. A separate user manual is provided with the program; additional technical documentation for the program is available from the National Technical Information Service (NTIS) in the publication *Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation* (EPA-600/3-82-023, NTIS PB 82 258096 (US \$34.00)) The given price is for purchasers on the

North American continent, who can obtain the document from the U.S. Department of Commerce, National Technical Information Service, Springfield, Virginia 22161 USA. NTIS also maintains overseas depositories for the convenience of non-USA organizations wishing to acquire their publications.

The EXAMS computer program can be obtained from the author at the address given above. The program is supplied on a microcomputer diskette containing an MS-DOS executable image for use on an IBM PC or "compatible." The PC/MS-DOS run-time version requires a microcomputer (IBM-PC or "Compatible") with at least 512 kilobytes of RAM (Random Access Memory), 3.5-inch diskette drive, and mass-storage device (5+ megabyte hard disk). The EXAMS executable image runs under MS-DOS 2.12+ on the Intel 8086 chip family (including DOS instances under Windows 3.1 or Windows 95/98); note that a Fortran compiler is not needed. In addition, the software is available through the Center for Exposure Assessment Modeling (CEAM) bulletin board system. The CEAM can be accessed at no charge at <http://www://epa.gov/ceam>.

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