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Fate and Exposure Modeling in Terrestrial Ecosystems: A Process Approach

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ABSTRACT

Pathways for exposure of birds to pesticides include soil, water, air, soil-dwelling organisms, and insects. A process approach to avian exposure calculates transport and transformation of agricultural chemicals through each of the exposure media. Differential equations calculating the time rate of change of chemical in each exposure medium are solved in this approach. Development of terrestrial exposure algorithms at the United States Environmental Protection Agency (U.S. EPA), Environmental Research Laboratory, Athens, GA, draws on validated technology where well-established methodologies do not exist.

Multimedia process models are data intensive. An integral part of developing a usable and useful exposure calculation framework is the incorporation of supporting databases in the system. Supporting data for soils, meteorology, crops and cropping scenarios, and species distribution data are being developed on a regional scale based on the 186 major land resource areas (MLRA) defined by the United States Department of Agriculture (USDA).

This chapter further describes the process-oriented, mechanistically based approach to avian exposure calculations, the supporting databases required for doing regional analyses, and the interactive system design for accessing this information.

KEY WORDS

exposure assessment, pesticide transport, process modeling

INTRODUCTION

Relating the pesticide exposure pattern of birds to environmental characteristics of the toxic chemicals involved is a prerequisite for predicting the long-term response patterns of avian populations. Direct measurement of the exposure of birds in a field situation is costly, and only a limited number of exposure scenarios will likely ever be evaluated in this manner. Extrapolation techniques in the form of mathematical models are required to supplement field and laboratory studies in performing comprehensive environmental exposure assessments and assisting in the choice of critical field tests.

Pathways for exposure of birds to pesticides include soil, water, air, soil-dwelling organisms, plants, and insects. Transport and transformation of agricultural chemicals through each of the exposure media, coupled with the behavioral and physiological attributes of the bird, determine the ultimate exposure patterns in a field situation. TEEAM, described by Dean et al.,[1] used a process-based approach in looking at the fate of pesticides in the physical environment and their ultimate movement into the biota. Processes originally represented in TEEAM included behavior of the spray, water, and pesticide movement in the soil; evapotranspiration and volatilization; plant growth and uptake; bioconcentration in soil organisms; and ingestion and inhalation by terrestrial vertebrates. The TEEAM project provided the initial prototype for a terrestrial exposure system that will be incorporated into the Pesticide and Industrial Chemical Risk Analysis and Hazard Assessment (PIRANHA)[2] modeling system. The current components of the PIRANHA system provide an exposure assessment methodology for aquatic systems.

The general approach of the PIRANHA system models is to combine the loadings, transport, and transformation of a chemical into a set of differential equations using the law of conservation of mass as an accounting principle. Generally, the process descriptions for transport of chemicals between environmental compartments and transformation of chemicals within those compartments are based on process-oriented mechanistic constructs or accepted empirical relationships. The discussion in this chapter describes the components to be incorporated into the PIRANHA system as part of the U.S. EPA EcoRisk program, which will expand the methodology to terrestrial exposure assessments.

SYSTEM ARCHITECTURE

Exposure assessment within PIRANHA is structured as a series of stand-alone programs linked together by input and output files. The modules are based on well-developed and tested technology. The terrestrial exposure algorithm structure is a series of four stand-alone components: (1) spray drift and deposition, (2) terrestrial exposure media, (3) surface water, and (4) avian exposure, which are linked as illustrated in Figure 1. The spray drift and deposition component provides the spray deposition on habitats and spray day inhalation concentrations. The terrestrial exposure media com-

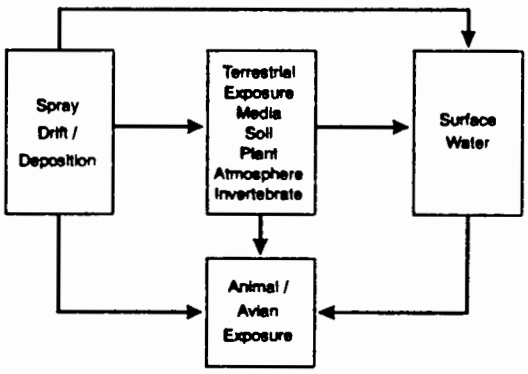

FIGURE 1. Architecture of a terrestrial exposure modeling system depicting the interactions between spray drift and deposition, terrestrial exposure media (soil, plants, invertebrates), surface water, and avian uptake.

ponent calculates the residues (soil, plants, invertebrates) to which the avian species may be exposed. The surface water component provides exposure concentrations via the drinking water.

There are several advantages to developing the terrestrial exposure system in this modular format. The primary advantage is the ability to incorporate updated versions of components easily and with a reduced risk of introducing errors in the integration process. Thus, the user can be confident that the validity of the components is not compromised in the transfer process and that the most recent versions of each component are included in the package. Finally, a major emphasis in the PIRANHA development is the linkage of the models to input databases. The mechanistic approach is data intensive and use of the process modeling approach outside of a research environment requires direct user access to parameter databases in developing input scenarios.

APPLICATION AND DEPOSITION

Evaluating the dynamics of toxicant application and deposition is the first step in determining the fate of pesticides. Pesticides are introduced in several ways: spray application to foliage or soil surfaces, incorporation into the soil, or deposition as time release granules or on seeds treated prior to planting. The type of initial application plays a large role in the type of environmental threat a pesticide may represent. Spray applications may contaminate offsite wildlife habitat; treated seeds or granules may provide a highly concentrated source of pesticide if ingested.

TEEAM used the USDA-Forest Service Spray Drift Model, FSCBG, to estimate deposition and offsite drift from aerial spray applications,[3] and the recent release, FSCBG 4.0, is a candidate for inclusion in PIRANHA. Offsite drift is a function of a variety of factors including aircraft type, speed, and application altitude; type and configuration of spray nozzles; weather conditions; and chemical formulation. Spray drift model algorithms calculate the spatial distribution of pesticide in the canopy and on the soil surface and, in addition, provide an estimate of the aerosol concentration that can be used to estimate inhalation dosage that could occur during the spray.

Wind tunnel tests provide the droplet size spectra, the most important equipment parameter, for spray nozzles under different application conditions. One of the biggest limitations in parameterizing spray drift models is estimating local meteorological conditions. Turbulence (i.e., atmospheric stability) is the most difficult model feature to accurately parameterize and lends the greatest uncertainty in modeling pesticide drift.

Two candidate spray drift models for inclusion in the PIRANHA system are FSCBG 4.0, the updated USDA-Forest Service model, and the Dow-Elanco spray drift model. Model testing efforts for FSCBG 4.0 have been reported previously,[4-6] but have not been oriented to performing exposure assessments. The Dow-Elanco model contains a more simplified algorithm for near-aircraft spray behavior and is simpler to parameterize. Both models require additional testing for use within a regulatory context. The spray drift model selection for incorporation within the PIRANHA system is coordinated with the spray drift task force, an industry coalition developing drift analysis tools for regulatory evaluations.

In addition to simulating aerial spray drift, pesticide application in the soil/plant component can be specified by the user as a direct application to the canopy, application to the soil surface, incorporation to a specified depth of the soil, or release from granules or treated seeds.

TRANSPORT AND TRANSFORMATION IN SOIL

Following application, a combination of chemical properties, soil properties, cropping practices, and meteorological conditions interact to determine whether a chemical will move into surface water via runoff and erosion, leach into the groundwater, volatilize into the atmosphere, move into the food chain via plants and soil-dwelling organisms, or degrade in the soil surface layers.

The Pesticide Root Zone Model (PRZM) forms the basis in TEEAM for calculating soil-associated movement of the pesticide.[7] PRZM is a one-dimensional compartmental model for use in simulating vertical chemical movement in unsaturated soil systems within and immediately below the plant root zone. PRZM processes are illustrated in Figure 2. PRZM allows the user to simulate movement of potentially toxic chemicals, particularly pesticides, that are applied to the soil or to plant foliage. Dynamic simulations allow the consideration of pulse loads, the prediction of peak events, and the estimation of time-varying mass emission or concentration profiles.

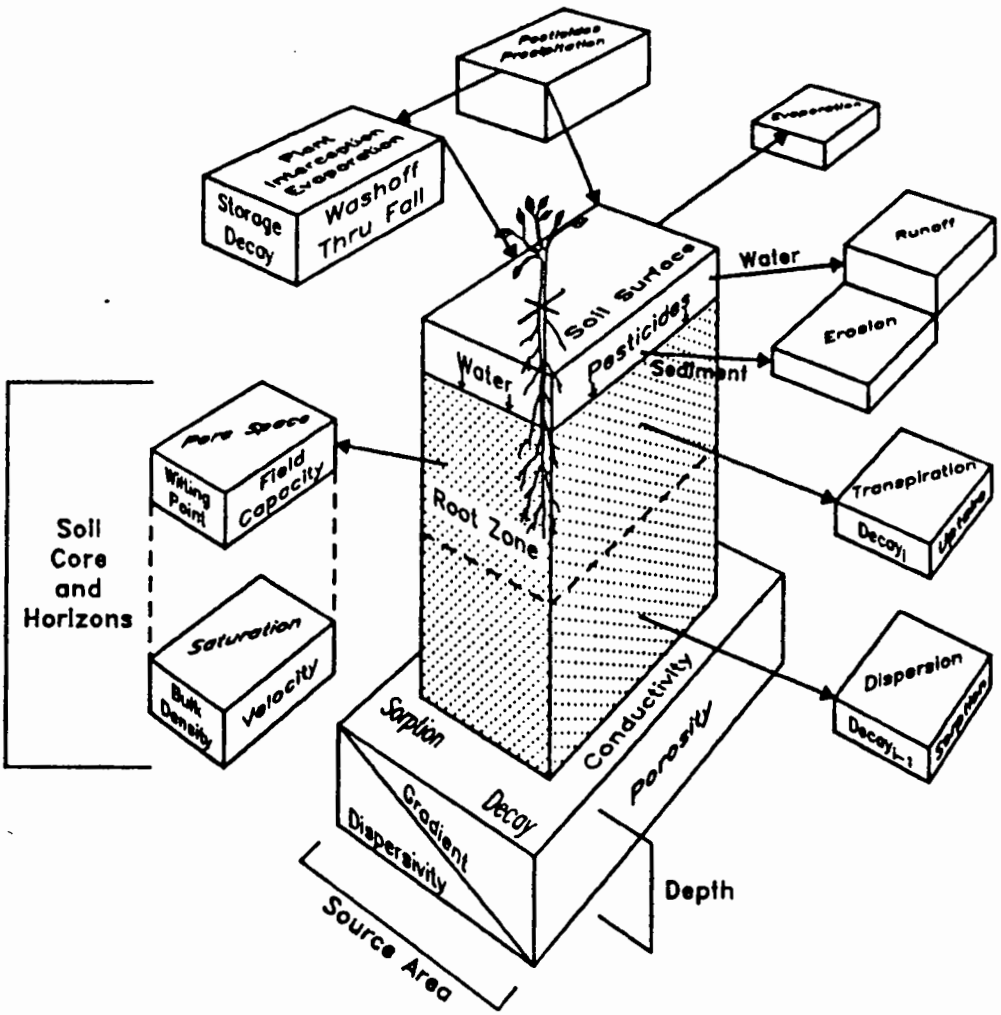

FIGURE 2. Process included in the pesticide root zone model (PRZM).

PRZM has two major components: hydrology 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 from pan evaporation data, or by an empirical formula if input pan data are unavailable. 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. Irrigation also may be considered. 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. Detailed descriptions of equation development, numerical solution techniques, and input variables may be found in the PRZM user's manual.[7]

PRZM performs calculations on a daily time step returning daily values of adsorbed, dissolved, and vapor phase pesticide concentrations in vertical soil layers; runoff volume and pesticide concentration in the runoff; eroded soil volume and pesticide concentration in the eroded particles; and volatilization loss from the soil surface and under canopy vapor concentrations. PRZM has been applied extensively and tested against field data.[8-10]

TRANSPORT AND TRANSFORMATION IN PLANTS

Exposure of plants to pesticide can occur either through direct application to the foliage or uptake of pesticide from the soil. On plants, the pesticide may wash off the leaf surface, photodegrade, or move into the plant cells and be translocated throughout the plant. Pesticides in soil water adsorb to root surfaces and move into the aboveground plant parts in the transpiration stream. The chemical may be either degraded by the plant or lost through the stomata to the atmosphere. Following application, pesticide concentrations in plants decline not only due to washoff, degradation, and volatilization but also due to growth dilution.

The plant growth simulations are based on the plant growth algorithm found in the USDA model EPIC.[11] Crop growth is calculated using crop-specific factors such as maximum leaf area index, heat units required for crop maturity, energy conversion efficiency, and optimal growth temperature along with environmental parameters such as solar radiation, temperature, and available water. Crop growth models for corn, wheat, soybeans, and other major field crops are relatively well developed and parameterized.

Uptake of pesticide from the soil and translocation into aboveground plant parts are simulated using a simple compartment model (Figure 3) applicable to neutral organic molecules passively transported by the plant. Uptake by the plant roots is parameterized based on studies[12] for a series of organic molecules with log K_{ow} values ranging from 1.2 to 5.0.

Individual components of the soil-plant transport system have been tested independently, and the combined system has been recently tested using field data.[10]

DRINKING WATER EXPOSURE

Drinking water exposure of birds to pesticides can be considered through two routes. When the soil surface layer is saturated following a rainstorm, this surface soil water is

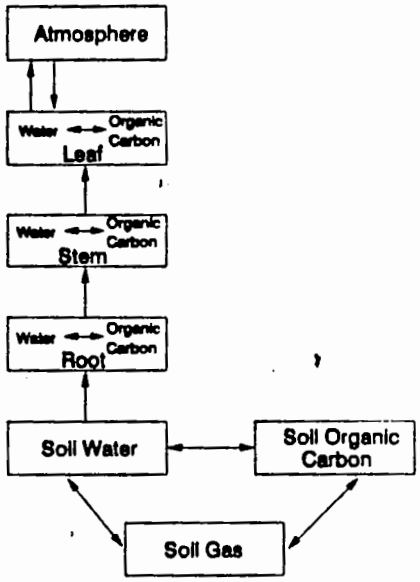

FIGURE 3. A simple compartment model simulating uptake of xylem-transported pesticides from the soil and translocation into aboveground plant parts.

assumed to be available to the bird. Additionally, they may drink from ponds or streams adjacent to treated areas.

EXAMS[13] is used to calculate pesticide concentration in streams or ponds. This model combines the loadings, transport, and transformations of a chemical in the body of water into a set of differential equations using the laws of mass balance. Loadings to the water body are measured from the runoff/erosion calculations of PRZM and direct deposition to the body of water. The chemical kinetics expressions in EXAMS are second order descriptions for transformations attributable to direct photolysis, hydrolysis, biolysis, and oxidation reactions. The model input has been designed to accept standard water quality parameters and system characteristics along with chemical data sets required by EPA regulatory procedures.

TERRESTRIAL FOOD CHAIN

The simulation of pesticide movement in soil, plant, air, and water provide the media concentrations for uptake by ecosystem fauna. Once environmental concentrations of toxicants are known, the behavior and physiology of the individual species interact to determine uptake and accumulation of the pesticide.

A simple Markov transition matrix is used to specify movement of animals between environmental compartments. Soil organisms are allowed to move vertically between soil horizons while aboveground dwellers move among the laterally defined habitats. For each organism, an $M \times M$ transition matrix is specified where M is the number of possible locations (horizons or habitats), and the transition probability specified within the matrix is the probability that an animal in a given location will move to a specific location given its current location.

Formulation of equations to describe the uptake and accumulation of chemicals in birds and other aboveground dwellers based on easily defined chemical properties and organism physiology is the ultimate goal for the development of uptake and exposure

algorithms. The pharmacokinetic approach used in the development of the Food and Gill Exchange of Toxic Substances (FGETS) model[14] to simulate accumulation of neutral organics in fish serves as a prototype for estimating accumulation in terrestrial species. An exposure model must be able to calculate internal concentrations to evaluate impacts of time-varying dosages of the contaminant before extrapolations can be made to population-level impacts. The original approach to modeling the uptake of pesticides in TEEAM incorporated a calibration factor, often referred to as an assimilation efficiency factor, to parameterize the amount of material retained in an organism following ingestion. A soil organism module recently developed for inclusion uses this physiological approach.

Soil-dwelling organisms are assumed to remain in a single lateral habitat but may move vertically between soil horizons. Initial development and testing of the uptake by soil-dwelling organisms has centered on earthworms. Uptake of pesticide may be through ingestion of soil material or diffusion of dissolved pesticide though the integument.

The two routes of uptake by the earthworm are illustrated in Figure 4. Chemical dissolved in the soil water solution diffuses through the cuticle. Chemical ingested with soil and litter is assumed to equilibrate between the gut and body of the worm as the material passes through the worm's digestive tract. Equilibration is controlled by the organic matter content of the soil and of the worm. Concentration in the organism may decrease due to internal degradation and growth dilution. As of this writing, the formulation is applicable only to neutral hydrophobic molecules, but plans are to expand it to accommodate polar and ionic compounds.

A substantial database exists on accumulation of toxicants in earthworms because they are an economically important species in agroecosystems as well as being an important food source for many species of birds. Both model and field data indicate that uptake of chemicals by earthworms is relatively rapid, with concentrations equili-

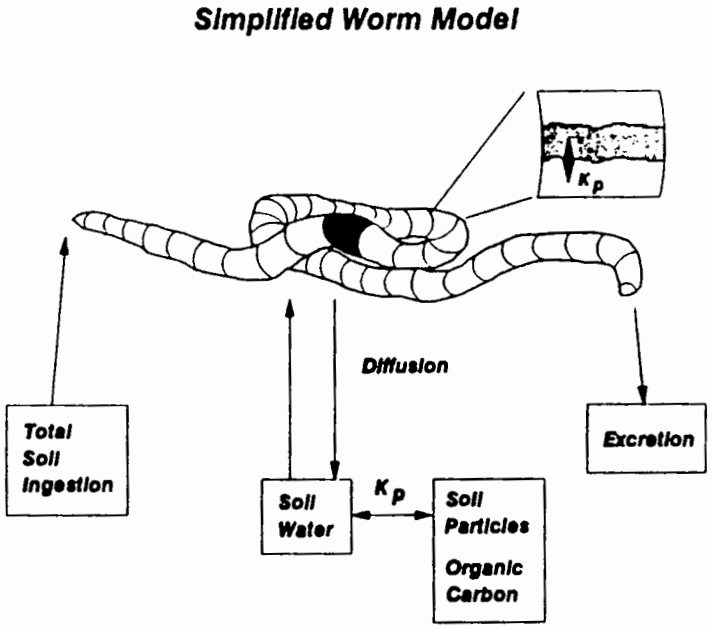

FIGURE 4. Routes of uptake by the earthworm where K_p is the partitioning coefficient of chemical between organic carbon and water.

brating within the worm in 10 to 20 days with a three- to tenfold organism concentration relative to soil concentration.

Aboveground organisms may move between different lateral habitats and take in pesticide from a variety of sources including water, air, plants, soil, pesticide granules, and prey. Daily drinking volumes and respiratory volumes are combined with water and air concentrations, respectively, to calculate dosage via the water and inhalation routes.

Total daily feeding rates along with preference factors for each food source are combined with each food type to calculate dosage via ingestion. In addition to food (plants, soil organisms, and prey animals), soil, pesticide granules, and coated seeds may be ingested. Capture of prey by a predator is simulated by basing capture on the probability that predator and prey are in the same habitat and a probability of capture for each predator/prey pair.

Development of a pharmacokinetic approach to estimating internal organism concentrations for bird is a precondition for adequately predicting impacts of field exposures on birds. Previous bioaccumulation modeling for birds[1] used an empirical assimilation factor, which has limited use in extrapolating between conditions, individuals, and species. The pharmacokinetic approach analogous to that used in FGETS, based on physiology of the organism and the properties of the chemical, is necessary to adequately predict the impact on a mixed population under multiple stresses.

INPUT DATA GENERATION

The input data requirements for performing mechanistic-based exposure calculations are extensive and include soil characteristics, chemical properties, crop and cropping practice information, meteorological conditions, animal behavior and physiology, and food chain interactions. Development of a utilitarian tool requires linkage of the model to databases for development of user input sequences. The PRZM Input Collator, Version 1.0 (PIC:V1)[15] is the first step in developing a comprehensive database support system for all elements of a terrestrial exposure system.

The geographical data in PIC:V1 are organized based on the 186 MLRAs defined by the U.S. Soil Conservation Service.[16] The delineation of MLRAs is based primarily on soils, climate, and hydrology of individual regions. The county-scale soil and crop data contained in NSSAD/SIRS (National Soil Survey Area Database/Soil Interpretations Record Database)[17] was overlaid onto the MLRA scale data.

PIC:V1 allows the user to enter the data generator by selecting either a crop or an MLRA. If a crop is selected, the program returns a list of MLRAs where this crop is potentially grown for user selection. Alternately, if an MLRA entry is selected, the program returns the list of potential crops grown in that area.

Based on crop and region selected, a list of soil names sorted by areal extent in the MLRA is returned to the user along with the number of hectares of the particular soil, hydrologic group, and soil textural class. The user then simply selects the soil of interest for input generation.

Selection of the MLRA also identifies the appropriate first order National Oceanic and Atmospheric Association (NOAA) meteorological station for the area. PIC:V1 contains a utility that allows the user to review 20 to 30 years of rainfall records to easily identify a specified 30-day period of interest. The user can then select the application date that represents the critical period for a particular evaluation.

Selection of the crop, MLRA, and soil specifies all PRZM input variables except the chemical properties and application scenarios. PIC:V1 requests input of the chemical

properties and application parameters. Following specification of these parameters, a PRZM input sequence is generated.

Incorporation of additional databases including information such as plant growth parameters, feeding rates and food preferences, physiological parameters, and aircraft and spray nozzle characteristics will expand preprocessing to exposure calculation for terrestrial species. Development of typical farm pond scenarios within each MLRA for use with the EXAMS model is an additional component of the PIRANHA system.

Specific scenario generation is another approach to increasing model accessibility. This approach has been successfully used in the inclusion of the canonical series developed for use with the EXAMS model.

MODEL VALIDATION

Mathematical models and computer simulation codes designed to aid in risk assessment must be verified and validated before they can be used with confidence in a decisionmaking context. The builders and users of ecological models are rightfully concerned that the models be valid, because decisions based on them have significant economic, public health, and ecological consequences. Structuring a system such as PIRANHA to incorporate, where available, developed technological components (e.g., EXAMS and PRZM), each characterized by a substantial history of validation testing and maintained to the extent possible in a stand-alone context—allows the package to be updated easily as the components are updated, with reduced risk of introducing errors in the process.

Individual process models developed for incorporation in PIRANHA must be subjected to validation testing. In addition to process-level testing, the model as a whole must be evaluated. This overall system testing includes use of the databases and parameter estimation or measurement techniques when the model is used in a risk assessment context. This level of validation will be an integral part of the continuing development of the terrestrial exposure model.

One of the difficulties in evaluating terrestrial exposure, whether through models or through field-based evaluations, is the lack of local homogeneity of the soil medium itself, of the pesticide distribution in the system, and of the population of organisms. The potential variability of pesticide concentration must be considered as it moves through all the components of the system. Model results must be evaluated within the context of this concentration variability. Field studies for use in testing model validity must be carefully designed with consideration for this sample variability.[10]

Objective criteria for model validity must be defined. Models are, due to inherent assumptions, incapable of predicting exactly the "true" values and can only be expected to get close to them. A model's validity must be considered in the context of producing values that are sufficiently close to true values. Hence, defining what is meant by "sufficiently close" in the context of the user's application is the essence of model validity. One way to pose the model validity question is using a criterion statement of the form of whether the model is capable of predicting within a factor (e.g., 2) of the true value in a given application context. This type of statement can be easily translated into a hypothesis statement that can be subjected to statistical tests.

SUMMARY

Calculating the exposure of terrestrial biota to pesticides is the first step in evaluating possible ecological impacts from the application of these pesticides in terrestrial sys-

tems. A series of models that calculate transport of pesticides in the exposure media and into the terrestrial biota is necessary in developing population effects modeling of field applications. In addition to algorithm development, parameter estimation utilities and validation testing are key requirements for success of a terrestrial exposure model in a risk assessment framework and use in a regulatory setting.

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Terrestrial Pollution Avian Exposure Fate Modeling		

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