NONLINEAR MODEL FOR PESTICIDE ACCUMULATION IN SELECTED ESTUARINE SPECIES

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ABSTRACT


Extensive testing has shown that pesticides, such as Kepone and endrin, are rapidly accumulated by estuarine animals from water, food, or sediment. After initial uptake, a pesticide can depurate rapidly or slowly, depending on its chemical composition, the test species, and temperature. Chemicals that depurate slowly can threaten aquatic animals and man in their movement through aquatic food webs. Simulated aquatic exposures of Kepone and endrin to estuarine shrimp and crabs were used to test our nonlinear statistical models for pesticide uptake, equilibrium, and depuration. The models describe biological data as a single equation, thus allowing variations due to many physical, chemical, biological, and random error factors to be analyzed simultaneously.

INTRODUCTION

Aquatic animals accumulate and depurate pesticides at varying rates due to their unique characteristics, length of exposure, temperature, and sources of contamination. Laboratory studies complement field surveys by determining the degree to which physical, chemical, and biological factors influence these rates; thus allowing optimization of field survey methods for greater return per unit effort. Often, pesticides are available to aquatic animals from water, food, and sediments; each species is impacted differently due to ventilation rates and feeding habits (whether the animal is planktonic or pelagic, burrows or ingests sediment). Variability in laboratory and field survey data caused by these factors can obscure trends and limit full utilization of pesticide residue data.

Several investigators (Blau and Neely, 1975; Branson et al., 1975) describe methods of analyzing laboratory-derived fish residue data, using kinetic models and in which exposure concentrations in water are closely monitored. With minimal uptake data, these kinetic models can accurately predict equilibrium residues in freshwater fish. However, their use for invertebrate residue data has yet to be demonstrated. When field residue data (exposure concentrations, length of exposure, temperature, pH, and salinity) are not known, several representative invertebrate and vertebrate species should be sampled or tested. Time-series analyses of residues obtained from laboratory depuration of field-exposed animals are valuable in determining how long biota will retain a chemical.

There has long been a need for a method to analyze field and laboratory uptake and depuration data, so differences in exposure concentration, species, size-class, or route of uptake in estuarine animals, could be statistically examined. Therefore, we developed a generalized mathematical equation that: 1) describes the available data and delineates rates; 2) describes uptake from water, food, or sediments; 3) describes uptake singly; 4) describes depuration singly; 5) describes uptake and depuration simultaneously. The equation is expandable to multidimensions (describing uptake and depuration simultaneously by a species exposed to several concentrations, or describing uptake and depuration simultaneously by one or several species exposed to one or several pesticides). The resulting one equation nonlinear statistical model was estimated by the SAS NLIN procedure.

METHODS

Model-Building Process

In general, initial uptake of persistent pesticides by estuarine animals is rapid, but the rate diminishes until a constant concentration is reached. On the other hand, depuration of pesticides does not follow a consistent pattern: rate of loss is dependent upon the nature of the pesticide and the test species. In most experiments, the data fluctuates with physical, chemical, and biological factors (temperature, pesticide concentration, animal size, molt cycle, and seasonal spawning cycles). Pesticide concentrations in water and food are the variables most critical in determining uptake/depuration and are easily controlled in the laboratory. Conversely, molting and spawning cycle variations are difficult to control, and often are affected by a pesticide's toxic properties. To analyze mathematically the uptake of pesticides by estuarine animals, we developed a statistical model that would describe laboratory-derived results, allow comparisons with field data, and permit use in larger ecosystem models to predict movement of pesticides in estuarine biota.

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Our nonlinear statistical model was designed to describe the uptake and depuration of pesticides because: 1) transformations of the data failed to provide an acceptable linear model; and 2) one equation was needed to describe simultaneously both uptake and depuration data. Effects, such as sublethal toxicity, should be distinguishable by statistically significant changes in parameter values of the model.

The general form of the model found to best fit the data is:

\[ Y = \left[A + 10^{(-C \times \text{DAY})}\right]^{-1} - \left[F + G \times e^{(-D \times \text{DAY} - E)}\right]^{-1}, \]

where \( A, C, D, F, \) and \( C \) are parameters estimated with the natural logarithm of pesticide residue, \( Y \), found at time, \( \text{DAY} \). The effects of parameters \( A \) and \( C \) are graphically illustrated (Figure 1a) as well as parameter \( D \) (Figure 1b). Parameter \( A \) has the value of the uptake curve. The asymptotic residue concentration (in the animal at the end of exposure), \( \text{RESIDUE} \), is determined by:

\[ \ln(\text{RESIDUE}) = 1/A \quad \text{or} \quad \text{RESIDUE} = e^{(1/A)}. \]

Parameter \( D \) (Figure 1b) determines the slope of the depuration, where \( D \) indicates no depuration and \( 0 < D < .7 \) indicates increasing rapidity of depuration. The parameter \( E \) is not estimated from the data but is fixed at \( \text{DAY} - '\text{beginning of depuration}' \). In extreme cases, parameters \( F \) and \( G \) are required to modify the shape of the curve so the model will describe the data with greater accuracy. We found that parameters \( F \) and \( G \) usually can be replaced by \( A \) and \( 10 \), respectively, yielding the model:

\[ Y = \left[A + 10^{(-C \times \text{DAY})}\right]^{-1} - \left[A + 10 \times e^{(-D \times \text{DAY} - E)}\right]^{-1}. \]

Results of this equation are shown graphically to indicate applicability to depuration data of different rates (Figure 1c, slow depuration; Figure 1d, rapid depuration).

Both models (1) and (2), non-linear in parameters, required an iterative method to estimate the parameters. The numerical analysis method of Marquardt (1963) was chosen primarily because of its wide acceptance and general use. A typical program dataset (exclusive of job control), using the SAS NLIN procedure, follows:

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DATA REPO; INPUT SPECIES $ CONC TISSUE $ RESIDUE DAY;
IF RESIDUE EQ 0 THEN Y = 0;
IF RESIDUE NE 0 THEN Y = LOG (1000*RESIDUE);
CARDS;
SPOT .4 FILLET 0.00 0
SPOT .4 FILLET 0.50 7
SPOT .4 FILLET 0.86 15
SPOT .4 FILLET 0.99 30
SPOT .4 FILLET 0.87 37
SPOT .4 FILLET 0.57 44
SPOT .4 FILLET 0.38 54
SHRIMP .023 WHOLE 0.000 0
SHRIMP .023 WHOLE 0.038 7
SHRIMP .023 WHOLE 0.072 9
SHRIMP .023 WHOLE 0.088 14
SHRIMP .023 WHOLE 0.120 21
SHRIMP .023 WHOLE 0.087 28
SHRIMP .023 WHOLE 0.100 30
SHRIMP .023 WHOLE 0.100 35
SHRIMP .023 WHOLE 0.084 42
SHRIMP .023 WHOLE 0.055 49
SHRIMP .023 WHOLE 0.023 56
PROC SORT; BY SPECIES CONC TISSUE;
PROC NLIN; BEST = 05 ITER - 200 METHOD = MARQUARDT;
BY SPECIES CONC TISSUE;
PARMS A = 0.1 TO 0.3 by 0.1;
C = 0.1 TO 0.7 by 0.2;
D = -.1 TO 0.3 by 0.2;
Q = (A + (10**(-C*DAY)));
R = (A + (10*EXP(-D*(DAY-E))));
MODEL Y = (Q**(-1) - R**(-1));
DER.A = -Q**(-2) + R**(-1);
DER.C = (Q**(-2)) * (10*EXP(-D*(DAY-E))) * DAY * LOG(10);
DER.D = -10*(DAY-E)**2*EXP(-D*(DAY-E)) * R**(-2);
WEIGHT = DAY;
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RESULTS AND DISCUSSION

The uptake/depuration statistical models (Equations 1 and 2) were validated with data from uptake and depuration of di-2-ethylhexyl phthalate by fathead minnows (Pimphales promelas) (Branson, Bluu J, and Moyer, 1977). Nine sample periods were represented with four replications for the seven concentrations tested. The parameter estimates for each concentration tested were generated from the five-parameter (Equation 1) and three-parameter (Equation 2) model equations; no lack-of-fit was evident. Our three-parameter model (Equation 2) was applied to laboratory results of experiments (Bahner et al., 1977; Bahner and Tyler-Schroeder, Environmental Research Laboratory, Gulf Breeze, FL, personal communication) with grass shrimp (Palaemonem argus) exposed to Kepone or endrin in water, fiddler crabs (Uca pugilator) exposed to Kepone in sediment, and blue crabs (Callinectes sapidus) exposed to Kepone in food. Results indicate that our model sufficiently describes the uptake, equilibrium, and depuration of these chemicals by these estuarine animals (Figure 2). The model was also used to describe the laboratory depuration of Kepone from grass shrimp collected from the Lafayette River, near Norfolk, Virginia. Application of our model to depuration-only data gave excellent results, indicating that data from field-exposed animals can be used to derive all parameter estimates except \( C \), the uptake rate parameter. Parameter \( C \) was arbitrarily set to 1.0 for these data (Figure 2a).

CONCLUSIONS

The statistical uptake/depuration model sufficiently described uptake and depuration of Kepone and endrin by estuarine shrimp and crabs in water, food, or sediments. In addition, the model described 'depuration only' data, allowing use of field-exposed animals to project depuration rates and to estimate time required for...
residues to non-detectable concentrations. With the three-parameter model (Equation 2), the ultimate residue concentration in exposed animals is predicted to depurate to zero concentration (if parameter D is greater than zero and time is sufficient). The exponential depuration portion of the model gives an accurate fit to data, regardless of the depuration rate. Given sufficient data, extrapolations can be made with caution. All parameters in the model have confidence intervals; therefore, statistical inferences (statistical significance) can be judged with joint confidence region comparisons. For example, the model can be used to determine if pesticide residues from laboratory exposures are statistically different than those from field exposures.

If expanded, the present single-species, single-concentration model should produce multidimensional models to describe chemical-species-dose-time interactions. Expansion of the number of parameters in the model will be limited by the availability of replicated data points. Because thorough, replicated sampling schemes testing multiple concentrations are not possible for all pesticides, attempts should be made to categorize parameter estimates for chemicals, species, and exposure concentrations. Successful categorization of the model parameters would allow use of generalized parameter estimates in dynamic ecosystem models.

REFERENCES


Figure 1. (a) Plot of generalized uptake equation. Parameter A (A=0.125) in this illustration denotes upper asymptote; parameter $A'$ illustrates effect of increase in value of A to 0.2. Parameter C determines initial uptake slope; normally, C varies from 0.1 (slow) to 2.0 (rapid).

(b) Plot of generalized depuration equation: parameter D determines loss slope and varies from 0.1 (top), 0.5 (mid), to 0.65 (lower); parameter E denotes onset of time depuration.

(c) Plot of generalized equation, indicating slow depuration.

(d) Plot of generalized equation, indicating rapid depuration.
Figure 2. (a) Model representation of Kepone bioconcentration by grass shrimp (Palaemonetes pugio) from water containing average measured concentrations of 0.023 or 0.40 μg/l. Exposure was for 28 days, followed by depuration of shrimp placed in Kepone-free water for 28 days. Intermediate curve represents depuration of Kepone from grass shrimp collected in the Lafayette River, Norfolk, Virginia, and held in Kepone-free seawater at the ERL, Gulf Breeze, for 21 days. Parameter estimates for shrimp exposed to 0.023 μg/l were: \( A=0.212, \ C=0.183, \) and \( D=0.098; \) for shrimp exposed to 0.40 μg/l: \( A=0.124, \ C=0.22, \) and \( D=0.099; \) for Lafayette River shrimp: \( A=0.155 \) and \( D=0.084. \) Lower limit of analytical detection was 20 ng/g.

(b) Model representation of endrin bioconcentration from water containing average measured concentration of 0.1 μg/l by grass shrimp exposed for 21 days, and its depuration by shrimp placed in endrin-free water for 4 days. Parameter estimates for shrimp exposed to 0.1 μg/l were: \( A=0.197, \ C=1.27, \) and \( D=0.92. \) Lower limit of analytical detection was 20 ng/g.

(c) Model representation of Kepone uptake from sediments containing average measured concentration of 0.25 μg/g by fiddler crabs (Uca pugilator) exposed for 28 days, and its depuration by crabs placed on Kepone-free sediments for 35 days. Parameter estimates for crabs were: \( A=0.181, \ C=0.49, \) and \( D=0.050. \) Lower limit of analytical detection was 20 ng/g.

(d) Model representation of bioaccumulation by blue crabs (Callinectes sapidus) exposed to Kepone-contaminated food and water for 28 days, followed by Kepone-free food and water for 28 days. Parameter estimates for crabs exposed to 250 ng/g were: \( A=0.211, \ C=0.136, \) and \( D=0.057; \) for crabs exposed to 250 ng/g plus 0.3 μg/l: \( A=0.202, \ C=0.123, \) and \( D=0.032. \) Lower limit of analytical detection was 10 ng/g.