Chlorpyrifos Release Rate from Clay Granules: Experimental Observations and Simple Algorithm Development for Use in Computer-Based Exposure Assessments

S. A. Cryer*

Dow AgroSciences LLC, 9330 Zionsville Road, Indianapolis, Indiana 46268

D. A. Laskowski

Dow AgroSciences LLC, Indianapolis, Indiana 46268

Environmental models can approximate pesticide mass leaving a treated field in runoff water and sediment but do not typically account for controlled-release formulations such as granules. Mathematical algorithms are developed from experimental observations to predict the environmental release rate of chlorpyrifos from a commercial formulation [Lorsban (trademark of Dow AgroSciences) 15G insecticide] into the surrounding soil environment. Chlorpyrifos release rates into flowing water were measured by HPLC analysis of water pumped through a column containing 15G granules. Analysis of these observations provides a basis for predicting water-induced release rates during natural precipitation events. Chlorpyrifos diffusion and volatilization rates from the granule in the absence of precipitation were determined from experimental observations using first-order kinetic modeling. Multiyear simulations and distribution analysis were performed using the GLEAMS model for the Midwestern corn belt region to determine release mechanism sensitivity and edge-of-field runoff potential for chlorpyrifos in 15G granules when the release mechanisms of advection, volatilization, and diffusion are accounted for. It is found that advection release was the dominate mechanism for chlorpyrifos release from clay granules, followed by diffusion and volatilization for Midwestern U.S. scenarios. Predicted losses of chlorpyrifos in runoff from soil incorporated applications are <1% of applied.

Keywords: *Lorsban 15G; rate of release; chlorpyrifos; runoff; GLEAMS*

INTRODUCTION

Pesticides can pose risk to nontarget organisms if off-site movement of a pesticide from the intended target area occurs. Pesticide-contaminated runoff water and sediment can potentially harm nontarget aquatic and terrestrial organisms if an organism's toxicity level of concern is exceeded. A prerequisite for estimating pesticide impact to nontarget organisms stems from approximation of estimated environmental concentrations (EECs) in neighboring fields or bodies of surface water. Runoff loadings from agricultural fields must first be determined before EECs can be estimated.

For granular or encapsulated formulations, the active pesticide must first be released into the environment from the release device before it is available for physical processes such as runoff and degradation. Current runoff models [GLEAMS (Knisel et al., 1987); SWRRB-WQ (Arnold et al., 1990); EPICWQ (Sharpley and Williams, 1990); and PRZM (Carsel et al., 1984)] can be used to predict pesticide mass in runoff water and sediment for liquid (or emulsifiable) formulations but are not written to account for controlled-release formulations or granules such as Lorsban 15G insecticide. There are limited numbers of studies investigating the direct release of chlorpyrifos from granules into the surrounding soil environment, but there is a large volume of literature that exists for chlorpyrifos degradation in soil (Racke, 1993). Algorithms based upon degradation work and physical principles are developed and incorporated for use with the USDA model GLEAMS. Diffusion into the surrounding soil matrix (i.e., soil, voids, pore water), advection due to water flowing past the granule, and volatilization from the granule into the atmosphere are the major release mechanisms accounted for. This methodology has been used in various geographical exposure assessments for chlorpyrifos (Cryer et al., 1998; Havens et al., 1998), where it is assumed that granules remain stationary and are not transported with runoff water or eroded sediment. This assumption is reasonable since a large majority of the chlorpyrifos applied to corn is T-band incorporated into soil [totaling nearly 3 million treated hectares each year between 1990 and 1992 (U.S. Environmental Protection Agency, 1996)], making the granules immobile in all but highly erosive storms.

Davis et al. (1996) explored water release rates for fenamiphos, atrazine, and alachlor using technology similar to that presented here. These researchers understood the coupling between water release rates and environmental fate of these materials but did not adequately implement experimental/theoretical reasoning of observations into predictive models. This work extends the work of Davis et al. by incorporating simple

* Author to whom correspondence should be addressed [telephone (317) 337-3428; fax (317) 337-3628; e-mail sacryer@dowagro.com].
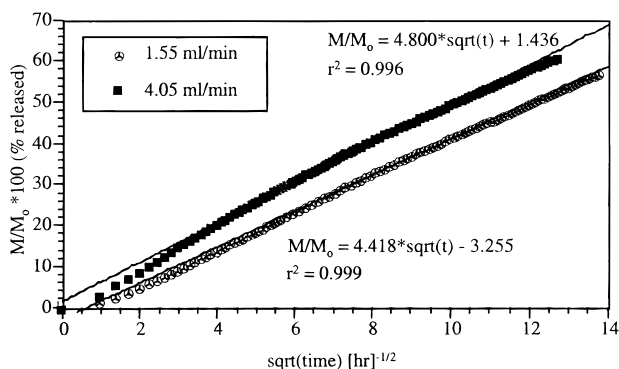
Chlorpyrifos Release Rate from Clay Granules

J. Agric. Food Chem., Vol. 46, No. 9, 1998 **3811**

Figure 1. Experimental observations for water induced chlorpyrifos rate of release from Lorsban 15G insecticide granules (mesh size 50/60).

mathematical descriptors and experimental observations to characterize water-induced release rates for granulated pesticides for subsequent use in environmental fate models. Examples using chlorpyrifos are provided.

Chlorpyrifos release from granules can occur by volatilization, diffusion into the surrounding environmental matrix, or advection loss as precipitation flows past a granule. Diffusion into the surrounding matrix can be approximated initially by classical one-dimensional, semi-infinite diffusion theory (for a slab or for a spherical particle with appropriate change of variable). The solution to this classical problem (eq 1) can be found in classical treatise (Bird et al., 1960) for a constant-source "slab" with an initial mass (M_o) of $M = M_o$ at $t = 0$, and boundary conditions of no mass or mass flux at $y = \infty$. Here, M_o represents a constant amount of mass.

$$\frac{M}{M_o} = \frac{2}{\sqrt{\pi}} \int_{\eta}^{\infty} e^{-\eta^2} d\eta \qquad (1)$$

where $\eta = y/\sqrt{4DT}$, y = distance from granule (cm), D = diffusion coefficient (cm²/s), and t = time (s).

A typical diffusion coefficient for a chemical species in water is on the order of 10^{-5} cm²/s. Equation 1 provides a simple estimate for diffusion of chemical into a homogeneous surrounding medium.

A simple kinetic approach can also be used to represent both the diffusion release of chlorpyrifos from a granule and the subsequent degradation in the soil environment. A kinetic approach for slow release formulations using this methodology has been described elsewhere (Leonard and Knisel, 1989).

MATERIALS AND METHODS

Water-Induced Release Rates (Advection). A 0.6 cm diameter by 6.0 cm long stainless steel column was half-filled with 40-μm glass beads. An equivalent of 7 μg of chlorpyrifos (as Lorsban 15G granules) was placed on top of the beads, and the remainder of the column was subsequently filled with the beads. The median particle size for the 15G granules is ~250–297 μm and contains a chlorpyrifos mass loading (by weight) of 15%. The column was connected to Milton-Roy high-pressure piston pumps. The volumetric flow rate of water pumped through the saturated column was held constant for each trial with experiments performed for flow rates between 1 and 17.5 mL/min. Effluent leaving the column passed through a C-18 reverse phase trap and was subsequently analyzed by reverse phase HPLC for chlorpyrifos residues. Observations of the cumulative amount of chlorpyrifos mass released versus time were recorded as indicated by Figure 1

Table 1. Experimentally Determined Values for $k(V_I)$ from Regression of Experimental Observations

flow rate Q [V_I] (Q in mL/min; V_I in cm/min)	$k(V_I)$ from regression of exptl observations (h$^{-1/2}$ day$^{-1/2}$)	R^2
1.55 [14.8]	4.800 (0.980)	0.996
4.05 [38.7]	4.418 (0.902)	0.999
8.60 [82.2]	4.715 (0.962)	0.992
17.5 [167]	4.385 (0.895)	0.989

for two different water flow rates. The release rate from a granule to a continually flowing stream of water passing the granule surface is found to scale linearly with the square root of time.

The linearity of the functions in Figure 1 indicates the percent of chlorpyrifos mass released can be written as

$$M/M_o = k(V_I)t^{1/2} \qquad (2)$$

where $k(V_I)$ is the experimentally determined constant (i.e., the slopes of the equations printed in Figure 1) which depends on the interstitial velocity (V_I), and M/M_o is the mass fraction released from the granule (M = mass released; M_o = total mass available). Collins (1974) has shown the $t^{1/2}$ scale is exact in the limit of $t \to 0$ for diffusion mass transfer from a one-dimensional semi-infinite slab/sphere source into the surrounding soil environment. Thus, water-induced release losses during a precipitation event can be linked to the storm's duration and intensity by translation into a certain velocity of water passing over the granule particle.

Convection of pesticide mass from the granular surface is governed by the magnitude of the interstitial velocity for this experimental setup. The interstitial velocity (V_I) is determined by

$$V_I = Q/A_S\epsilon \qquad (3)$$

where Q = volumetric flow rate (mL/min), A_s = cross-sectional area of column = $\pi D^2/4$, D = diameter of column (cm; 0.60 cm for this experiment), ϵ = porosity of glass beads in column.

The void volume and/or porosity within the glass bead column can be readily determined for spherical particles of equal size. The porosity (ϵ) can vary between $0.26 \le \epsilon \le 0.48$ depending on the packing of the solid spheres. An intermediate porosity value of 0.37 was used for determining the interstitial velocity for water passing around the Lorsban 15G insecticide granules. The interstitial velocity range is determined as 9.6 cm/min < V_I < 167 cm/min for flow rates ranging over 1.0 mL/min < Q < 17.5 mL/min. A linear line was fit through each experimental data set to determine the constant $k(V_I)$, with results summarized in Table 1.

Rate constant dependence on V_I is expected as water passing the granule surface removes chlorpyrifos mass and subsequently increases the net concentration gradient between the granule and water stream. However, this was not seen experimentally, indicating all experimental observations were diffusion-limited. This necessitated the development of a procedure for estimation of the magnitude of $k(V_I)$ in diffusion-limited mass transfer.

Diffusion-Limited Water Release Rate. Precipitation events are highly variable in terms of intensity and duration and, thus, in their uniqueness to transport pesticide mass away from the granule. An expression was developed for the constant $k(V_I)$, under conditions of diffusion-limited mass transfer, to account for storm variability. The rate constant dependence on interstitial velocity can be easily determined via experimental observations (Figure 1). However, this experimental method cannot be used in the limit of the flow rate approaching zero. In this case classical one-dimensional semi-infinite diffusion theory (eq 1) is used to estimate a value for $k(V_I)$ in the limit of $V_I \to 0.0$.

The resulting cummulative mass release profile for diffusion-limited transport of chlorpyrifos from a granule and into a stagnant water layer surrounding the granule (eq 1) is given in Figure 2 (for $y = 1.0$ cm and $D = 1.0 \times 10^{-5}$ cm²/s). Figure

3812 *J. Agric. Food Chem.,* Vol. 46, No. 9, 1998
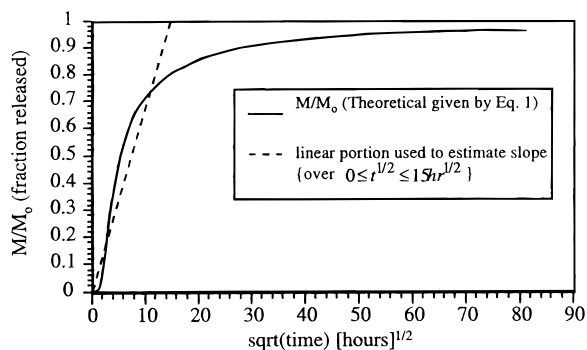
Cryer and Laskowski

Figure 2. Theoretical prediction for rate-limiting diffusion of chlorpyrifos from clay granules into immobile surrounding water.

Table 2. Nonlinear Regression Analysis for Determining the Rate Constant k_1 from the Experimental Observations of Walgenbach and Getzin

	first-order diffusion constant k_1 (fitted to exptl data)	first-order degradation constant k_2 from exptl data of liquid sprays
Getzin (incorporated)	2.08×10^{-2}	3.10×10^{-2}
Getzin (surface)	3.73×10^{-2}	1.08×10^{-1}
Walgenbach (laboratory)	3.90×10^{-2}	4.704×10^{-2}
Walgenbach (field)	3.26×10^{-2}	4.704×10^{-2}

2 includes the integrated theoretical function (eq 1) for M/M_o dependence on the square root of time. The nonlinearity of this function in Figure 2 indicates that the assumptions on which eq 2 is based do indeed break down for large times. The postulated model (i.e., eq 2) assumes a linear form, and it is clear from Figure 2 that the diffusion-limited advection is not linear for all "square roots" of time. To obtain a linear range consistent with the postulated model of eq 2, the "linear range" was assumed to be $0 \text{ h} \leq t \leq 225 \text{ h}$ ($0 \leq \sqrt{t} \leq 15 \text{ h}^{1/2}$). This time interval was chosen to be consistent with our experimental observations where linearity was observed.

The slope of the linear curve in Figure 2 (dashed line) was determined by comparing the analytical solution (i.e., eq 1) with a linear equation (with zero intercept) over the linear time interval (assumed $0 \leq \sqrt{t} \leq 15 \text{ h}^{1/2}$). By minimizing the sum of the squared residuals (i.e., the squared difference between linear and analytical results), a value of $0.0636 \text{ h}^{-1/2}$ for the slope was determined to yield the best fit over this time interval. The diffusion-limited water rate of release was therefore approximated by $k_{(VI=0)} = 0.0636 \text{ h}^{-1/2}$. From the experimentally determined values for $k(V_I)$ in Table 2, it is clear that convection dominates diffusion for flow rates greater than zero. Only in the limit of $V_I \rightarrow 0$ will diffusion and convection be of similar magnitudes.

A semiempirical function was constructed to account for the effect of water flow rate on $k(V_I)$. Observed results for $k(V_I)$ with the theoretical value for $V_I \rightarrow 0$ are given in Figure 3, along with the function used to predict $k(V_I)$ once a water velocity is known (eq 4). Equation 4 was chosen on the basis of curve-fitting and not on any physical mechanism. However, the function was forced to pass through the diffusion limit for $k(V_I)$ while minimizing the error between observation and prediction. The coefficients in eq 4 were evaluated using linear regression.

$$k(V_I) = 4.52(1.014 - e^{-V_I}) \qquad (4)$$

Equation 4 is empirical with units for V_I of cm/min and $k(V_I)$ of $h^{-1/2}$ and can be used in conjunction with eq 2 to predict water-induced release rates for chlorpyrifos. Note that $k(V_I)$ increases sharply between 0 and 5 cm/min and remains
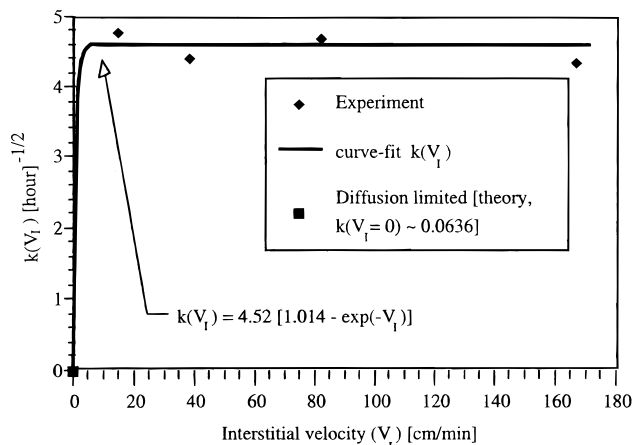

Figure 3. Dependence of the constant $k(V_I)$ on the flow rate of water passing over the granule. symbols represent experimental observations and diffusion limit. solid line represents curve fit of closed form solution which describes $k(V_I)$ dependence on V_I.

approximately constant above 5 cm/min indicating the intensity of the rainfall event is mass transfer-limited at or near this threshold value for V_I. However, it is anticipated most soil pore water interstitial velocities occurring in nature are between 0 and 5 cm/min, where the release of chlorpyrifos mass is a strong function of water flow rate.

Determination of Interstitial Velocities (V_I) for Soil-Incorporated Granules. The weather generator CLIGEN [WEPP program listing (Nicks, 1989)] is used to predict storm duration and intensity, and thus can produce estimates for V_I. Daily rainfall duration and intensity predicted by CLIGEN were converted into a velocity for use in deducing the water release rate of chlorpyrifos from granules within the environment. For surface-applied granules, the velocity used to predict $k(V_I)$ was the rainfall intensity [amount (mm)] divided by the storm duration (h). The units were converted to yield velocities in cm/min.

The determination of V_I for soil-incorporated granules was not as straightforward as that for surface-applied granules. A certain percentage of rainfall can run off a field, the remainder can infiltrate into the soil, and thus a value for V_I based on infiltration must be estimated. Surface runoff was estimated using the SCS curve number equation (Knisel, 1980). This is an empirically derived expression for estimating the volume of precipitation that infiltrates (I) into the soil. The interstitial velocity can be calculated as

$$V_I = I/\tau\epsilon_S \qquad (5)$$

where $I =$ infiltration amount (cm), $\tau =$ storm duration (min), and $\epsilon_s =$ porosity of soil.

Porosity is a property of the soil type and can vary between soils and geographic regions. Thus, geographically referenced soil porosity and runoff curve numbers are used to determine V_I in soil via eq 5 for numerical simulation purposes for specific regions.

Kinetic Approach for Volatilization. Chemical volatilization can be important in soil-incorporated and surface-applied granules. However, because of the typical lumped-sum analysis for degradation rates in soil, volatilization is accounted for indirectly in most experimental observations. However, in one study F. Hamburg (Dow AgroSciences, personal communication, 1990) performed experiments that measured volatilization losses of chlorpyrifos from Lorsban 15G insecticide granules at room temperature. This experiment consisted of spreading 0.25 g of granules onto Petri dishes. Granules on the dishes were subsequently assayed at various dates by extraction of the granules with 100 mL of acetonitrile followed by spectrophotometric measurement of the acetonitrile to determine chlorpyrifos concentrations. The data indicate volatilization loss can be accurately modeled
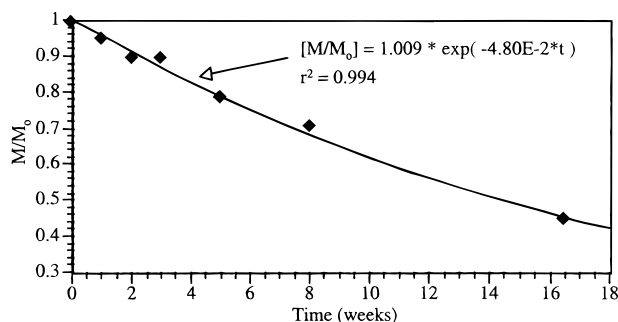
Figure 4. Volatilization of chlorpyrifos from 15G granules (Hamburg, personal communication, 1990).
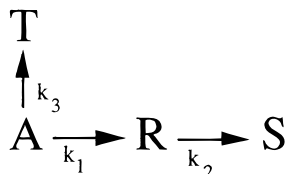

Figure 5. Kinetic representation for volatilization and diffusion into soil.

using first-order kinetics (Figure 4). The first-order rate constant for volatilization (ω) was determined to be 4.80×10^{-2} week^{-1} (6.85×10^{-3} day^{-1}).

It is pointed out that these experiments were performed under conditions different from that of a field setting. Physical properties affecting volatilization release rates include such things as air temperature, humidity, wind speed, and transient soil moisture conditions. Thus, the experimental observations of Hamburg can be treated as an estimate for volatility of chlorpyrifos from dry surface-applied granules. The volatilization rate constant may be influenced by climatic properties and soil moisture conditions, and ideally, this influence could be described mathematically. However, we are unaware of any volatilization experiments performed specifically with the 15G formulation of chlorpyrifos to address this limitation.

Kinetic Approach for Diffusion into Soil. The approach used by Leonard and Knisel (1989) to describe the release of a pesticide from a formulation carrier mimics the metabolic process for formation/degradation of a metabolite from parent material. In Figure 5, the letter A represents chlorpyrifos within the granule, T represents chlorpyrifos that has volatilized, R represents chlorpyrifos released from the granule and now in soil, and S represents chlorpyrifos degradation products. A disadvantage of Leonard and Knisel's approach is the independence of soil properties, specifically organic carbon content and the sorption of the molecule. The consecutive sequence of events as illustrated by the proposed transport pathway in Figure 5 dictates that k_2 (the degradation rate constant of chlorpyrifos in soil) will influence the value of k_1 (the rate constant for release of chlorpyrifos mass into the soil). Sorption is indirectly incorporated in the rate constant k_1 if actual field/laboratory observations are properly used to define k_1.

A kinetic approach can qualitatively account for all of the various mechanisms responsible for release of a pesticide from a granule carrier. However, the uniqueness and quantification of these mechanisms are lost in the magnitude of the rate constant k_i. The numerical values for k_i can be estimated from experimental data. Analytical solutions for the ordinary differential equations describing the first-order kinetic mechanism listed in Figure 5 can be found in most elementary texts in reaction kinetics (Holland and Anthony, 1979).

Relating Net Kinetic Diffusion Constant to Degradation. Rate constants representing diffusion and degradation were determined using the experimental data of Walgenbach (1979) and Getzin (1985). These researchers performed degradation experiments using both 15G granules and a liquid (spray) formulation of chlorpyrifos where both formulations
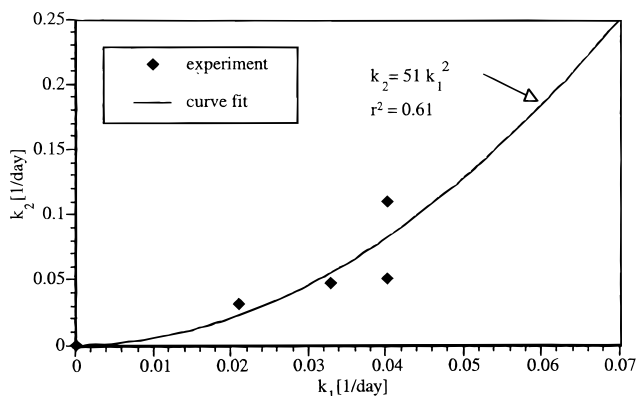

Figure 6. Plot of degradation rate constant of chlorpyrifos in soil (k_2) vs the first-order diffusion release constant (k_1). A nonlinear expression was assumed to model the data dependency.
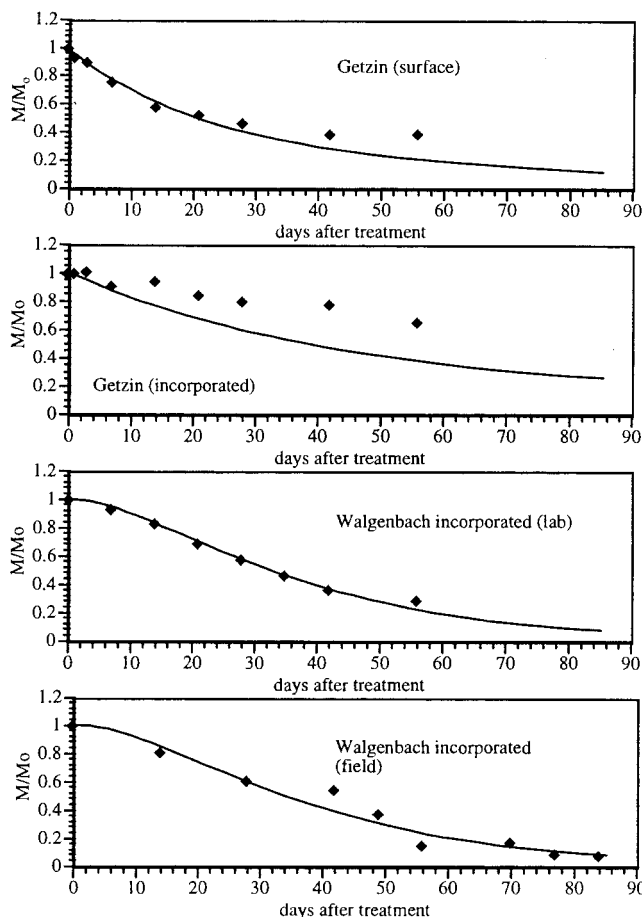

Figure 7. Comparison of kinetic model predictions (solid line) with experimental observations (symbols).

are studied under identical environmental conditions. The kinetic first-order rate constant for chlorpyrifos degradation in soil (k_2) can be determined independently from the spray data (i.e., technical or liquid formulation chlorpyrifos) of Getzin and Walgenbach for both field and laboratory experiments. The value for degradation from the surface experiments of Getzin is $k_2 = 0.108$ day^{-1} and $k_2 = 0.031$ day^{-1} for incorporated spray. The value from Walgenbach's experiments suggests the degradation rate constant of technical grade chlorpyrifos in soil (k_2) equals 0.047 day^{-1}. This single value from Walgenbach's observations (k_2) is used with two different data sets of Walgenbach (field and laboratory) to estimate the release constant (k_1). This accounts for the two data points in Figure 6 having the same value for k_2 but different values for k_1. The pseudo rate constants obtained from the experimental obser-

Table 3. Description of Chlorpyrifos Pesticide Properties Utilized in the GLEAMS Simulations

description	value
water solubility (ppm)	1.39
foliar degradation half-life (days)	1.5
soil degradation half-life (days)	15
K_{oc} (mL/g)	8753
plant washoff fraction	0.65
application rate (kg/ha)	2.24
Julian application date	105

vations of Getzin for surface granules were adjusted for volatilization using the half-life predicted from Hamburg's experiments to yield an actual apparent soil degradation rate constant. Nonlinear regression analysis comparing experimental observations and kinetic (analytical) solutions yielded values for k_1, which are summarized in Table 2.

Several field experiments have been analyzed to describe the dependence of the diffusive rate constant for chlorpyrifos mass release from a granule (k_1) with the chlorpyrifos degradation rate in soil (k_2) (Table 2). A nonlinear expression is used to fit the data for a plot of k_2 versus k_1 (Figure 6). The fictitious data point $k_2 = 0.0$ when $k_1 = 0.0$ was added on the basis of physical arguments. No degradation will occur for any chlorpyrifos released from the granule into the soil for the soil degradation half-life of chlorpyrifos approaching ∞ (i.e., $k_2 = 0.0$). Any chlorpyrifos mass released from a granule will be confined near the granule/soil interface because of the sorptivity of this molecule to solids. Chlorpyrifos water solubility is small (1.39 ppm), which will keep concentrations in soil pore water (and any water within the granule) small. Therefore, the concentration gradient for diffusion is small when chlorpyrifos degradation is negligible, and the physics of the problem dictate that for $k_2 = 0.0$, $k_1 = 0.0$. The resulting equation based on experimental evidence (Getzin, 1985; Walgenbach, 1979; Table 2) and nonlinear regression is

$$k_2 = 51k_1{}^2 \qquad (6)$$

Equation 6 is an experimentally derived empirical equation that relates the first-order degradation constant for chlorpyrifos in soil (k_2) to a "pseudo" diffusion constant for diffusion from the granule into the soil environment (k_1). Once k_2 is known, k_1 can be determined and the amount of active chlorpyrifos mass left in soil can be calculated using the

material balance equations associated with the kinetic pathway given by Figure 5. Results from using eq 6 with the data from Getzin and Walgenbach can be seen in Figure 7.

The kinetic approach describing release rates has the benefit of (i) conserving mass and (ii) incorporating a functional dependence of chlorpyrifos half-life in soil with the release rate from a clay carrier into the soil environment. Chlorpyrifos rate constant dependence on soil moisture and temperature can also be easily incorporated using this methodology if field and laboratory degradation data are available for different soil moisture and temperature conditions. Thus, the kinetic model approach should prove useful for probabilistic modeling where regional properties can and do change (Laskowski et al., 1990). The modeling of the volatilization and precipitation-induced advection release remains unchanged.

GLEAMS Modeling Accounting for All Release Rate Mechanisms. The sum of all release mechanisms (i.e., volatilization, advection into a water stream due to water passing the granule surface, and diffusion into the surrounding soil pore water and pore void) represent the total amount of mass released from a granule particle as a function of time within the environment. A computer program was written to couple the chlorpyrifos release rate methodology presented here with the GLEAMS model. A GLEAMS pesticide input file contains information such as depth of pesticide incorporation, multiple application dates, and initial quantity of pesticide mass applied on each application date. This interface program reads a standard GLEAMS input file for this information, coupled with daily weather information generated by the weather generator program CLIGEN. Precipitation-induced release rates are then accounted for on days when precipitation occurs through the constant $k(V_l)$, where V_l is a function of weather data, soil porosity, curve number, and granule location (i.e., surface applied or soil incorporated). Using the nominal or general information from the original GLEAMS pesticide input file, the interface program creates a new GLEAMS pesticide input file that accounts for the various release mechanisms and appropriate chlorpyrifos mass predicted to be released on a given day. The original application dates and rates are then replaced by daily "release" rates for chlorpyrifos mass as dictated by the independent mechanisms representing diffusion, advection, and volatilization.

Definition of Standard Scenario for GLEAMS Modeling. The single-site scenario developed to illustrate the environmental behavior of Lorsban 15G insecticide in a typical Midwest corn field is made up of average values from a subset
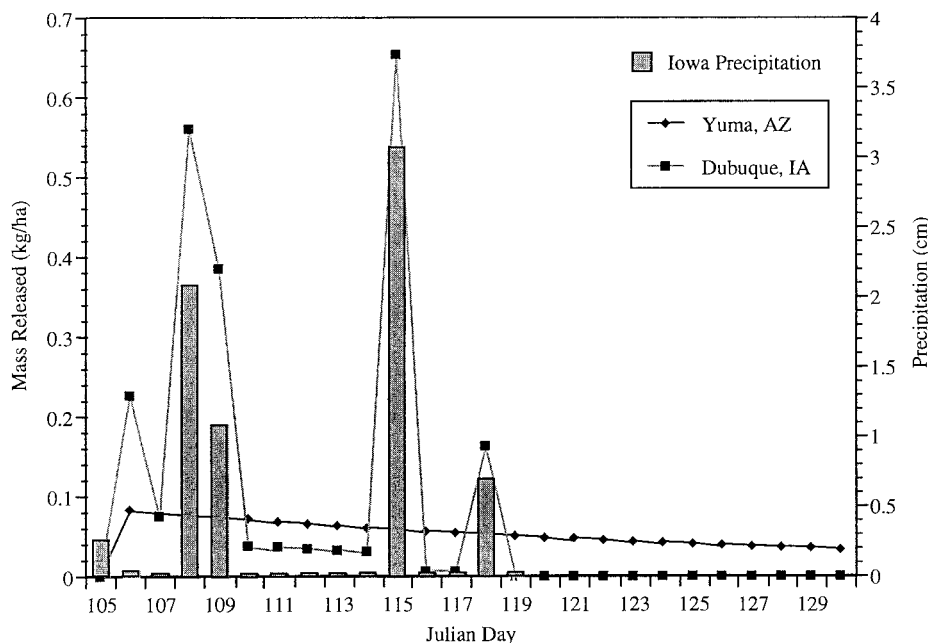

Figure 8. Predicted chlorpyrifos mass released through advection, diffusion, and volatilization for an average Midwest soil with weather patterns from Iowa and Arizona.
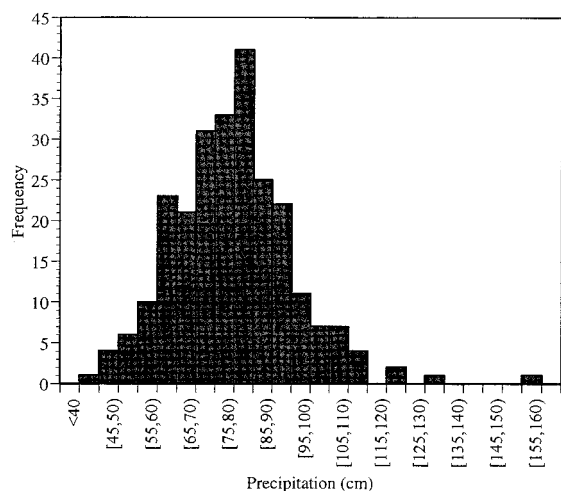
Chlorpyrifos Release Rate from Clay Granules

J. Agric. Food Chem., Vol. 46, No. 9, 1998 **3815**

Figure 9. Precipitation frequency distribution beginning with application date (Julian day 105) to the end of the year (EOY) for Dubuque, IA, as generated by CLIGEN.

of a multistate region. The U.S. corn-growing market was delineated from the 1987 census of agriculture data for all state counties where >20 000 acres of corn was planted. This was limited to the Midwestern states (Texas and Colorado excluded). The soil properties within these counties were acre-weight-averaged to obtain single values. These acre-weight average values were utilized to create a GLEAMS hydrology and erosion file. Thus, the single scenario modeled in this paper represents a "numerical" average soil that may be typically found in the Midwest. This approach provides an unbiased mechanism for choosing a single soil that is representative of a typical soil found in the region of interest. However, actual soil properties are used when regional assessments are performed using the GLEAMS model to simulate runoff potential for Lorsban 15G insecticide granules (Havens et al., 1998).

A single simulated application of chlorpyrifos is made on Julian day 105 at a rate of 2.24 kg/ha. The soil was assumed to be bare of all vegetation so that 100% of the target application rate was achieved (for both surface-applied and soil-incorporated applications). The physical properties for chlorpyrifos used in the simulation are given in Table 3, and a typical weather year for Dubuque, IA, is used in the simulation. A single weather year from Yuma, AZ, is also used to contrast the difference in release mechanisms when little/ no rainfall is present.

Monte Carlo Analysis for Weather. Two hundred and fifty years of simulated weather were generated for the GLEAMS simulations using CLIGEN, which was modified to include statistical analysis of variables associated with the weather years generated (i.e., key period precipitation, frequency distributions for precipitation, storm duration, wind speed, storm duration, etc.). The weather station chosen was for Dubuque IA.

RESULTS AND DISCUSSION

Figure 8 represents results for the chlorpyrifos release rate from Lorsban 15G insecticide granules as predicted
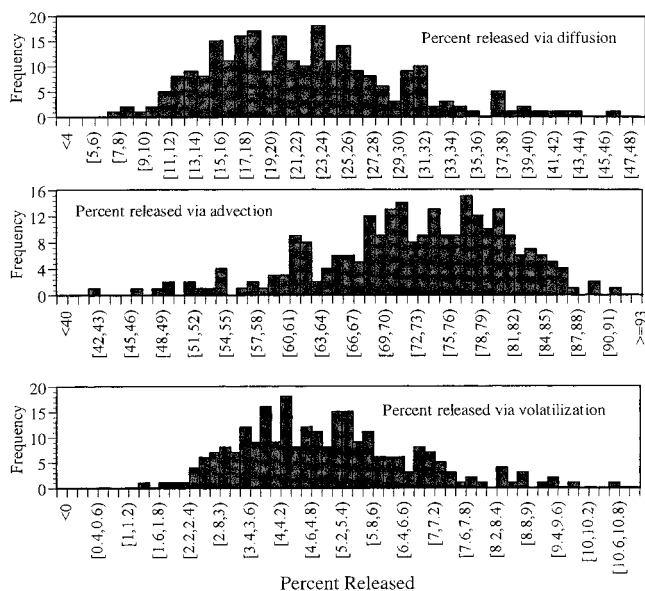

Figure 10. Example of chlorpyrifos release mechanisms given as a percentage for 250 years of simulated weather.

by the algorithms presented in this study for a single weather year. The precipitation-induced release rate was found to dominate the "controlled" release from the granules when a precipitation event occurred. Therefore, for comparative purposes with the example problem presented, two different weather files were utilized (Dubuque, IA, and Yuma, AZ). The "key period" precipitation beginning with the first application date and ending 30 days after the last application for Yuma and Dubuque were 0.01 and 7.20 cm, respectively. The results for the two different weather files can be seen in Figure 8. The large mass release rates seen in Figure 8 were due to advection transport occurring on precipitation days. For the single-year Dubuque simulation, the release percentages due to diffusion, advection, and volatilization were 18, 78, and 4%, respectively. For the Yuma weather simulation, the relative percentages were 80, 2, and 18% for diffusion, advection, and volatilization, respectively.

The frequency distribution for precipitation beginning with Julian day 105 and continuing to the end of the year (EOY) can be seen in Figure 9. The weather files making up the distribution of weather years were used as input to the GLEAMS model for comparative output predictions. From Figure 9 it is clear that there was always >40 cm of precipitation during the Julian interval 105−365. Each precipitation event had an associated storm duration as predicted by CLIGEN.

Frequency distributions for overall percent of chlorpyrifos mass released by the three mechanisms for surface applied granules (with a degradation half-life of 15 days once in soil) are given in Figure 10. From

Table 4. GLEAMS Simulation Results for the Total Annual Amount of Chlorpyrifos Predicted To Leave the Field in Runoff Water and Bound to Eroded Sediment (Granules Incorporated 4 in. into Soil)

percentile	runoff water (% of applied), $t_{1/2} = 7$ days	eroded sediment (% of applied), $t_{1/2} = 7$ days	total losses (% of applied), $t_{1/2} = 7$ days	runoff water (% of applied), $t_{1/2} = 30$ days	eroded sediment (% of applied), $t_{1/2} = 30$ days	total losses (% of applied), $t_{1/2} = 30$ days
25	0.001	0.002	0.002	0.009	0.018	0.027
50	0.004	0.006	0.011	0.020	0.041	0.062
75	0.013	0.016	0.030	0.041	0.097	0.136
90	0.024	0.032	0.058	0.074	0.222	0.287
95	0.032	0.061	0.101	0.105	0.309	0.393
99	0.065	0.154	0.187	0.228	0.785	0.996

3816 *J. Agric. Food Chem.,* Vol. 46, No. 9, 1998

Cryer and Laskowski

this figure it is clear that advection drives the chlorpyrifos release rate from the 15G granules for the Midwest weather station chosen for simulation purposes. The averages for diffusion, advection, and volatilization are 22.3, 72.7, and 5.0%, respectively.

Table 4 represents typical GLEAMS simulation results for the total annual amount of chlorpyrifos predicted to leave the field in runoff water and bound to eroded sediment. In this example, the 15G granules are incorporated 4 in. into the soil, and the simulation includes the average Midwest soil with 250 years of simulated Dubuque, IA, weather patterns. A soil degradation half-life for chlorpyrifos of either 7 or 30 days is used to illustrate the effect of degradation on release rate. As the chlorpyrifos degradation half-life in soil increases, the amount of chemical transported off the field in runoff water and erosion also increases. The loss of chlorpyrifos from field edge is <1.0% of applied, which corroborates findings of other researchers for highly sorbed pesticides (Wauchope, 1979).

CONCLUSION

Current models for simulating pesticide fate in the environment do not distinguish between formulation type. Researchers have understood the importance of different formulation types and the impact they may have on off-target environmental exposures. A simple method is proposed and implemented to account for transient water release, diffusion, and volatilization of chlorpyrifos from clay-based granules with easy couplings to current environmental fate models. Many of the coefficients required for mathematical descriptions of physical processes are obtained experimentally, and chlorpyrifos release mechanisms specific for the Lorsban 15G insecticide formulation are incorporated into the GLEAMS model. Refined estimates for controlled release should yield more realistic estimates for edge-of-field runoff, both in model prediction and in field study interpretation.

This work indicates that precipitation-induced release is the largest driving mechanism for all of the individual mechanisms available for chlorpyrifos release from a clay carrier when a Midwest weather station (Dubuque, IA) and an average Midwest soil are used in the simulation. Advection is followed by diffusion and volatilization for release mechanism importance under Midwestern U.S. weather patterns. Predicted losses of chlorpyrifos in runoff from soil incorporated applications are <1% of applied.

There is always uncertainty associated with laboratory observation and extrapolation to field prediction. The uncertainty associated with the physical descriptors for mass transport can be quantified only through both repetition of experiments and execution under a variety of parameter conditions. Error associated with volatility losses is probably greatest in this analysis simply because the results presented were obtained from analysis of a single data set under artificial conditions. However, volatility was found to be the least important mode of release for typical chlorpyrifos applications made in the Midwest corn belt region, and thus the error associated with this prediction is not a sensitive parameter governing a refined exposure assessment.

LITERATURE CITED

Arnold, J. G.; Williams, J. R.; Nicks, A. D.; Sammons, N. B. *SWRRB: A Basin Scale Simulation Model for Soil and Water Resources Management*; Texas A&M Press: College Station, TX, 1990; 255 pp.

Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena;* Wiley: New York, 1960.

Carsel, R. F.; Smith, C. N.; Mulkey, L. A.; Dean, J. D.; Jowise, P. *User's Manual for Pesticide Root Zone Model (PRZM).* release 1; EPA-600/3−84/109. U.S. EPA: Athens, GA Dec 1984; 216 pp.

Collins, R. L. A Theoretical Foundation for Controlled Release. Presented at the Controlled Release Pesticide Symposium, Engineering and Science Division Community and Technical College, The University of Akron, Akron, OH, Sept 16−18, 1974.

Collins, R. L.; Doglia, S.; Mazak, R. A.; Samulski, E. T. Controlled Release of Herbicides-Theory. *Weed Sci.* **1973**, *21* (1) 1−5.

Cryer, S. A.; Havens, P. L.; Rolston, L. J.; Swearingen, R. A.; Laskowski, D. A.; Blau, G. E. Addressing Regional Exposure of Crop Protection Chemicals to Non-Target Aquatic Organisms Resulting from Agricultural Runoff. In *Ecological Risk Assessment of Pesticides: Enhancing the Process*; Ingerson, C., Ed.; Lewis: Boca Raton, FL, 1998; in press.

Davis, R. F.; Wauchope, R. D.; Johnson, A. W.; Burgoa, B.; Pepperman, A. B. Release of Fenamiphos, Atrazine, and Alachlor into Flowing Water from Granules and Spray Deposits of Conventional and Controlled-Release Formulations. *J. Agric. Food Chem.* **1996**, *44*, 2900−2907.

Getzin, L. W. Factors Influencing the Persistence and Effectiveness of Chlorpyrifos. *Soil. J. Econ. Entomol.* **1985**, *78*, 412−418.

Havens, P. L.; Cryer, S. A.; Rolston, L. J. Tiered Aquatic Risk Refinement: Case Study At−Plant Applications of Granular Chlorpyrifos to Corn. *Environ. Toxicol. Chem.* **1998**, *17* (7), 1313−1322.

Holland, D. D.; Anthony, R. G. Fundamentals of Chemical Reaction Engineering. *Prentice Hall International Series in the Physical and Chemical Engineering Sciences*; Prentice-Hall: Englewood Cliffs, NJ, 1979.

Knisel, W. G., Ed. *CREAMS: A Field-Scale Model for **C**hemicals, **R**unoff, and **E**rosion from **A**gricultural **M**anagement **S**ystems*; USDA Conservation Research Report 26; U.S. GPO: Washington, DC, 1980; 640 pp., illus.

Laskowski, D. A.; Tillotson, P. M.; Fontaine, D. D.; Martin, E. J. Probability modelling. *Philos. Trans. R. Soc. London B* **1990**, *329*, 383−389.

Leonard, R. A.; Knisel, W. G. Groundwater Loadings by Controlled-Release Pesticides: A Gleams Simulation. *Trans. ASAE.* **1989**, *32* (6), Nov−Dec.

Leonard, R. A.; Knisel, W. G.; Still, D. A. GLEAMS: Ground Loading Effects of Agricultural Management Systems. *Trans. Am. Soc. Agric. Eng.* **1987**. *30* (5), Sept−Oct.

Nicks, A. CLIGEN weather generator program (version 1.0); USDA−ARS WEPP Water Erosion Project, Durant, OK, 1989.

Racke, K. D. Environmental Fate of Chlorpyrifos. *Rev. Environ. Contam. Toxicol.* **1993**, *131*.

Sharpley, A. N.; Williams, J. R., Eds. *EPIC−Erosion/Productivity Impact Calculator: Model Documentation*; U.S. Department of Agriculture Technical Bulletin 1768; U.S. GPO: Washington, DC, 1990; 235 pp.

U.S. Environmental Protection Agency. Final benefits evaluation of the use of at-plant insecticides on field corn; Washington, DC. 1996.

Walgenbach, D. D. Draft report on chlorpyrifos residual study in the field and laboratory; South Dakota State University, Brookings, SD, 1979.

Wauchope, R. D. The Pesticide Content of Surface Water Draining from Agricultural Fields-A Review. *J. Environ. Qual.* **1979**, *7*, 459-472.