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Mathematical Modeling of Controlled-Release Systems of Herbicides Using Lignins as Matrices

A Review

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Abstract

The herbicides applied in soils can be easily lost, owing to leaching, volatilization, and bio- and photodegradation. Controlled-release systems using polymeric matrices claim to solve these problems. The movement of the herbicides in the soil is also an important phenomenon to be studied in order to evaluate the loss processes. The development of mathematical models is a relevant requirement for simulation and optimization of such systems. This study reviews mathematical models as an initial step for modeling data obtained for controlled-release systems of herbicides (diuron, 2,4-dichlorophenoxyacetic acid, and ametryn) using sugarcane bagasse lignin as a polymeric matrix. The release kinetic studies were carried out using several acceptor systems including a water bath, soil, and soil-packed columns. Generally, these models take into account phenomena such as unsteady-state mass transfer by diffusion (Fick's law) and convection, consumption by several processes, and partitioning processes, resulting in partial differential equations with respect to time and space variables.

Index Entries: Mathematical modeling; controlled-release formulations; lignins.

Introduction

Mankind is living the beginning of a new millennium, but fundamental problems including the supplementation of water and food have not been solved yet. The distribution of aliments is one of these problems whose difficulties have been increased owing to limited cultivable areas and

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growth of the world population. The new concepts to solve such problems require the development of advanced technologies in agriculture that should cause no impact to the environment.

The large plantation of monocultures favored the increased utilization of pesticides for weed and pest control. This implies elevated risks for the environment, as well as health risks for the appliers and consumers of the aliments produced *(1)*.

The controlled release of herbicides is a technology that, in recent years, is proving to be very attractive for the solution of problems with the application and contamination of herbicides. Polymeric and macromolecular matrices are often utilized as support for the herbicide, and among the various materials used as support, lignin is an interesting alternative since it can be obtained from most agroindustrial residues, such as sugarcane bagasse, kraft liquor, rice, and wheat straw.

Controlled-release formulations can be obtained by the chemical or physical immobilization of the herbicide (active ingredient [AI]) in a polymeric or macromolecular matrix from which it will be gradually released to the soil.

In our research group, controlled-release systems of the herbicides diuron, 2,4-dichlorophenoxyacetic acid (2,4-D) and ametryn have been developed utilizing sugarcane bagasse lignin as macromolecular matrix. The release kinetics was evaluated monitoring the amount of AI released into several acceptor systems, including a water bath, soil, and soil columns *(2–9)*.

The necessity to describe the main phenomena involved in such systems has favored the development of mathematical models able to simulate the movement of herbicides in the soil *(10)*. This study reviews the mathematical models of controlled-release systems as an initial step for modeling the laboratory and field data obtained in our research group.

Obtention of Lignins and Formulations for Controlled Release of Herbicides

Controlled-release formulations can be obtained utilizing several polymers and macromolecules, synthetic or natural, such as polyvinyl chloride, starch, cellulose, and lignin *(1)*. Lignin is an interesting alternative material to be used because it has important advantages for controlled release and is also available in large quantities in several parts of the world, especially in tropical areas.

Lignin is basically formed by the radical polymerization of *p*-coumaryl, coniferyl, and sinapyl alcohols, and the result is a macromolecule with remarkable etherified-aromatic nature *(11)*. Technical and industrial lignins can be obtained as a byproduct in several processes of conversion of vegetal biomass, including the production of kraft pulp, sugar, and ethanol.

Obtention of Lignins

Various procedures are utilized to obtain lignin from vegetal biomass. These are the most important processes:

1. *Alkaline pulping process*: Alkaline lignins are produced by kraft- and soda-pulping processes (60% of the worldwide production of pulp is based in the kraft process). The obtained lignin is a macromolecule insoluble in water with low mol wt (2–15 kDa). Approximately 20×10^6 t of kraft lignin are produced each year in the United States *(12,13)*, and in Brazil this production reaches 3×10^6 t/yr *(14)*.
2. *Sulfite pulping process*: The sulfite process is still largely used for the separation of the lignin from biomass and produces lignin derivatives (lignosulfonates). Opposite to the kraft lignin, lignosulfonates have high mol wt (above 20 kDa) and are very soluble in water. The yearly production of lignosulfonates in the United States is lower than 1×10^6 t and is decreasing owing to economical restrictions *(12)*.
3. *Milling in ball mill*: Milled wood lignin is produced by milling of wood in a rotatory or vibratory ball mill. Lignin can be extracted from the resultant dust using appropriate solvents such as dioxane *(12,15)*. The milling process releases mildly 60% of the lignin present in the wood; nevertheless, modifications in the lignin structure can be promoted by the milling *(12,16)*. Despite the limitations, milling seems to be an effective process to obtain lignins from plants with small changes in the macromolecular structure *(12)*.
4. *Enzymatic release*: Hydrolytic enzymes, which hydrolyze polysaccharides, can be utilized to act over plant fibers and to release lignin. After carbohydrate removal, lignin is solubilized in dioxane *(12,17)*. Extensive analytical studies support the fact that in the enzymatic release no further modifications in lignin occur *(12,18)*.
5. *Acidic hydrolysis*: The acidic hydrolysis of the polysaccharides from bagasse, wood, and other lignocellulosics releases lignin but also causes condensation reactions in the lignin. Ether linkages are cleaved and substituted by carbon-carbon bonds. Condensation can be minimized by using hypochloric acid instead of stronger mineral acids *(12)*.
6. *Extraction with organic solvents*: Lignin can be extracted by solvent mixtures as an alternative to commercial pulping processes. This group of alternative pulping processes is called Organosolv, and their advantages are small environmental impact and the possibility of recovering the solvent *(19)*. The modifications in the Organosolv lignin are smaller in comparison with other pulping processes *(12)*.
7. *Steam explosion*: This process is proposed for the production of pulps from both hardwoods and softwoods even from gramineae such as sugarcane bagasse *(20)*. First, the material is impregnated with acids, bases, or organic solvents and introduced in a high-pressure reactor, pressurized with steam at 180–200°C. After short time periods, the

reactor is decompressed and the material refined for the production of pulp *(20)*. Lignin can be extracted with NaOH solution and recovered from the black liquor after precipitation with concentrated sulfuric acid *(20)*.

Steam explosion was the main process employed for our research group to obtain lignin to be utilized as matrix in the controlled-release formulations *(21)*. Kraft and Organosolv lignins were also used *(8,21)*.

Obtention of Formulations for Controlled Release of Herbicides

There are basically three different methods with respect to the immobilization of agricultural defensives using lignocellulosics to produce controlled-release formulations *(1)*:

1. Through the formation of a solid matrix with or without the utilization of physical modifiers
2. By chemically bounding the active ingredient to the lignin
3. By retention of the active ingredient in modified materials through crosslinking

The most adequate immobilization method depends on several factors *(1)*:

1. Nature and persistence of the agrochemical
2. Availability of the lignocellulosics
3. Costs involved in the modifications and refining processing
4. Most appropriate application
5. Potential market of the final product

The formation of solid matrices is the simplest method and has more advantages over the other ones, since chemical modifications in the matrix are not necessary and formation of new structures by chemical bonds occur *(1)*. The process for registration of herbicides by regulatory organizations (e.g., Food and Drug Administration) is simpler for formulations in which the matrix interacts only physically with the active ingredient.

Studies employing formulations of 2,4-D with kraft lignin obtained from pinewood as support (melting with 50% AI) showed that the weed control in forests was efficient for 14 mo after only one application of the formulation *(1)*.

Formulations of 2,4-D with lignin extracted from rice straw were prepared by melting *(22)*, and the release of 2,4-D in water was monitored for 150 d, the time necessary for complete release.

Riggle and Penner *(23–25)* developed a systematic study for the controlled release of metribuzin, chloramban, and alachlor, using different kraft lignins as macromolecular support. Formulations were obtained by a simple adsorption system of the AI in the lignin. In soil-column assays, these formulations presented elevated efficiency to prevent losses by leach-

ing. For the most part, the work developed until now utilized kraft lignin from pinewood (INDULIN-AT, Westvaco) as macromolecular matrix.

Recently, Ferraz et al. *(21)* observed different release rates for formulations of 2,4-D when different types of lignin and different conditions of processing were employed during the obtention of these formulations. This result was attributed to the different physical and chemical properties of the lignins used. The development of formulations using lignins from different sources and the control and modifications of the processing conditions can also be useful for the obtention of formulations with different release rates of a specific AI *(2–7,21)*.

Kinetic Aspects of Controlled Release from Matrices

The release rate of an AI from a matrix can be controlled by several sequential or simultaneous mechanisms that are generally difficult for a mathematical analysis *(26)*. However, an overall apparent order to the release kinetics in these complex systems can be experimentally determined. Table 1 presents the main kinetic models used to describe the release rate of an AI from a matrix to an acceptor medium, usually a water bath. Each kinetic model corresponds to a specific controlling mechanism of the release rate, as will be shown for the (–1)-order kinetics *(5,9,27,28)*.

In the zero-order kinetics, the release rate is constant and independent of the time. The first-order kinetics is observed when the release rate declines with the time and is proportional to the amount of AI remaining in the matrix. In the second-order kinetics, the release rate is proportional to the square of the amount of AI contained in the matrix. For the kinetics of order –1, the release rate is inversely proportional to the amount of AI released.

For monolithic systems in which the AI is physically dissolved in a nonerodible polymeric matrix, several studies showed that the integral form of the (–1)-order kinetics better describes the cumulative amount of AI released at the time *(5,7,9,28–34)*. This kinetics can be explained by a diffusion mechanism through the matrix pores. Aiming the mathematical description of the diffusion mechanism the following hypotheses are assumed *(35)*:

1. The matrix is an isothermal slab.
2. The AI is dissolved in the solvent (water) contained in the matrix pores at a concentration less than the saturation concentration (c_s).
3. The release occurs through the two faces of the slab.
4. The total sum of the individual volumes of the pores is εAl.
5. The AI concentration in the matrix pores (c_p) varies with depth x into the matrix and with time t: $c_p = c_p(x,t)$.
6. The initial concentration of AI in the pores is $M_0/\varepsilon Al$.
7. Perfect sink conditions are at $x = 0$ and $x = l$ (two situations in which this hypothesis may not be valid are the release into a relatively small volume, or when a stagnant unstirred layer exists at the interface between the monolith and the release medium).

Table 1
Kinetic Models Used
to Describe the Release Rate of an AI from a Matrix[a]

Order	Differential form	Integral form
0	$\frac{dM_t}{dt} = k_0$	$M_t = k_0 t$
1	$\frac{dM_t}{dt} = k_1(M_0 - M_t)$	$\ln\left(\frac{M_0 - M_t}{M_0}\right) = -k_1 t$
2	$\frac{dM_t}{dt} = k_2(M_0 - M_t)^2$	$\frac{M_t}{M_0 - M_t} = M_0 k_2 t$
–1	$\frac{dM_t}{dt} = \frac{K^2}{2M_t}$	$M_t = Kt^{1/2}$

[a] t = time (d); M_t = cumulative amount of AI released at the instant t (g); M_0 = initial amount of AI in the matrix (g); k_0 = rate constant for zero-order kinetics (g/d); k_1 = rate constant for first-order kinetics (d^{-1}); k_2 = rate constant for second-order kinetics (g/d); and K = rate constant for (–1)-order kinetics ($g/d^{1/2}$).

Considering the previous assumptions, using the following equation:

$$\frac{\partial c_p}{\partial t} = D_{eff}\frac{\partial^2 c_p}{\partial x^2} \tag{1}$$

subject to the following initial and boundary conditions:

$$c_p(x, t = 0) = \frac{M_0}{\varepsilon A l} \tag{2}$$

$$c_p(0, t) = c_p(l, t) = 0 \tag{3}$$

describe the spatial and temporal profiles of the herbicide concentration in the matrix pores. In Eqs. 1–3, c_p is the AI concentration in the pores (g/cm^3); D_{eff} is the effective diffusion coefficient (cm^2/d); ε is the matrix porosity; A is the slab area (cm^2); and l is the slab thickness (cm).

The solution of Eq. 1 satisfying the initial and boundary conditions is given as follows *(35)*:

$$c_p(x, t) = \frac{4M_0}{\varepsilon A l \pi}\sum_{n=0}^{\infty}\left\{\frac{1}{2n+1}\exp\left[\frac{-(2n+1)^2\pi^2 D_{eff} t}{l^2}\right]\sin\left[\frac{(2n+1)\pi x}{l}\right]\right\} \tag{4}$$

The mass flow rate (Q_t) of herbicide at time through the face of the slab at $x = l$ may be evaluated using Eq. 5:

$$Q_t = -A\varepsilon D_{eff} \left.\frac{\partial c_p}{\partial x}\right|_{x=l} \tag{5}$$

Since release occurs through both faces of the slab, the cumulative amount of AI released at time t is given by:

$$M_t = -\int_0^t 2A\varepsilon D_{eff} \left.\frac{\partial c_p}{\partial t}\right|_{x=l} dt \tag{6}$$

Solving the integral in Eq. 6, Eq. 7 is obtained *(35)*:

$$M_t = M_0 \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left(\frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 D_{eff} t}{l^2} \right] \right) \right] \tag{7}$$

At early times, Eq. 7 may be replaced by the simpler Eq. 8:

$$M_t = \frac{4M_0}{l} \sqrt{\frac{D_{eff} t}{\pi}} \tag{8}$$

which is analogous to the integral form of the (–1)-order kinetics since $K = (4M_0/l)\sqrt{(D_{eff}/\pi)}$.

Eq. 8 may not be valid to describe the first data points owing to the removal of AI by direct solubilization from the surface of the matrix and owing to the time required for water to penetrate into the matrix *(7)*. Furthermore, Eq. 8 is valid until about 60% of the herbicide is released. Above this value, the release rate is related to the time using the following empirical equation *(36)*:

$$\frac{dM_t}{dt} = c_1 \exp(-c_2 t) \tag{9}$$

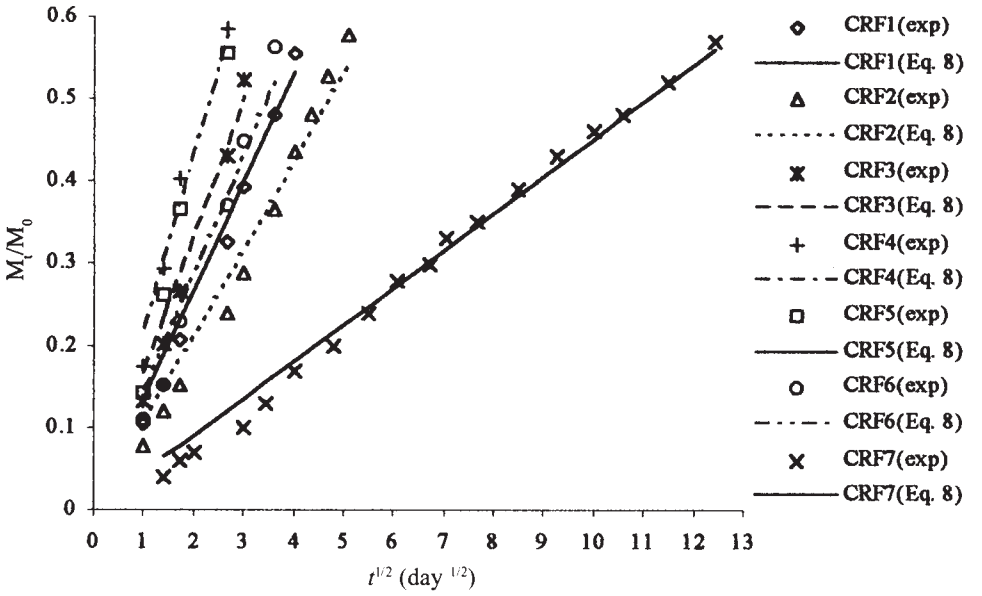
in which c_1 and c_2 are constants. The solution of Eq. 9 satisfying the condition

$$t \to \infty, \quad M_t \to M_0 \tag{10}$$

is given by

$$M_t = M_0 - (c_1/c_2) \exp(-c_2 t) \tag{11}$$

Figure 1 shows the validity of Eq. 8 to describe some of our kinetic data of herbicide release in a water bath for 2,4-D and diuron formulations obtained from different sources of lignins *(21)*. According to Fig. 1, release of herbicides from lignin-based formulations follows a diffusion-controlled



Symbol	Herbicide	Lignin Source	Lignin Production Process	Precipitant Agent	Herbicide Concentration
CRF1	2,4-D	Bagasse	Steam Explosion	HCl	45%
CRF2	2,4-D	Bagasse	Steam Explosion	H_2SO_4	45%
CRF3	2,4-D	Eucalyptus*	Kraft	H_2SO_4	45%
CRF4	2,4-D	Eucalyptus**	Kraft	H_2SO_4	45%
CRF5	2,4-D	Eucalyptus**	Kraft	HCl	45%
CRF6	2,4-D	Pinus	Kraft	***	45%
CRF7	Diuron	Bagasse	Steam Explosion.	HCl	50%

*from kraft liquor containing 14% solids, **from kraft liquor containing 37% solids, ***pinus kraft lignin (INDULIN AT, Westvaco).

Fig. 1. Comparison between experimental data and Eq. 8 predictions for 2,4-D and diuron formulations until 60% of herbicide release.

mechanism in which a linear response of released herbicide as a function of the square root of time is observed for data until $M_t/M_0 = 0.6$.

When the AI has an initial amount higher than that corresponding to saturation, a moving front separates the core of undissolved AI from the outer part of the slab through which the dissolved AI diffuses. Higuchi *(37)* originally treated this case using a pseudo-steady-state approximation and developed the following equation:

$$M_t = 2A\left[D_{eff}\varepsilon c_s\left(\frac{2M_0}{Al} - \varepsilon c_s\right)t\right]^{1/2} \quad (12)$$

An exact solution to this problem, in which the pseudo-steady-state approximation is relaxed, was developed by Miller and Peppas *(38)*:

$$M_t = \frac{4A\varepsilon c_s}{erf(\zeta)}\sqrt{\frac{D_{eff}t}{\pi}} \quad (13)$$

in which *erf* is the error function and ζ is the root of the following implicit equation:

$$\zeta \exp(\zeta^2)\,\mathrm{erf}(\zeta) - \varepsilon c_s / \left\{\pi^{1/2}\left[(M_0/Al) - \varepsilon c_s\right]\right\} = 0 \quad (14)$$

The exact solution is useful when M_0/Al is not much greater than εc_S. For $M_0/Al >> \varepsilon c_S$, the exact and approximate solution are equivalent, so Higuchi's *(37)* equation (Eq. 12) may be safely used. Equations 12 and 13 are valid as long as the undissolved AI core remains. This will be the case at least until $M_t = M_0 - \varepsilon Alc_S$.

Mathematical Models of Transport and Degradation of Herbicides in Soils

The mathematical modeling of transport and degradation of herbicides in soil requires several process descriptions *(39)*:

1. Flux models describing the mass transport through soil
2. A mass storage description, identifying where and in what form the herbicide resides in the soil volume
3. Interphase mass-transfer relations, to describe the mass exchange between soil phases
4. Degradation models, describing chemical and biological transformation processes

Herbicides are transported through the soil by two main transport processes *(40)*:

1. Vapor-phase transport
2. Hydrodynamic transport including mechanisms of diffusion, convection, and dispersion as soluble constituents of the aqueous phase

Other processes such as chemical degradation, biological degradation, photodegradation, and interphase mass transfer (partitioning processes) affect the herbicide transport in soil. The relative importance of each transport and degradation process is dependent on several factors such as the following *(40)*:

1. Physical and chemical properties of the herbicide
2. Properties of the soil and water with which the herbicide comes in contact
3. Prevailing climatic conditions

Vapor-Phase Transport

The herbicide transport in the vapor phase is assumed to occur by diffusion in the air contained in the soil pores. This transport process is described by the Fick's law in which an effective diffusion coefficient ($D_{eff,v}$) is used to account for the increased path length and decreased cross-sectional area restricting vapor flow in soil compared to free diffusion in air:

$$J_v = -D_{eff,v} \frac{\partial C_v}{\partial Z} \tag{15}$$

in which J_v is the herbicide-vapor flux through gaseous phase (g/[cm^2 · d]); $D_{eff'v}$ is the effective diffusion coefficient of the vapor in air (cm^2/d); C_v is the herbicide concentration in the gaseous phase (g/cm^3); and Z is the soil depth (cm).

The gas-phase transport will be more significant for compounds presenting low solubilities and high vapor pressures *(41)*.

Hydrodynamic Transport

Herbicides dissolved in the soil solution may be transported either by bulk flow of soil solution (convective transport) or by diffusion and dispersion through the solution phase. The dispersion process is modeled formally as analogous to the diffusion process (dispersive flux is set proportional to the concentration gradient). Equation 16 describes the herbicide hydrodynamic transport in soil *(10,38)*:

$$J_l = -D_{eff,l} \frac{\partial C_l}{\partial Z} - D_h \frac{\partial C_l}{\partial Z} + C_l\, q_w \tag{16}$$

in which J_l is the dissolved-herbicide flux by hydrodynamic transport (g/[cm^2 · d]); q_w is the area-averaged water flux (cm/d); $D_{eff,l}$ is the effective diffusion coefficient of herbicide in the solution phase (cm^2/d); and D_h is the hydrodynamic dispersion coefficient (cm^2/d).

Since the dispersion coefficient cannot be estimated separately from the diffusion coefficient using Eq. 16, the terms involving these coefficients usually are combined to result as follows:

$$J_t = -D_d \frac{\partial C_l}{\partial Z} + C_l\, q_w \tag{17}$$

in which D_d is the effective dispersion-diffusion coefficient.

Another convective flux of soil solution is that owing to water evaporation *(42)*. Water evaporation from the surface induces an upward flow of soil solution, which carries with it herbicide and other solutes. The mass flux of herbicide to the surface (J_S, g/[cm^2 · d]) depends on the evaporation rate (E, cm/d) and the herbicide concentration in soil solution *(42)*:

$$J_S = C_l E \tag{18}$$

This convective flux will be more significant in wet soil than in dry soil.

Partitioning Processes

The herbicide transport in soil occurs always in unsteady-state conditions. In such conditions, the herbicide concentration in each soil phase (solid, aqueous, and vapor) varies with soil depth Z and time t. Equation 19 describes the spatial and temporal profiles of total herbicide concentration in soil *(10)*:

$$\frac{\partial C_t}{\partial t} = -\frac{\partial J_t}{\partial Z} - \phi \tag{19}$$

in which $C_t = \rho C_S + \theta C_l + \alpha C_v$ is the total herbicide concentration (mass/soil volume); $J_t = J_v + J_l + J_S$ is the total herbicide flux in soil (g/[cm^2 · d]); C_S = adsorbed herbicide concentration (mass/mass of solids); C_l is the dissolved herbicide concentration (mass/liquid volume); C_v is the herbicide vapor concentration (mass/air volume); ρ is the volumetric density of the soil (soil mass/soil volume); θ is the volumetric water content (volume/soil volume); α is the volumetric air content (volume/soil volume); and ϕ is the volumetric degradation rate by several processes including hydrolysis and biodegradations (herbicide mass/liquid volume/time).

The partitioning process is an important interphase mass-transfer process that determines the relative fraction of the herbicide that is present in each soil phase (solid, aqueous, and vapor). The herbicide concentration in each phase in turn influences other transport and degradation processes as follows. The herbicide partitioning to the stationary solid phase slows the rate of transport by processes of aqueous-phase convection and dispersion, and vapor-phase mass transfer. Furthermore, the portion of herbicide that is sorbed is usually assumed not to be available for degradation processes.

As with all interphase mass-transfer processes, description of the partitioning processes requires information about the equilibrium achieved between phases and the rate as the equilibrium is attained.

Partitioning Between Dissolved and Adsorbed Phases

Partitioning between the dissolved and adsorbed phases is modeled mathematically using an adsorption relationship, which may be expressed by the following general equation *(39)*:

$$C_S = f(C_l) \tag{20}$$

The form of $f(C_l)$ that describes well the adsorption of many nonionic compounds over a large range of concentrations is the Freundlich's adsorption isotherm:

$$C_S = K_F C_l^{1/N} \tag{21}$$

in which K_F is the Freundlich's adsorption coefficient and the power coefficient $1/N$ is a constant that is generally less than unity. Many herbicides that have been characterized in the laboratory show deviation from linearity in their adsorption behavior. Hamaker and Thompson *(43)* obtained the following average values of power coefficient $1/N$ for some common pesticides tested on different soils: 0.82 (simazine), 0.71 (atrazine), 0.81 (prometon), 0.86 (prometryn), 0.77 (monuron), and 1.03 (parathion).

The simplest form of $f(C_l)$ is the so-called linear adsorption isotherm, which is given by the Eq. 22 *(10,39)*:

$$C_S = K_d C_l \tag{22}$$

in which K_d is the distribution coefficient, which is a function of the properties of both soil and herbicide. The linear adsorption isotherm has been shown to apply reasonably well at low concentration for nonionic organic compounds *(44)*.

Partitioning Between Dissolved and Gaseous Phases

The partitioning between dissolved and gas phases for an organic compound is modeled mathematically using the modified form of Henry's law *(10,39)*:

$$C_v = K_H C_l \tag{23}$$

in which K_H is the modified Henry's constant. Henry's law is assumed to be valid at all times because the phases are considered to be in equilibrium. Thus, modified Henry's constant may be estimated from Eq. 24:

$$K_H = \frac{C_v^*}{C_l^*} \tag{24}$$

in which the asterisk refers to the saturated state of the phases. Since both vapor density and solubility are dependent on the temperature, K_H is also a function of the temperature.

An implicit hypothesis assumed in the previous models is that the state of equilibrium between phases is instantaneously achieved. However, at relatively high water contents in the soil, equilibrium may not be reached if water is flowing. Also, the adsorption process may be limited by the rate of diffusion from the surrounding solution to the stationary adsorption sites, mainly at high water flow rates. These situations lead to somewhat more complex equations, which are discussed by Jury and Ghodrati *(39)*.

From the equations describing the herbicide partitioning between the soil phases, Eq. 19 can be written as a function of C_l, which is a variable more easily measured. Moreover, the diffusive flux from the matrix is computed as an input term in the soil, in this way coupling both systems (matrix and soil).

Herbicide Degradation Processes in Soils

Nonbiological Degradations

The main nonbiological degradation processes of herbicides in soil are hydrolysis, oxidation-reduction, and photodecomposition *(45)*. Photodecomposition is significant in the soil region very near to the soil-atmosphere interface, occurring during and after application of the herbicide *(46)*. However, this degradation process is insignificant below the top few centimeters of soil because sunlight irradiation is absent *(39)*. The relative importance of redox degradation processes for organic compounds in soil is not understood quantitatively *(39)*.

On the other hand, hydrolysis is a significant degradation process in determining the fate of a herbicide in the environment. For many herbicides, hydrolysis can be the main process for their degradation in the soil *(47)*. Often, hydrolysis of specific functional groups is required before microbial degradation can be initiated. However, some organic functional groups are relatively or completely inert with respect to hydrolysis under reaction conditions existing in most soils. The functional groups potentially susceptible to hydrolysis are amides, carbamates, epoxides, aliphatic and aromatic esters, alkyl and aryl halides, nitriles, and phosphorous esters *(47)*.

The hydrolysis rate can be a function of chemical parameters such as pH, dissolved organic matter, and dissolved metal ions. In general, hydrolysis of organic chemicals in water under pH-buffered conditions is pseudo-first-order in the concentration of the organic compound *(45,48)*:

$$(-r_H) = k_{obs} C_l \tag{25}$$

in which $(-r_H)$ is the hydrolysis rate; and k_{obs} is the observed pseudo-first-order rate constant that can include contributions from acid-catalyzed or base-mediated hydrolysis, nucleophilic attack by water, or catalysis by buffers in the reaction medium.

Hydrolysis processes in soil can be mediated by microorganisms (biotic hydrolysis). In these cases, hydrolysis rate is often proportional to microbial biomass and/or specific concentration of enzyme (activities) in the medium. For many compounds, both abiotic and biotic hydrolysis processes contribute to the degradation of herbicides in soil. Unfortunately, the hydrolysis rate constant is measured in such a mode that it is not possible to discriminate between abiotic and biotic contributions. However, biotic hydrolysis kinetics is often, but not always, characterized by an initial lag period during which little or no change in concentration occurs,

followed by a more rapid change in concentration in which its natural log is generally linear with time *(48)*. Several herbicides, including dalapon, chloridazon, and 2,4-D, have been reported to exhibit this kind of kinetics *(49)*. For abiotic hydrolysis under pH-buffered conditions, a lag period is generally not observed.

Biological Degradations

The degradation of a particular organic substrate by microorganisms can occur under one of the following conditions *(50)*:

1. The microorganisms are growing at the expense of the substrate and using it as a source of carbon, energy, or possibly another nutrient element needed for growth.
2. The microorganisms are growing at the expense of another organic nutrient that is used as a source of carbon, energy, or both. The substrate of interest is metabolized but not used to supply building blocks for cell synthesis.
3. The microorganisms do not grow as long as they metabolize the substrate.

The biodegradation kinetics is a function of the herbicide's nature and concentration, the organisms responsible for the degradation, and a variety of environmental factors. A model describing the biodegradation kinetics is extremely useful because it permits prediction of the herbicide levels present at some future time, and allows assessment of whether the herbicide will be degraded before it is transported to a site where susceptible humans, animals, or plants may be exposed. Several models have been proposed to represent the kinetics of biodegradation in soil, including empirical and theoretical models *(51–53)*.

Empirical Kinetic Models of Herbicide Biodegradation

The modeling of biodegradation kinetics in soil has usually been empirical, reflecting the low level of knowledge about microbial populations and their activities in soil. An extensively used empirical model is the power law in which the degradation rate is proportional to a power of the substrate concentration *(50,53)*:

$$(-r_S) = kS^n \tag{26}$$

in which S is the substrate concentration; t is the time; k is the rate constant for nth-order kinetics; and n is a fitting coefficient. This model can be fitted to experimental data of substrate concentration by varying n and k until a good fit is achieved. When $n = 1$, the model is equivalent to first-order kinetics, and it often has been used in this form *(53)*. When $n = 0$, the model reduces to the zero-order kinetics, and when $n = 2$, second-order kinetics is represented. Values of n greater than unity are commonly observed in soil *(53)*. The power law model allows a discrimination between different curves, but gives no insight into the reasons for their shapes.

Theoretical Kinetic Models of Herbicide Biodegradation

Substrate concentration and initial cell density are certainly important factors in determining the kinetics of biodegradation in soil. Under special circumstances, information on these factors may be sufficient to describe the kinetics of biodegradation. However, it is not clear whether these variables are enough to explain the biodegradation kinetics for most compounds or for many soils.

Biodegradation Processes Coupled to Cell Growth

Growth is a biological process in which the substrate is used as a source of carbon and energy, and is converted to cell mass and metabolites. To simplify the kinetic modeling of the cell growth process, the following hypotheses are assumed:

1. A pure culture of a microorganism's population is growing.
2. The organic substrate is water soluble and nontoxic for the microorganism.
3. The organism is growing in well-aerated liquid media.
4. The inorganic nutrients and growth factors needed by the microorganisms are present in excess of the organism's need.
5. No barriers exist between the substrate and the cells.

The growth rate, like a chemical reaction rate, is a function of chemical concentration. The chemicals in this case are the essential nutrients or substrates for growth. The form of the relationship between specific growth rate and substrate concentration (S) was first established by Monod *(54–56)*:

$$\mu = \frac{\mu_{max} S}{K_S + S} \tag{27}$$

The Monod model is based on empirical observations, but it is frequently rationalized by analogy with Michaelis-Menten enzyme kinetics *(54–56)* with the hypothesis that a single, rate-limiting, enzyme-catalyzed step controls the growth rate. Furthermore, some physical and biological meaning can be attributed to the model constants: μ_{max} (h^{-1}) is the maximum specific growth rate (which occurs at the higher range of substrate concentrations), and K_S(g/cm^3) is inversely proportional to the affinity of the microorganism for its substrate. Focht and Shelton *(57)* found higher K_S values for biodegradation of 3-chlorobenzoate in soil than in pure culture, which they attributed to a lower degree of contact in soil between the substrate and the organisms responsible for its degradation. Pure cultures and microbial communities may have two K_S values for a single substrate *(58,59)*. Two affinity constants have also been observed for phenol-degrading microorganisms *(60)*. The presence of more than one affinity constant in nature may reflect the activity of a single population or of different species with dissimilar affinities for the same organic substrate.

Cell growth occurs only in the presence of substrate and other nutrients. Thus, the substrate utilization rate can be related to specific cell growth rate by Eq. 28 *(54–56)*:

$$\left(-r_s\right) = \left(\frac{\mu_{max} S}{K_S + S}\right) \frac{X}{Y_{X/S}} \tag{28}$$

in which $Y_{X/S}$ is a yield coefficient expressed as the mass of cells formed per mass unit of substrate consumed.

When $S >> K_S$, an exponential cell growth is observed and the concentrations of cells and substrate during the growth are given by Eqs. 29 and 30 *(50,55)*:

$$X = X_0 \exp(\mu_{max} t) \tag{29}$$

$$S = S_0 + (X_0 / Y_{X/S}) [1 - \exp(\mu_{max} t)] \tag{30}$$

in which X_0 and S_0 are the initial concentrations of substrate and cells, respectively. Exponential kinetics have been observed for the consumption of benzoate in cultures of a *Pseudomonas* sp. *(61)* and apparently for the formation of $^{14}CO_2$ from ^{14}C-2,4-D added at high concentrations to soil *(62)*.

When $S << K_S$, a logistic cell growth is observed and the concentrations of cells and substrate are given by *(50,55)*:

$$X = \frac{X_0 \exp(a_1 t)}{1 + (a_2 / a_1) X_0 [1 - \exp(a_1 t)]} \tag{31}$$

$$S = S_0 / \{[1 + (b_1 / b_2) S_0] \exp(-b_2 t) - (b_1 / b_2) S_0\} \tag{32}$$

in which

$$a_1 = \frac{\mu_{max}}{K_S} \left(S_0 + \frac{X_0}{Y_{X/S}}\right); \quad a_2 = -\frac{\mu_{max}}{K_S Y_{X/S}}; \quad b_1 = -Y_{X/S} a_2; \quad b_2 = -a_1$$

Logistic kinetics provided the best fit to the rate of nitrification in a soil perfusion column *(63)*, apparently because of first growth and then saturation of the population of nitrifying bacteria at a fixed number of sites where nitrification could occur.

When simplifications cannot be made in the substrate degradation kinetics ($S_0 \sim K_S$), the following implicit equation describing the substrate concentration with time t is obtained *(50,55)*:

$$X_0 + Y_{X/S} (S_0 + K_S) \ln \frac{X_0 + Y_{X/S} (S - S_0)}{X_0} - K_S Y_{X/S} \ln \frac{S}{S_0} = \mu_{max} (X_0 + Y_{X/S} S_0) t \tag{33}$$

Equation 33 describes the metabolism of benzoate by *Pseudomonas* sp. at benzoate levels near K_S *(61)*.

At high concentrations, many compounds are toxic to the very microorganisms that use them as carbon sources *(62)*. A relationship between growth rate and concentration of a potentially toxic substrate is given by the modified form of the Monod model *(50,55)*:

$$\mu = \{\mu_{max} S/[\, K_S + S + (S^2/\, K_I)]\} \tag{34}$$

in which K_I is an inhibition constant that reflects the reduction of the growth rate by high-substrate concentrations. This equation has been used for describing the kinetics of phenol and pentachlorophenol metabolism by microorganisms *(64,65)*.

Biodegradation Processes Without Cell Growth

If the cell concentration is high relative to the substrate concentration, little or no cell growth occurs. As a consequence, the cell concentration at time t is assumed to be equal to the initial cell concentration [$X(t) = X_0$]. Under this condition, the substrate degradation kinetics resemble enzyme reactions because growth is not involved.

For nongrowing cells, the kinetics when $S_0 >> K_S$, $S_0 \sim K_S$, and $S_0 << K_S$ are so-called pseudo-zero-order, Monod-no-growth, and pseudo-first-order kinetics, respectively, because cell concentration is a constant *(50)*. The integral forms of these kinetics are expressed mathematically as follows:

Pseudo-zero-order:

$$S = S_0 - k_2 t; \quad k_2 = \mu_{max}(X_0/\, Y_{X/S}) \tag{35}$$

Monod-no-growth:

$$K_S \ln(S/\, S_0) + S - S_0 = -k_2 t \tag{36}$$

Pseudo-first-order:

$$S = S_0 \exp(-k_1 t); \quad k_1 = (\mu_{max} X_0/\, K_S Y_{X/S}) \tag{37}$$

First-order kinetics has been observed for the metabolism of hexazinone *(66)*, 2,6-dichlorobenzonitrile *(67)*, chlorosulfuron *(68)*, and a number of other compounds. Monod-no-growth kinetics has been reported to describe the kinetics of biodegradation of picloram in soil *(52,69)*.

Scow et al. *(70)* found that the models derived from the Monod model did not provide good fits to the kinetic data of degradation at low concentrations of phenol, 4-nitrophenol, aniline, 2,4-dichlorophenol, benzylamine, nitrilotriacetic acid, and cyclohexylamine. These models also did not fit satisfactorily kinetic data of degradation of atrazine, linuron, and picloram *(51)*. The fact that the models derived from the Monod model do not adequately describe biodegradation in soil is not surprising since two assumptions of these models are not very realistic. The existence of other communities of microorganisms in soil and a limitation to degradation owing to sorption or slow diffusion of the substrate from inaccessible to accessible sites are possible reasons for the lack of fit of such models. How-

ever, it is important to consider the utility of the theory derived from models of pure cultures of bacteria growing under controlled conditions on high concentrations of freely available substrates to environmental conditions. A more sophisticated approach concerns substrate availability to the microorganisms. In this approach, the substrate is assumed to be distributed in two compartments. In one compartment, the substrate is freely available to microorganisms and subject to rapid degradation. In the other compartment, the substrate is not readily available because it is adsorbed to colloidal surfaces or deposited in inaccessible micropores. After the substrate in the first compartment is depleted, the subsequent biodegradation rate is limited by the rate of desorption or diffusion of the substrate from the inaccessible micropores to sites containing the active microorganisms.

Conclusion and Further Advances in Technology of Controlled Release of Herbicides Using Lignins as Matrices

Controlled release of herbicides using lignin as the matrix proved to be a promising and alternative technology for weed control. The main limiting factor for an industrial application is the scale-up of the formulation's production.

The release of herbicides is governed by partial differential equations that can be solved by appropriate numerical methods and using available information about model parameters. Our research group obtained a series of data for controlled release of herbicides in water, soil, and soil columns. Recently, an empirical modeling of the soil-leaching profiles of ametryn applied as conventional and lignin controlled-release formulations resulted in equations with exponential and square root terms in time *(71)*. Further analysis of these profiles should be made employing the phenomenological approach discussed in this article.

Experimental release data of herbicides from controlled-release formulations are usually modeled by the simplified equation $M_t = K \cdot t^{1/2}$, which is valid only until 60% of the release. For the modeling of the release process in all its extension, more terms of the series that originates the simplified equation should be employed.

Generally the models available are useful only for some specific process treated separately. Most of the published studies are based on experimental data that on controlled-release systems applied to soils are extremely laborious to be obtained. An integral modeling including all release and degradation processes can allow a more effective development of this technology with less experimental effort.

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