Environ. Sci. Technol. **2003**, *37,* 2257−2261

Modeling Controlled Nutrient Release from a Population of Polymer Coated Fertilizers: Statistically Based Model for Diffusion Release

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A statistically based model for describing the release from a population of polymer coated controlled release fertilizer (CRF) granules by the diffusion mechanism was constructed. The model is based on a mathematical-mechanistic description of the release from a single granule of a coated CRF accounting for its complex and nonlinear nature. The large variation within populations of coated CRFs poses the need for a statistically based approach to integrate over the release from the individual granules within a given population for which the distribution and range of granule radii and coating thickness are known. The model was constructed and verified using experimentally determined parameters and release curves of polymer-coated CRFs. A sensitivity analysis indicated the importance of water permeability in controlling the lag period and that of solute permeability in governing the rate of linear release and the total duration of the release. Increasing the mean values of normally distributed granule radii or coating thickness, increases the lag period and the period of linear release. The variation of radii and coating thickness, within realistic ranges, affects the release only when the standard deviation is very large or when water permeability is reduced without affecting solute permeability. The model provides an effective tool for designing and improving agronomic and environmental effectiveness of polymer-coated CRFs.

Introduction

Controlled release fertilizers, CRFs, based on coating with hydrophobic organic polymers are perceived as the ones providing the best control over release (*1*−*3*). The release from such CRFs is by the diffusion mechanism (*4*). The temporal patterns of release from a population of well performing coated CRFs are generally sigmoidal (*4, 5*). These match the temporal patterns of nutrient uptake by plants and thus significantly reduce environmental pollution due to fertilizer application (*1*, *3*, *6*). Shaviv et al. (*4*) developed a mechanistic-mathematical model which describes the release from a single coated granule under the diffusion mechanism. The release is controlled by the mass transfer properties of the coating material, properties of the active agent (fertilizer) within the granule, and coating thickness and granule radius. The release from a single granule of a polymer coated CRFs, in which the diffusion mechanism dominates, consists of three stages: an initial stage during which no release is observed (lag period); a stage of constant release; and finally a phase of gradual decay of the release rate. The model succeeds in describing the complex and "non-Fickian" (or mathematically nonlinear) nature of the cumulative release from a single granule, which basically features a sigmoidal pattern. Yet, the release pattern determined for populations of coated granules is in most cases significantly different from the one expected for one single granule (*7*−*9*). This is due to a large variation in properties such granule radius, coating thickness, or permeability of water or solute through the coating (*3*, *5*, *7*, *8*). No attention was paid to the modeling of fertilizer (or other agrochemicals) release from a population of CRF granules, which practically is very important. Some efforts were done with controlled release drugs in which a statistical model was applied on a mechanistic model of release from single granules (*10*). An alternative approach was offered in which release characteristics and chemophysical features of controlled release drugs were linked statistically allowing performance-optimization of the drugs (e.g., ref *11*).

In this paper a statistical model for release from a plurality of CRFs granules is developed on the basis of the mechanistic model of diffusion release from a single granule (*4*). The model is verified using data obtained by Raban (*7*) and by Zaidel (*8*). It is then used to perform a sensitivity analysis to the major factors, which affect the release from a population of granules and to statistical characteristics such as mean value, standard deviation, and distribution type.

Development of the Statistical Model

A large population of *N* coated granules is considered. The granules differ one from the other by two main geometrical factors: granule radius *r* and coating thickness *l*. The release from such a system could be described by solving simultaneously *N* differential equations, which numerically and practically does not appear to be an effective approach. Alternatively, a statistical treatment is presented which accounts for the effects of variation in CRF properties (e.g., coating thickness, granule radius, permeability) on the release from a large population of granules.

The statistical approach presented below is a modification and elaboration of the treatment of a population of coated granular drug proposed by Dappert and Thies (*10*). The model is based on the following assumptions: all granules in the population are spherical and the granules contain the same active component (fertilizer) and are coated with the same coating material.

The fractional release from the *i*th granule at time *t* is described by the function $g(r_i, l_i, t)$ which is basically the same for all individual granules and only the radius r_i and thickness l_i differ among granules. The formulation of the release function $g(r_i, l_i, t)$ depends on the release mechanism and takes different forms for the diffusion and for the "failure" release mechanisms (*3*, *5*). It is also assumed that the release from individual granules is unaffected by its neighbors. This is based on the assumption that the concentration of the released nutrient outside the granules is negligible. An assumption, which is fairly justified for release into free water (the common case in practical assessment of CRFs) or even for nitrogen release into soil where intensive nutrient uptake, transformations, and leaching take place (*4*).

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10.1021/es0205277 CCC: $25.00

To obtain the cumulative release from a population at time t, one should sum up $g(r_i, l_i, t)$ over $i = 1,...N$

$$C(t) = \sum_{i=1}^{N} g(r_i,l_i,t)w_i \tag{1}$$

where $C(t)$ is the fractional release of the total nutrient-load at time t, and w_i is the fraction of granules characterized by the release function $g(r_i, l_i, t)$. A continuous distribution function for the radius r and coating thickness l is introduced through a continuous probability density function $\psi(r,l)$. In this case w_i is replaced by $\psi(r,l)\,\mathrm{d}r\mathrm{d}l$ that stands for the weight fraction of the total mass released from the population represented by granules with the radius between r and $r+\mathrm{d}r$, and the thickness between l and $l+\mathrm{d}l$. In a real population of coated granules the probability density function $\psi\,(r,l)$ should be defined for a definite range of the radii, $r_{\min} \le r \le r_{\max}$, and the coating thickness, $l_{\min} \le l \le l_{\max}$, and thus eq 1 transforms into

$$C(t) = \int_{r_{\min}}^{r_{\max}} \int_{l_{\min}}^{l_{\max}} g(r,l,t)\psi(r,l)\mathrm{d}r\mathrm{d}l \tag{2}$$

Equation 2 represents the cumulative release from a group of granules, at time t, each being characterized by the general function $g(r, l, t)$.

Assuming, as first approximation, that the two variables r and l are independent (namely, the coating thickness is not affected by granule radius), the probability density function $\psi(r,l)$ can be expressed as a product of the two probability density functions of each of the variables

$$\psi(r,l) = \varphi_r\,(r)\,\varphi_l\,(l) \tag{3}$$

where, φ_r and φ_l are the probability density functions of the radius and the thickness, respectively. Accordingly eq 2 transforms to

$$C(t) = \int_{r_{\min}}^{r_{\max}} \int_{l_{\min}}^{l_{\max}} g(r,l,t)\varphi_r(r)\varphi_l(l)\mathrm{d}r\mathrm{d}l \tag{4}$$

At $t \rightarrow \infty$, the quantity of released mass should be close to the total payload, i.e., $C(t) \rightarrow 1$.

For the simple case of the diffusion release mechanism the function $g(r,l,t)$ takes the form of eq 14 given by Shaviv et al. for the release from a single CRF granule (*4*).

Lupo (*12*) found that when imperfections are caused during the coating process, solute permeability inversely depends on coating thickness: $P_s = \tilde{P}_s/l$. In such a case the release function takes a somewhat different form becoming nonlinear with respect to the thickness l and nonsymmetric with respect to the product $r \times l$ (*4*)

$$\tilde{g}(r,l,t) = \begin{cases} 0, t < t' \\ \dfrac{3\tilde{P}_s C_{\mathrm{sat}}}{rl^2}(t - t'), t' \le t < t^* \\ \left(1 - \dfrac{C_{\mathrm{sat}}}{\rho_s}\right) \exp\left[-\dfrac{3\tilde{P}_s}{rl^2}(t - t^*)\right], t \ge t^* \end{cases} \tag{5}$$

where $t' = (\gamma rl/3P_h\Delta P)$ is the duration of the lag-period [day]; $t^* = t' + (1 - (C_{\mathrm{sat}}/\rho_s))(rl^2\rho_s/3\tilde{P}_s C_{\mathrm{sat}})$ is the duration of the linear release period; $\tilde{P}_s$ is the specific solute permeability of the coating [cm^3 day^{-1}]; γ is the total fraction of voids within the granule; ΔP is the difference between vapor pressure of water and saturated urea solution (Pa); P_h [cm^2 day^{-1} Pa^{-1}] and P_s [cm^2 day^{-1}] are water and solute permeability coefficients of the coating, respectively; ρ_s [g cm^{-3}] is the density of the solid fertilizer; and C_{sat} [g cm^{-3}] is the saturation concentration of the fertilizer solution.

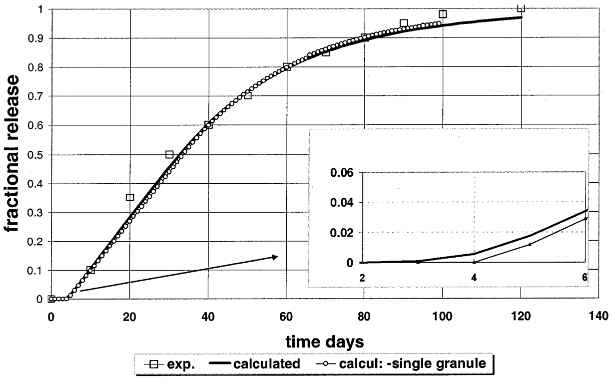

FIGURE 1. Comparison of (squares) experimentally measured cumulative release of urea granules coated with PULC (*7*); (solid line) release calculated applying the statistical approach ($\mu_r = 0.2$ [cm] and $\sigma_r = 0.02$; and $\mu_l = 0.011$ [cm] and $\sigma_l = 0.002$); and (triangles) release calculated for a single granule (eq 14 in ref *4*) characterized by the mean values (μ_r, μ_l) used for the statistical approach.

Model Verification

Experimental results obtained for the release from populations of urea granules coated with a polyurethane-like coating (PULC) and granules coated with modified polyolefin (MPO) coatings (*7*) were compared with the results obtained numerically (e.g., Figure 1) by solving eq 4 with $g(r,l,t)$ developed by Shaviv et al. (eq 14 in ref *4*). The calculations were done assuming normal distributions of the radii, r, and coating thickness, l. The values of the water and urea permeability (at 30 °C), mean radius μ_r and coating thickness μ_l, were evaluated experimentally by Raban (*7*). Good agreement between the calculated curves and the experimental ones was observed with standard errors of estimate, SEE, of 0.032 and 0.038 for the PULC and MPO coatings, respectively. The results demonstrate the possibility to model properly the release from a population of coated granules once the mean values of the normally distributed main governing factors are determined. Noteworthy is the fact that inserting the mean values μ_r and μ_l in a simple model of release from a single granule (e.g., eq 14 of ref *4*) yields also good agreement with the release from a population having a relatively narrow and normal distribution of μ_r and μ_l (Figure 1). The fact that only spherical CRF granules were selected and sieved for these experiments (*7*, *8*) supports this result. In the following analysis several realistic scenarios, some of which introduce significant changes in the release curves, are examined.

Sensitivity Analysis

a. Effect of Water and Solute Permeability. The influence of water and solute permeability on the release from a population of coated granules is analyzed, including analysis of the special case where solute permeability depends, inversely, on coating thickness demonstrated by Lupo (*12*).

Figure 2 illustrates the influence of water, P_h, and solute, P_s, permeability coefficients on the cumulative release (calculated according to eq 14 of ref *4*). Realistic values of water and solute permeability determined by Raban (*7*) for the two different coating materials MPO − 2.6×10^{-9} [cm^2 day^{-1} Pa^{1-}] and 1.0×10^{-5} [cm^2 day^{-1}] and PULC − 5.0×10^{-9} [cm^2 day^{-1} Pa^{1-}] and 2.5×10^{-5} [cm^2 day^{-1}], respectively, were used for this analysis. The same radius and thickness mean values and distribution characteristics (normal) were

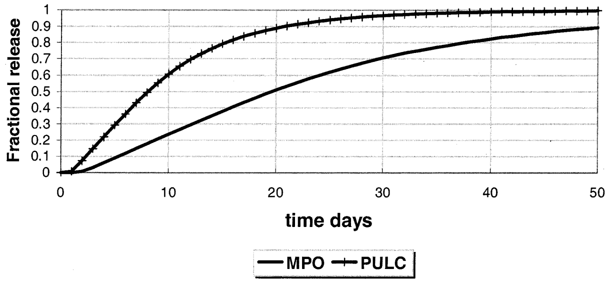

FIGURE 2. Comparison of calculated cumulative release from a population of urea granules coated with MPO and PULC films. Permeability coefficients, for water and solute of the PULC are 5.0 × 10^{-9} [cm^2 day^{-1} Pa^{-1}] and 2.5 × 10^{-5} [cm^2 day^{-1}], and the ones of the MPO are 2.6 × 10^{-9} [cm^2 day^{-1} Pa^{-1}] and 1.0 × 10^{-5} [cm^2 day^{-1}], respectively.

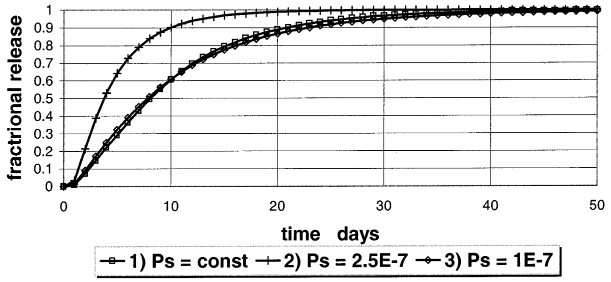

FIGURE 3. Influence of P_s, solute permeability, on the cumulative release for (1) constant $P_s = 2.5 \times 10^{-5}$ (cm^2 day^{-1}); and coating dependent $P_s = \tilde{P}_s/l$ with (2) $P_s = 2.5 \times 10^{-7}$; and 3) $P_s = 1.0 \times 10^{-7}$ (cm^2 day^{-1}).

used for both populations. Expectedly, the lag-period of release from the MPO coated granules (2 days) is about twice as long, in comparison with the release from PULC coated granules. The period of about 25 days of linear release calculated for the MPO is about 2.5 times larger compared to that of the PULC. This ratio conforms with the ratio of solute permeability of the coatings of the CRFs. The fraction of linear release expected, for a single urea granule, is 0.5. Due to the distribution of *r* and *l* one could expect a shorter lag and linear period for the smaller *r* × *l* values, as compared to other granules, thus reducing the "effective" time of linear release. On the other hand large values lead the system in the opposite direction and thus inducing some "smearing" of the "characteristic periods" of release. This does not occur in this case, presumably due to the narrow and symmetric distributions of *r* and *l* (see also statistical versus single granule approach in Figure 1).

The results demonstrate the importance of choosing or designing the coating of a CRF with permeability values of water and solute, which can assist in providing the desired pattern and rate of release.

The influence of dependence of solute permeability on coating thickness, $P_s = \tilde{P}_s\, l^{-1}$, was analyzed considering the observation that water permeability in some CRFs does not change significantly within the population (*12*). In those cases solute permeability was found inversely proportional to coating thickness due to its high sensitivity to imperfections in the coating (*12*). The resulting curves of urea release calculated for different solute permeability coefficients are represented in Figure 3. The calculations were performed for populations of coated granules in which the permeability coefficients were as follows: (*i*) $P_s = 2.5 \times 10^{-5}$ [cm^2 day^{-1}] (constant as in eq [14] in ref *4*); and two cases in which P_s inversely is proportional to the coating thickness, $P_s = \tilde{P}_s\, l^{-1}$ (eq 5), where (*ii*) $\tilde{P}_s = 2.5 \times 10^{-7}$ [cm^{3}day^{-1}]; and (*iii*) $\tilde{P}_s = 1.0 \times 10^{-7}$ [cm^3 day^{-1}]. The mean coating thickness in this case was $\mu_l = 0.004$ [cm], and the distribution was assumed to be normal. The dependence of P_s on thickness, *l*, did not change the nature of the release curve. In this case, the rate was determined mainly by the mean value of P_s given by $P_s = \tilde{P}_s\, \mu_l^{-1}$. Comparison of the curve that corresponds to the constant $P_s = 2.5 \times 10^{-5}$ [cm^2 day^{-1}] with case *iii* in which $P_s = 1.0 \times 10^{-7} \times 0.004^{-1}$ shows little difference between the two. This indicates that the thickness distribution (relatively narrow) in this case has a negligible effect on release characteristics, and it is the "effective mean value" − $P_s = \tilde{P}_s\, \mu_l^{-1}$, which influences release characteristics.

TABLE 1: Parameters of Normal Distribution of Coating Thickness Used To Analyze Their Influence on Diffusion Release

cm			
effect of μ_l		effect of σ_l	
μ_l	σ_l	μ_l	σ_l
0.004	0.001	0.006	0.0005
0.006	0.001	0.006	0.002
0.008	0.001	0.006	uniform

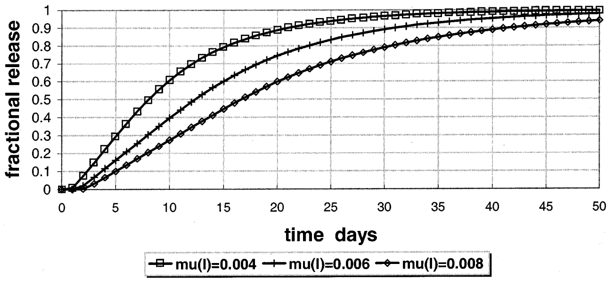

FIGURE 4. Cumulative release from a group of granules having different values of mean thickness of coating, μ_l, (mu(l)) as shown in Table 1.

b. Effect of Distribution Parameters of Granule Radius and Coating Thickness. The sensitivity of the release to the distribution parameters of the two independent variables, mean granule radius and mean coating thickness (μ_x, $x = r, l$,), was analyzed. The variation of the values for each parameter is characterized by their standard deviation (σ_x, $x = r, l$). All other parameters are assumed to be constant over the population. When testing model sensitivity to the variables μ_x, ($x = r, l$), it was assumed that they are normally distributed.

Results are shown for a population of urea granules coated with membranes having water and solute permeability typical to those obtained for PULC and within the realistic ranges of radius and coating thickness: $r = 0.05 \div 0.25$ cm and $l = 0.001 \div 0.011$ cm, respectively.

In the first series of numerical experiments the influence of μ_l on release was tested (Table 1), keeping the standard deviation of coating thickness constant, $\sigma_l = 0.001$. In the second series (Table 1) the mean value of the thickness was fixed ($\mu_l = 0.006$) and the effect of changes of σ_l on the release was examined for two values of the water permeability, P_h and 0.1 × P_h. The curves of cumulative release calculated for different mean μ_l and σ_l are shown in Figures 4−6.

The mean thickness, μ_l, has a strong influence on release rate (Figure 4) as it does in case of a single granule (*4*): smaller μ_l induces a faster release and shorter period of the linear release and shorter lag-periods. Half-life time, $t_{50\%}$, of the release from the population increases linearly with μ_l, as could be expected from eq 14 of ref *4*. The effect of coating thickness variation, expressed by σ_l, on the release is small with the value of $P_h = 5.0 \times 10^{-9}$ [cm^2 day^{-1} Pa^{-1}] as seen in Figure 5. Reduction of the water permeability coefficient, P_h, independent of P_s (*12*), introduces significant differences in

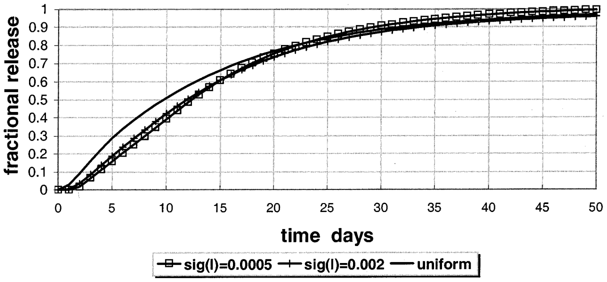

FIGURE 5. Cumulative release from a group of granules having different values of σ_l (sig(l)) − [0.0005, 0.002, uniform}, obtained for $P_h = 5.0 \times 10^{-9}$ [cm^2 day^{-1} Pa^{-1}].

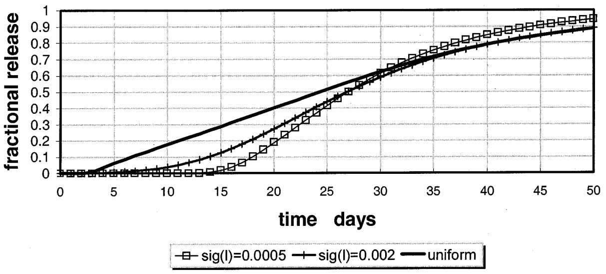

FIGURE 6. Cumulative release from a group of granules having different values of σ_l (sig(l)) − [0.0005, 0.002, uniform}, obtained for $P_h = 5.0 \times 10^{-10}$ [cm^2 day^{-1} Pa^{-1}].

TABLE 2: Types of Thickness Distributions and Their Characteristic Parameters as Used To Analyze Their Influence on Diffusion Release

distribution type	μ_l	σ_l	other characteristic parameters
normal	0.006	0.00135	
log-normal	0.006	0.00135	$\mu_{\ln l} = -5.14$; $\sigma_{\ln l} = 0.224$
polynomial	0.006	0.002	$a_0 = -0.156$; $a_1 = 111.2$; $a_2 = -8741.2$; $a_4 = -44677$
uniform	0.006		

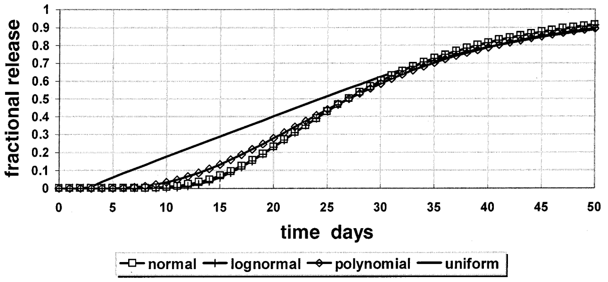

FIGURE 7. Cumulative release from a group of granules having different types of thickness distribution (Table 2), obtained for $P_h = 5.0 \times 10^{-10}$ [cm^2 day^{-1} Pa^{-1}].

the release curves due to changes in σ_l: larger σ_l induce shorter lag and $t_{50\%}$-periods, on one hand, and somewhat prolong the period of 80% release, $t_{80\%}$, on the other (Figure 6). In such a case the pattern of release shifts from sigmoidal type with the smallest σ_l to almost linear release with the uniform distribution. A reduction of P_h without affecting P_s can be achieved with materials in which P_s depends mainly on the defects induced in the coatings during their manufacture, whereas P_h depends mainly on the hydrophobicity (i.e., can be changed by additives) of the coating material (*12*).

A similar analysis was done for the effect of radius distribution parameters (μ_r and σ_r). Expectedly, the influence of μ_r and σ_r on release behavior is *similar* to that of parameters of thickness distribution: larger μ_r induces longer lag-periods, longer periods of linear release, and decaying release and an overall lower rate of release. This result was expected since the product $r \times l$ is eventually the factor that affects the release when both the radius and coating thickness are considered. From a manufacturing point of view it should be easier and much cheaper to increase granule radius as compared to coating thickness. Controlling the "width" of the standard deviation of granule radius is also expected to be easier than controlling it for coating thickness. Yet, there are practical limitations to the desired granule size and its distribution due to the following: a. the need to optimize the delivery of fertilizer granules between plants or plant roots (= optimize overlapping between sources and sinks) and b. constrains due to bulk blending requirements and physical distribution in the field (*2, 3*).

c. Effect of Distribution Type. The influence of distribution type on release, whether symmetric (e.g. normal, uniform) or nonsymmetric (e.g. log-normal, polynomial), was tested keeping the other governing factors constant. To test model sensitivity to the distribution type of a chosen variable it was assumed that the other variable is normally distributed.

As in the previous cases the permeability coefficients of the population of urea granules are the ones characteristic of the PULC. The influence of the type of coating thickness distribution on release was analyzed for a normal radius distribution having $\mu_r = 0.138$ [cm] and $\sigma_r = 0.0126$. Four different types of thickness distributions were considered (Table 2), all with the same first moment $\mu_l = 0.006$ cm (thickness varies in the range $l = 0.001 \div 0.011$ cm). The release curves obtained for water permeability values of $P_h = 5.0 \times 10^{-9}$ were similar in nature to those observed in Figure 5 and thus not shown: The release curves obtained with the symmetric (normal) and the nonsymmetric (log-normal) distributions of thickness were quite similar, and only the polynomial distribution induced a "smearing effect" as did the uniform spreading in Figure 5. The curves obtained for the smaller water permeability − $P_h = 5.0 \times 10^{-10}$ [cm^2/day Pa] are shown in Figures 7. The reduction of the water permeability without changing the solute permeability significantly amplified the effect of distribution type on the release. The polynomial distribution has, effectively, a wider range of thickness distribution in comparison with the normal and log-normal distributions thus inducing a "smearing" effect and hence a shorter lag-period. The uniform distribution (Figure 7), which effectively indicates that the CRF population has the widest spreading of coating thickness, induces a very different pattern of release compared to the other types of distributions. Reduction of P_h without changing P_s, in a population of coated CRFs with uniformly distributed coating thickness, changes the release pattern from sigmoidal to almost linear.

Expectedly, changes of the types of radius distribution have a similar effect on the release as does the type of thickness distribution. Obviously, the magnitude of the impact is expected to depend on the range of radius ($r_{\min} \le r \le r_{\max}$) and coating thickness ($l_{\min} \le l \le l_{\max}$) values. From a practical point of view changing the type of radius distribution from normal to a nonsymmetric one or to a very wide one should be a much easier task (e.g., by sieving) to do than controlling the type of distribution of the coating thickness.

The results above demonstrate the important role of the ratio P_h/P_s in affecting release characteristics from a population of granules and in amplifying the effects of radius and coating-thickness distribution type or SD. In general, CRFs populations having P_h/P_s that induces lag periods in the order of magnitude of $t_{50\%}$ are expected to be sensitive to the distribution types and degree of uniformity of granule radii and/or coating thickness.

Discussion

The statistically based model of release can be successfully used to describe nutrient release by diffusion from polymer coated CRFs using chemophysical parameters which were evaluated experimentally. The statistical approach singles itself out by allowing a more realistic way of modeling nutrient release from populations of polymer-coated granules having very broad distributions of parameters, which govern the release. Once the release model from a single granule is established (*4*) the statistical model provides an effective tool for improved design and prediction of release characteristics in accordance with agronomic and particularly environmental demands.

The sensitivity analysis of the model demonstrates the possibility to affect the release pattern by controlling the distribution of granule radius or coating thickness. When the values of σ_x within a given population are relatively small (e.g. 10−20% of the mean values), the effects on release are small, and the differences between symmetric (normal distribution) and nonsymmetric (log-normal) are practically nonsignificant. Breaking the symmetry in regard with the product $r \times l$ can be done in cases where the solute permeability is inversely dependent on the coating thickness, l: $P_s = \tilde{P}_s l^{-1}$ (*12*). This effect may become a significant means for affecting release characteristics only in combination with a large distribution of coating thickness.

A most effective tool for controlling release characteristics is the induction of changes in the ratio of P_h/P_s combined with changes of the distributions of r or l. CRF populations with P_h/P_s ratios that induce similar orders of magnitude of the lag period and that of $t_{50\%}$ (or period of linear release) are expected to be very sensitive to changes of r or l. The larger the spreading of these values, the more distinct will be the shift from sigmoidal to almost linear release ("smearing"). The opposite holds as well: in cases where P_h/P_s induces a short lag-period (e.g., days) while the period of linear release is at least 1 order of magnitude larger, population sensitivity to distribution parameters is small. For normally or log-normally distributed r or l with σ_x lower than 10−20% of their mean values, one can successfully apply the model of release from a single granule inserting the mean values μ_r and μ_l instead of r and l (e.g., eq 14 in ref *4*). In such cases the conclusions made regarding the factors affecting release from a single CRF granule (*4*) are applicable for a population characterized by the mean values.

The statistical model assumes no interactions between neighboring granules. This can be justified in cases where the concentration of the released nutrient in the external solution is negligible compared to the one inside the granule. Conditions for these situations are discussed by Shaviv et al. (*4*) for single CRF granules and are particularly relevant for nitrogen. For many practical situations the statistical model can be inserted into "nutrient dynamics models" as a source term in the relevant continuity equations, representing the release into a given soil domain that contains a plurality of CRF granules.

The paper focuses on the effects of varying r and l, while the water and solute permeability P_h and P_s are assumed constant. The estimation of P_h is based on evaluation of the lag period (eq [3] in ref *4*) and that of P_s is based on the linear period of release (eq 9 in ref *4*). In both equations, the permeability is divided by l implying that the accuracy of their estimation strongly depends on the accuracy of coating thickness determination (*4*). Alternatively, one can define the arguments P_h/l and P_s/l as "effective" fluxes of water and solute, $P_h$eff and $P_s$eff, respectively. In such case one could replace the variables P_h, P_s, and l with $P_h$eff and $P_s$eff. For the simple cases where the deviations are not large and the distribution is narrow and symmetric this may be a convenient "trade off". One could then simply apply the mean values of the radius and the "effective" water and solute fluxes in the model of release from a single granule. However, for populations with a large variation one would need to deal with the distribution characteristics of three or four parameters: $P_h$eff, $P_s$eff, r, and even l (e.g., eq 5 for $P_s = \tilde{P}_s/l$), which may introduce complications.

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Received for review January 15, 2002. Revised manuscript received October 6, 2002. Accepted January 3, 2003.

ES0205277