Application of Parametrization Using the Richards Function to Nitrogen Release from Coated Urea and Growth of Rice Seeds

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Abstract
The Richards function can describe the cumulative frequency distribution accurately because the function has a high flexibility owing to the presence of the 4 functional parameters. Accordingly, the frequency distribution can be characterized by the 4 functional parameters. The parametrization was applied to the nitrogen release from coated urea and the growth of rice seeds with the passage of time. The Richards function accurately described these responses. For the analysis of nitrogen release, one of the 4 functional parameters reflected the nitrogen content of fertilizer, another one was calculated from the other parameters, and another one followed the Arrenius equation. Accordingly, the nitrogen release from each type of coated urea at various temperatures could be characterized by 2 release parameters. Because the growth of rice seeds was too complex to be represented by the Arrenius equation and the functional parameters were sensitive to a small deviation, 4 functional parameters were transformed into 4 population parameters that were stable and comprehensive. Several factors affecting the growth could be analyzed using the population parameters although they may not affect the viability. Therefore, the analysis of nitrogen release and seed growth showed that the parametrization of the frequency distribution of responses using the Richards function could be applied.

Discipline: Soils, fertilizers and plant nutrition
Additional key words: Arrhenius equation, curve fitting, germination, parameter, seed vigor

Introduction
The Richards function is an asymmetric growth function with such a high flexibility that it can be substituted for the Bertalanffy, Gompertz and logistic functions, which are known to be growth functions. However, the complex calculation of the 4 functional parameters had limited the application hitherto. Presently, since personal computers can perform the calculation easily, the Richards function can be conveniently applied. The growth function is often applied to describe changes in the cumulative response with the passage of time. In this paper, the Richards function was applied to studies on the nitrogen release from coated urea and the growth of rice seeds.

The Richards function consists of 4 parameters (N, d, k, t). The cumulative frequency (n) of responses at time (t), which corresponds to the time interval after the stimulation, is represented by Eq. 1. If d > -1 , n is represented by a sigmoid curve with an inflection point at t = t. If d ≤ -1 , n is represented by a simple saturation curve without inflection points.

\[ n = N \cdot \left[ 1 + d \cdot \exp \left\{ -k \cdot (t - t) \right\} \right]^{1/d}. \] (Eq. 1)

Nitrogen release from coated urea
The use of coated urea saves farm labor since basal application of the whole amount can be performed. As many types of coated urea with various release patterns are currently being developed, the estimation of the amount of nitrogen released may contribute to the development of an efficient combination of coated urea types for various cropping systems.

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Received 18 December 2000, accepted 10 January 2001.
Nitrogen release can be considered to reflect the response to the application (i.e. soaking) of coated urea. The cumulative amount of nitrogen released from a slow-release fertilizer (LP group) can be well described by the Bertalanffy function represented by a simple saturation curve. Although the release from a delayed-release fertilizer (LPS group) is represented by a sigmoid curve, it used to be described by the Bertalanffy function despite the difference in the shape of the curve. Because the Richards function can describe both simple saturation and sigmoid curves, the function can be applied to describe the nitrogen release from both slow-release (LP group) and delayed-release fertilizers (LPS group). Accordingly, the Richards function was applied to analyze the amount of nitrogen released from coated urea.

1) Materials and methods

Fifteen types of polyolefin-coated urea were tested, consisting of 7 slow-release fertilizers (LP30–180) and 8 delayed-release fertilizers (LPS40–200, LPS5100). The cumulative percentage of the released nitrogen expressed as a percentage of the certified content (40% by weight) was obtained with the passage of time at constant temperatures (15–35°C). The Chisso-Asahi Fertilizer Corporation provided these data.

The Richards function was applied to the time-dependent cumulative percentage of released nitrogen for each fertilizer at each temperature. The optimum values of 4 parameters and the standard error expressed as a percentage of the certified content were calculated by the least squares method using a multipurpose spreadsheet program.

2) Functional parameters

The average standard error was 0.4%, a value sufficiently small. Examples of fitting for LP100 and LPS100 are depicted in Fig. 1. The good fits also indicate that the Richards function can accurately describe the nitrogen release from coated urea.

The maximum amount of released nitrogen (N) was approximately 100% for all the types of coated urea, which indicates that N is equivalent to the nitrogen content of fertilizer. The curve shape parameter (d) depended on the type of fertilizer and the temperature. The value was –0.8–0.4 for the LP group and 0.8–1.2 for the LPS group, except for LPS100. The temperature affected the value of d less conspicuously than the type of fertilizer.

The time to the inflection point (t) corresponds to
the time to the point of the maximum release per unit time and became shorter with increasing temperature. There was a linear relationship between \( d \) and \( \ln (k t / 1 + d) \), regardless of the group of fertilizer and the temperature (Fig. 2). Substituting the relationship, \( \ln (k t / 1 + d) = d + 1 \), into Eq. 1 to eliminate \( t \), gives

\[
N = N \cdot \left[ 1 + d \cdot \exp \left\{ \exp \left( d + 1 \right) - 1 - k \cdot t \right\} \right]^{-1/d}.
\]

(Eq. 2)

Accordingly, the nitrogen release from coated urea can be described with 3 parameters \((N, d, k)\). The curves described by Eq. 2 as \( d \) changed are shown in Fig. 3.

The rate constant \((k)\) which indicates the release rate increased as the nitrogen release was accelerated. There were linear relationships between \( \ln k \) and \( 1 / T \) as the absolute temperature \((T)\) changed (Fig. 4), which indicates that the value of \( k \) follows the Arrhenius equation:

\[
\ln k = \ln A - \left( E_a / R \right) / T.
\]

In addition, the slopes of the regression lines were similar in all the types of coated urea, which indicates that the apparent activation energy \((E_a)\) was independent of the type of coated urea. Accordingly, the value of \( k \) at any temperature can be calculated with \( k \) at 25°C \((k_0)\), \( E_a \) and the gas constant \((R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1})\) as follows:

\[
\ln k = \ln k_0 - \left( E_a / R \right) \cdot \left\{ 1 / T - 1 / \left( 273 + 25 \right) \right\}.
\]

(Eq. 3)

3) Release parameters

When the optimal values of the 3 parameters \((N, d, k)\) for each type of coated urea and the optimal value of a constant \((E_a)\) for all the fertilizers were calculated, the average standard error of fitting to describe the release was 1.6% for all the fertilizers. Accordingly, the nitrogen release from coated urea at various temperatures could be described with 3 parameters \((N, d, k)\) and a constant \((E_a)\). Since \( N \) indicates the quantity of released nitrogen and the value was approximately 100%, the qualitative characteristics of the nitrogen release were represented by 2 release parameters \((d, k)\) other than \( N \). The scatter diagram of the release parameters is shown in Fig. 5. The value of \( d \) was \(-0.8\sim0.4\) in the LP group, increasing with the release rate, and it was about 1 in the LPS group, except for LPS100 and LPS100.

As an example of application of the release parameters, the fertilizer with complex release was obtained by mixture. The cumulative release percentages of the mixed fertilizer were arbitrarily designed with the passage of time (Fig. 6). The total percentage of the nitrogen release among the 15 types of coated urea tested above was fitted to the designed values by the least squares method using a multipurpose spreadsheet program. The goodness of fit was high except for the early phase, pre-
sumably due to the lack of a suitable type of coated urea releasing nitrogen fast after a long suppression of release. Only 3 types of fertilizers were selected, which indicates that the combination of only 3 types of fertilizers enables the production of mixed fertilizer with such a degree of release complexity. Accordingly, the release parameter can contribute to the development of efficient combinations of several types of coated urea for various cropping systems.

4) Practical application

In practice, it is necessary to estimate the nitrogen release at fluctuating temperatures as in the case of field conditions. Nitrogen release at fluctuating temperatures can be analyzed using the numbers of days transformed at a standard temperature because the nitrogen release follows the Arrhenius equation.

Although the $E_r$ value remained constant for all the tested fertilizers, some may show different values of $E_r$. In addition, this method may be useful for nitrogen release from other materials than coated urea, because the behavior of nitrogen release from organic matter and soil is similar to that of coated urea. Accordingly, nitrogen release could be characterized by the use of 3 release parameters including $E_r$.

Growth of rice seeds

Unstable establishment of seedlings is presently one of the major constraints on the dissemination of direct sowing of rice plants in Japan. It is important to sow vigorous seeds to improve the establishment. Seeds growing fast are considered to be vigorous because plants growing fast tend to survive in adverse environments. Accordingly, seed vigor can be approximately estimated based on the growth rate.

Seed growth to a given stage reflects the response to sowing of seeds. The time-dependent cumulative numbers of seeds grown up to a given stage (ex. germination) can also be fitted using the Richards function. However, the functional parameters are too sensitive to characterize the growth because seed growth consisting of many stages is very complex. Accordingly, the 4 functional parameters were transformed into 4 population parameters that comprehensively characterized the growth properties of a seed lot, and they were used to evaluate the seed vigor.

1) Population parameters

Four population parameters were calculated from the 4 functional parameters of the Richards function (Table 1). The 4 population parameters were described using a sample for germination (Fig. 7). $V_i$ which is the final number of germinating seeds, indicates the viability of germination. $Me$ is the median time to germination and it is equal to $t$ when $n = V_i / 2$. It reflects the rate of germination and increases when the germination is delayed. $Qu$ is the quartile deviation of the time and it indicates the dispersion of time. The average half of seeds germinates in the range of $Me \pm Qu$ approximately. $Sq$ is the quartile skewness of time, and it indicates the skewness in the frequency distribution of the germination time. If $0 < Sq < 1$, it is negatively skewed (mode < median). If $-1 < Sq < 0$, it is positively skewed.

<table>
<thead>
<tr>
<th>Characteristics of growth</th>
<th>Characteristics of response curve</th>
<th>Population parameters</th>
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<tbody>
<tr>
<td>Viability</td>
<td>Amount of responses</td>
<td>$Vi = N$</td>
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<tr>
<td></td>
<td>= Cumulative amount of responses at infinity</td>
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<tr>
<td>Time</td>
<td>Average of response time</td>
<td>$Me = t_i + \frac{1}{k} \cdot \ln \frac{d}{2^{d-1}}$</td>
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<tr>
<td></td>
<td>= Median of response time</td>
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<tr>
<td>Dispersion</td>
<td>Dispersion of response time</td>
<td>$Qu = \frac{1}{2k} \cdot \ln \frac{4^d - 1}{(4/3)^d - 1}$</td>
</tr>
<tr>
<td></td>
<td>= Quartile deviation of response time</td>
<td></td>
</tr>
<tr>
<td>Skewness</td>
<td>Skewness of response time</td>
<td>$Sq = \frac{\ln \frac{(4/3)^d - 1}{2^{d-1}}}{\ln \frac{4^d - 1}{2^{d-1}}} + \ln(2^d + 1)$</td>
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<tr>
<td></td>
<td>= Quartile skewness of response time</td>
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Richards function

$n = N \cdot \left[1 + d \cdot \exp\{-k \cdot (t-t_i)\}\right]^{-1/d}$

Differential equation

$\frac{dn}{dt} = k \cdot n \cdot \left(1 - (n/N)^d\right) / d$

The value of $n$ corresponds to the cumulative amount of responses at time $t$ after the stimulation (ex. seed soaking).
are useful as indices of seed growth.

2) Materials and methods

Seeds (ca. 3 g) of rice (Oryza sativa L. cv. Dontaiko) selected at the specific gravity of 1.13, unless otherwise stated, were soaked in an unlit incubator at 20 ± 0.1 °C. The number of germinating seeds was counted at 1-day intervals. The Richards function was applied to the time-dependent cumulative number using the least squares method to determine the optimum values of the population parameters for germination.

3) Reproducibility

The population parameters of an identical seed lot for germination were calculated at 8-, 16-, or 24-hour intervals for 24 replications. The largest residual was about 2% on the average, which indicates that the fitness was good. The mean value and standard deviation were not influenced by the count interval except for Sq. Without replication, the expected confidence intervals for Vt, Me and Qu were likely to correspond to the measured value ± 2.3%, ± 3.7 h and ± 1.6 h, respectively.

4) Effects of several factors

Specific gravity: Two seed lots obtained from fields with a different amount of applied nitrogen (High-N and Low-N) were classified by the specific gravity (SG), and population parameters of the classified seeds for germination were obtained. Although Vt amounted to 100% at a SG of more than 1.00, the Me and Qu values decreased with the SG (Fig. 9). The Sq value decreased with the SG, due to the thinning of light seeds growing slowly. Accord-

Fig. 9. Effect of specific gravity on population parameters
Averages among 16 high-N lots (10–20 g N m⁻²) and 7 low-N lots (0–5 g N m⁻²) were described.
ingly, vigorous seeds growing fast and uniformly could be selected based on a high SG even if the viability was not affected. However, the amount of selected seeds also decreased with the SG. The level of SG should be determined depending on the amount of selected seeds.

**Temperature:** Population parameters of 4 seed lots for germination were investigated under various temperature conditions. $Vi$ decreased slightly with the decrease of the temperature and exceeded 92% at the lowest temperature (10°C). Accordingly, the decrease of the temperature may not lead to a decrease of the viability unless the seeds are affected by diseases. $Me$ decreased with the increase of the temperature, and the relationship between the reciprocal of temperature and the logarithm of $Me$ was not linear but was represented by a curve (Fig. 10). Accordingly, the germination time, which may consist of several phases with a varying degree of dependence on the temperature may not strictly follow the Arrhenius equation.

**Storage period:** Averages of population parameters for germination among seed lots stored at about 6°C for various durations were obtained (Fig. 11). The prolongation of the duration of the storage period did not lead to a decrease of $Vi$ but reduced the $Me$ and $Qu$ values. According to Takahashi[9], the prolongation of the duration of the storage period shortens the period during which water absorption stops temporarily, which implies that the reactions occurring originally during this period may gradually proceed during the storage period. Since the prolongation of the duration of the storage period may shorten the growing time and the dispersion before it decreases the viability, storage for an appropriate duration may enhance the seed vigor.

**Environment:** Population parameters for germination were obtained among identical seed lots soaked in a solution with various amounts of a pesticide, i.e. sodium hypochlorite (NaClO) solution. There was a linear relationship between the logarithm of the pesticide concentration and $Me$ although $Vi$ was not affected (Fig. 12). Accordingly, the population parameters may be also useful to quantify factors that can not affect the viability.

5) Indices of seed vigor

The germination curve can be accurately fitted by the Richards function. Population parameters can be calculated with a reproducibility sufficient to measure the germination at 1-day intervals without replication. Accordingly, the population parameters for germination...
can be used as indices of seed vigor.

Vi may be the main index of seed vigor, although sometimes it did not enable to differentiate vigorous seeds. Me enabled to evaluate seed vigor, even when Vi could not. The effect of the seed nitrogen content on seed vigor was successfully examined using Me because there was a close relationship between Me for germination and the establishment percentage\(^{2,3}\). Qu is also useful because uniformity of growth is another important aspect of seed vigor. Qu reflected the effect of the duration of seed soaking on the uniformity of emergence\(^{4}\). Although Sq reflects the composition of a population, the low reproducibility should be improved by measuring the tail of the germination curve more accurately.

The population parameters can also be used as indices of the subsequent growth of a seed lot. The progression of the growth stages led to a decrease of Vi and prolonged Me and Qu\(^{4}\), presumably due to the complexity of the growth processes.

**Conclusion**

The Richards function enables to parametrize the frequency distribution of responses. The applicability was confirmed by the analysis of the nitrogen release from coated urea and the growth of rice seeds. The flexibility may enable the Richards function to describe the frequency distribution of values for various measurements for other conditions than the passage of time. Therefore, the Richard function could be applied to various studies.

**References**