

Assessment of fertilizer efficacy utilizing the substitution rate methodology

Avaliação da eficácia do fertilizante utilizando a metodologia da taxa de substituição

Evaluación de la eficacia del fertilizante utilizando la metodología de la tasa de sustitución

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ABSTRACT

The substitution rate method describes the relative effectiveness of fertilizers according to the amount of nutrient required to produce a given crop yield. The two main reasons in which this method has had restricted use are: a) the model needs to be solved iteratively, thus, it is necessary an optimization program, and b) methods considering only a single point from response curves, such as the agronomic efficiency index, have been adopted for the sake of simplicity. However, these simple measures cause loss of data, and the interpretation of results may be impaired. We compared goodness-of fit measures from a published work with those generated by an optimization spreadsheet developed in Excel. We proposed changes in the equation from the mentioned work that rendered better goodness of fit. The Excel spreadsheet, with embedded statistical decision support is made available for download to encourage the testing of additional fertilizers by using the substitution rate method.

Keywords: Curve Comparison. Agronomic Efficiency Index. Optimization Program. Phosphate. Fertilizer.

RESUMO

O método da taxa de substituição descreve a eficácia relativa dos fertilizantes com base na quantidade de nutriente necessária para produzir uma determinada produtividade de cultura. As duas principais razões pelas quais esse método tem sido de uso restrito são: a) o modelo precisa ser resolvido iterativamente, exigindo, portanto, um programa de otimização, e b) métodos que consideram apenas um único ponto das curvas de resposta, como o índice de eficiência agrônômica, têm sido adotados por questões de simplicidade. No entanto, essas medidas simplificadas resultam em perda de dados e podem comprometer a interpretação dos resultados. Comparamos medidas de qualidade de ajuste de um trabalho publicado com aquelas geradas por uma planilha de otimização desenvolvida no Excel. Propusemos alterações na equação do trabalho mencionado que resultaram em uma melhor qualidade de ajuste. A planilha do Excel, com suporte estatístico para tomada de decisão integrado está disponível para download a fim de incentivar o teste de fertilizantes adicionais utilizando o método da taxa de substituição.

Palavras-chave: Comparação de Curvas. Índice de Eficiência Agronômica. Programa de Otimização. Fosfato. Fertilizante.

RESUMEN

El método de la tasa de sustitución describe la eficacia relativa de los fertilizantes en función de la cantidad de nutriente necesaria para producir un determinado rendimiento del cultivo. Las dos principales razones por las cuales este método ha tenido un uso restringido son: a) el modelo debe resolverse de manera iterativa, lo que requiere, por lo tanto, un programa de optimización, y b) se han adoptado métodos que consideran solo un único punto de las curvas de respuesta, como el índice de eficiencia agronómica, por razones de simplicidad. Sin embargo, estas medidas simplificadas provocan una pérdida de datos y pueden comprometer la interpretación de los resultados. Comparamos medidas de calidad de ajuste de un trabajo publicado con aquellas generadas por una hoja de cálculo de optimización desarrollada en Excel. Propusimos modificaciones en la ecuación del trabajo mencionado que resultaron en una mejor calidad de ajuste. La hoja de cálculo de Excel, con soporte estadístico integrado para la toma de decisiones, está disponible para su descarga con el fin de incentivar la prueba de fertilizantes adicionales utilizando el método de la tasa de sustitución.

Palabras clave: Comparación de Curvas. Índice de Eficiencia Agronómica. Programa de Optimización. Fosfato. Fertilizante.

1 INTRODUCTION

The substitution rate method expresses the effectiveness of a fertilizer product as a proportion of an equivalent high-performing reference (Colwell, 1994). The method, also known as horizontal approach, indicates the amount of one product that might be used for substituting another to reach a desired yield. According to this method, coefficient values for products are estimated by a regression procedure. Using a reference equation, successive approximations of the substitution rate (sr) values are calculated iteratively to minimize the residual mean squares for a product equation. This simple scale adjustment makes the response curves coincide along their entire length. Estimates of sr , thus, can be used to evaluate fertilizers performance, among other applications, in which response curves may be compared. The substitution rate method could be applied with experiments which results in two or more comparable curves, such as soybean yield with water insoluble P compounds and with water-soluble

monocalcium phosphate (Chien *et al.*, 2011), corn yield grown with ammonium nitrate and with urea (Copperi *et al.*, 2013), animal manures, pathogen control, etc.

Comparisons of the effectiveness of fertilizers could be made by the substitution rate instead of the used single point method, such as the agronomic efficiency index. Single point comparisons, by instance, are arbitrary. The point to be compared depends on the user's choice, often remarkably close to an optimum fertilizer rate. Other sections of the curves are waived unless the results are paralleled straight lines. Prochnow *et al.* (2006) work rendered straight lines, which were successfully compared using the ratio of slopes. Those authors used multiple regression to reach a common intercept to compare phosphorus (P) concentrations in plant yield. The intercept was obtained with increasing doses of P, in the linear region of response curves, up to 100 mg.kg⁻¹ P.

Despite the limitations of using the single point method, researchers might elect to sacrifice precision for the sake of simplicity. Single rate has been widely used for vertical (relative response) (Oliveira Junior *et al.*, 2011; Souza *et al.*, 2014) as well as for horizontal axis comparisons (Chien *et al.*, 2011).

Efforts were made to overcome single point constraints. A substitution ratio was proposed by Chien *et al.*, (1990) to describe the curvilinear response to P fertilizers. They used an exponential rise to the maximum curve containing only one-term coefficient in the x-independent variable, which was linearized and the regression coefficients from two sources were related. Mendoza *et al.*, (2009) estimated the ratio between log-transformed response curves of P sources to enable substitution rate calculations. Debnath *et al.* (2010) used the maximum yield plateaus and the slope of the Mitscherlich equation to compare the relative effectiveness of P sources. Wang *et al.* (2012) used a modified Mitscherlich equation to describe the yield and nutrient uptake by plants due to direct application of P. Some researchers (Fageria *et al.*, 2014) split their results in low, medium, and high doses to avoid losing data from the response curve.

Along with the single point, the substitution rate method also presents limitations. The procedure assumes that the *sr* is constant when the effect of the evaluated nutrient is isolated from other variables, such as variations in pH, other

nutrients, presence and absence of mycorrhiza, nutrient losses to the environment, etc. Another limitation, pointed out by Chien *et al.* (1990), is that P fertilizers differ in solubility, and it is commonly observed that crop response to these fertilizers varies widely under the same soil and crop conditions, and often do not share a common maximum yield. However, as shown by Mendoza *et al.* (2009), for some phosphate sources, applying higher rates of some products other than the reference material may reach the same maximum yield. A supplemental statistic, therefore, is useful to measure errors and misinterpretations during method application.

The aim of this work was to develop a tool suited for ranking the performance of fertilizer products using the substitution rate method.

2 MATERIAL AND METHODS

The data used in the present work was obtained from Goedert *et al.* (1988). The authors used a soluble triple superphosphate as a reference source, referred here as “reference” (REF) and a partially acidulated rock phosphate, referred as “product” (PROD), through a four-year experiment growing soybeans. P₂O₅ doses were 30, 60, 90, and 120 kg.ha⁻¹.yr⁻¹, using three replicates. Further details on the experiment are found at Goedert *et al.* (1988). After adjusting the data to a four-parameter model, such as:

$$ax^m + bx + c \quad (1)$$

where:

the exponent m is adjusted to an overall, REF and PROD, best fit ($0.5 \leq m \leq 2.0$; precision = 0.01).

The parameters for equation 1 for the REF and the PROD are adjusted. Excel's Generalized Reduced Gradient (GRG2) algorithm was used to minimize the Sum of the Squared Errors (SSE):

$$SSE = \sum_{i=1}^N [Si - \hat{Si}]^2 \quad (2)$$

where:

SSE is the objective function to be minimized, N is the number of observations, Si is the ith measured value of the dependent variable, and \hat{Si} is the ith model-predicted value of the dependent variable.

Coefficients for equation 1 were estimated for each data set (REF and PROD), using the m exponent, using Excel's solver to minimize SSE in both equations, using a common m value to both, as follows:

$$SSE_{M_m}^j = \sum_{i=1}^n REF_{M_m}^j \quad (3)$$

$$SSE_m^j = SSE_{REF_m}^j + SSE_{PROD_m}^j \quad (4)$$

where:

M = REF or PROD

m = 0.5 ... 2

j = 1 ... n1

$$n_1 = \frac{m_{final} - m_{initial}}{\gamma} + 1 \quad (5)$$

where:

$\gamma = 0.01$

To generate coefficients for REF and PROD equations, data were adjusted by:

$$y_{REF} = a_{REF} X_{REF}^m + b_{REF} X_{REF} + c_{REF} \quad (6)$$

$$y_{PROD} = a_{PROD}X_{PROD}^m + b_{PROD}X_{PROD} + c_{PROD} \quad (7)$$

The substitution rate (*sr*) is obtained using an Excel (2013) macro, which searches for the smallest SSE value within a simultaneous set of equations. Coefficients *a*, *b* and *c* for both REF and PROD were used to estimate values for *y*_{REF_estimated} and for *y*_{PROD_estimated} using the original values for the *x* axis. The *m* coefficient controls the response curvature.

$$y_{REF_estimated} = a_{REF}(X_{REF_SR}^m) + b_{REF}(X_{REF_SR}) + c_{REF} \quad (8)$$

For *y*_{PROD_estimated} optimized *X* values were estimated as follows:

$$y_{PROD_estimated} = a_{PROD}(X_{PROD_SR}^m) + b_{PROD}(X_{PROD_SR}) + c_{PROD} \quad (9)$$

$$X_{PROD_SR} = \frac{1}{SR} \times \text{optimized } X \quad (10)$$

An iterative process takes place deriving from the optimization of *X* (optimized *X*). The macro works with two sequential iterative calculations using Excel's solver. The first minimizes differences, one by one, among *y* coefficients rendering the value of the optimized *X* as follows:

$$\text{Min}(y_{PROD_estimated} - y_{REF_estimated}) \quad (11)$$

$$y_{REF_est_2} = a_{REF}(X_{optimized}^m) + b_{REF}(X_{optimized}) + c_{REF} \quad (12)$$

The second solver minimizes the difference among *y* coefficients estimated from a second round of *y* adjustments around the new *optimized X*, as follows:

$$\text{Min} \left[\sum_{i=1}^{n_2} (y_{i\ REF_est_2} - y_{i\ PROD_est_2})^2 \right] \quad (13)$$

where:

$$y_{PROD_est_2} = a_{PROD}(X_{PROD_SR}^m) + b_{PROD}(X_{PROD_SR}) + c_{PROD} \quad (14)$$

This iterative process allows finding the *sr* value. Coefficients for the final equation (unified equation) describing new *y* data (y_{PROD_SR}), adjusted by *sr* is as follows:

$$y_{PROD_SR} = a_{PROD} \times SR^m(X_{PROD}^m) + b_{PROD} \times SR^m(X_{PROD}) + c_{PROD} \quad (15)$$

Generated graphs were not standard from Excel; thus, graphs were drawn using a series of 1000 points in the *x* scale. An increment (*dx*) for the *x* scale was calculated following the equation:

$$dx = \left(\frac{x_{100} - x_1}{99} \right) \quad (16)$$

where:

x_1 denotes the first value, and x_{100} the last in the *x* scale.

An analysis of residual errors for P uptake by plants was used to evaluate model performance. The root mean square error (RMSE), and the modeling efficiency (EF), a dimensionless statistic, which ranges from minus infinity to 1.0, with higher values indicating better agreement (Borus *et al.*, 2018) were used to compare observed and predicted values. The EF is the best overall indicator of model fit (Marchi *et al.*, 2016).

$$RMSE = \left\{ \frac{\sum_{i=1}^N (\hat{y}_i - y_i)^2}{n} \right\}^{0.5} \quad (17)$$

where:

y_i represents observed values, \hat{y}_i represents simulated values, and n represents the number of pairs.

$$EF = 1 - \frac{\sum_{i=1}^N (\hat{y}_i - y_i)^2}{\sum_{i=1}^N (\hat{y}_i - \bar{y})^2} \quad (18)$$

where:

\bar{y} represents the observed mean.

Additional statistical indexes were used to evaluate the performance of the model, as the agreement index (d) (Willmott *et al.*, 2012),

$$d = 1.0 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n |\hat{y}_i - \bar{y}|^2 + |y_i - \bar{y}|^2} \quad (19)$$

Mean absolute error (MAE) (Chai and Draxler, 2014),

$$MAE = [n^{-1} \sum_{i=1}^n |e_i|] \quad (20)$$

Maximum error (Loague and Green, 1991),

$$ME = \text{Max} |\hat{y}_i - y_i|_{i=1}^n \quad (21)$$

The coefficient of residual mass (CRM), which indicates when the model overestimates (negative values) or underestimates (positive values) the simulated variables (Loague and Green, 1991),

$$CRM = \frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{n \bar{y}_i} \quad (22)$$

Akaike's Information Criterion (AIC), which allow best fit comparisons among models (Dziak *et al.*, 2019),

$$AIC = N \ln \left(\frac{SSE}{N} \right) + 2(p + 1) + \frac{2(p+1)(p+2)}{N-p-2} \quad (23)$$

3 RESULTS AND DISCUSSIONS

Data from Goedert *et al* (1988) were used to calculate *sr* values (Figure 1), and the results were different from the presented in Goedert *et al* (1988) for all years. Substitution rate values obtained by these authors for the first to the fourth year were, respectively: 0.39, 0.41, 0.35, and 0.43. Ultimately, these values mean that the PROD dose is equivalent to 0.39, 0.41, 0.35 and 0.43 times the REF dose. A 1:1 *sr* indicates that the tested product has the same efficiency as the standard. A *sr* value higher than 1 indicates that more of the tested product is necessary to reach the same yield, suggesting lower efficiency. A *sr* value lower than 1 indicates that the product has lower efficiency than the standard. The difference in *sr* values obtained among the years occurred because the y-intercept parameter on the Excel spreadsheet, obtained for the unified equation [15] was equalized to the y-intercept obtained in the equation nº 8, “estimated REF”. This mathematical adjustment prevents that a second product being tested (under the same conditions) could generate a different unified equation, and allows comparing multiple products, one by one, against the REF, using a single, unified equation. Simultaneous comparison of curves could decrease the weight of model REF. Materials being compared with the same REF will always produce the same unified equation if *m* is constant. The *sr* value will be modified for each product, but the equation will remain the same. Of course, there is an associated error when estimating equations for more than one product, regarding the intercept. Using the same dataset, Colwell and Goedert (1988) avoided the error by excluding values from the initial dose of P (0 kg.ha⁻¹), and estimated a common intercept value for both REF and PROD equations. The methodology adopted by these authors, although valid, is centered on the relevant part of the data after fertilizers were applied. Estimates found by Colwell and Goedert (1988), ultimately, extrapolated lines beyond the range of the data.

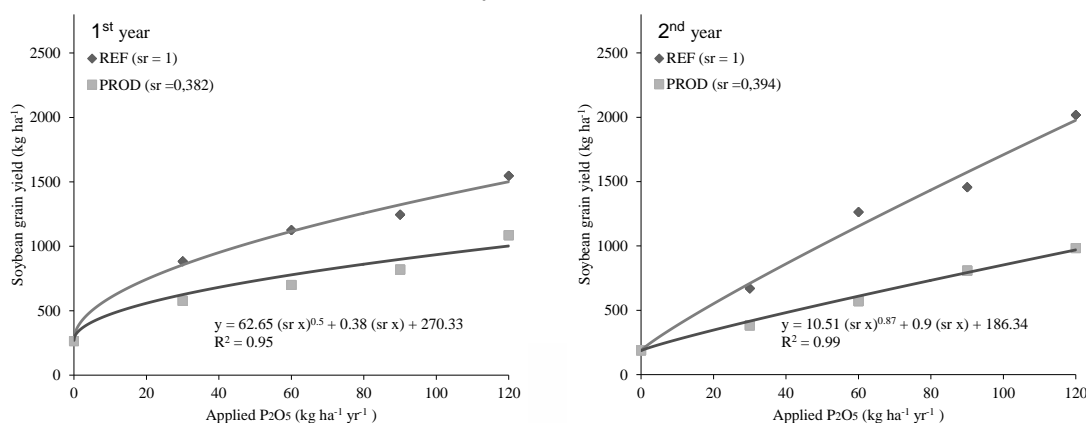
The Excel spreadsheet suggested an exponent *m* = 0.87 for the second-year estimates (Figure 1) while suggested *m* was equal to 0.5 for first, third, and

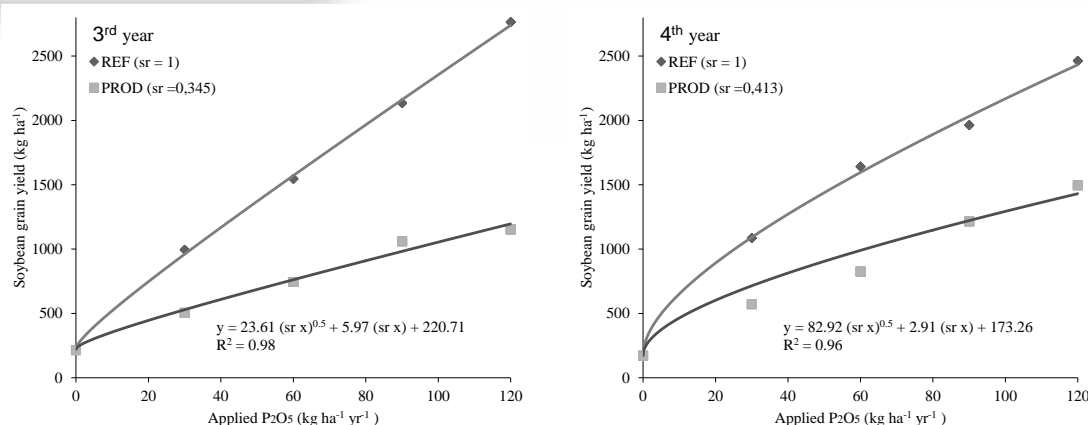
fourth-year estimates. The best fit for m exponent is estimated on the “coefficients” tab from Excel spreadsheet and is the first step of the calculation procedure (equations 1 – 4). The model for PROD for the second-year data using $m = 0.5$ would be

$$18.08 (sr x)^{0.5} + 4.86 (sr x) + 185.98, R^2 = 0.99; sr = 0.394,$$

and the statistical indexes would be $SSE = 19300$; $AIC = 144.94$, $RMSE = 5.34\%$, $MAE = 12.22$, $ME = 47,76$, $CRM = -2.08\%$, $EF = 0.99$, “d” index = 0.99. Although R^2 was the same for $m = 0.87$ and for $m = 0.5$, the increase in precision was shown by the other statistical indexes (Figure 3, 2nd year). These indexes yielded a very good adjust for the model using $m = 0.5$, however, while varying m , estimates with the lowest SSE are those that were better adjusted to the data (Figure 3, 2nd year), and, ultimately, a further end estimate for the unified equation presenting the lower AIC (132.07; $m = 0.87$) is considered to be the most likely to be the correct. SSE value for $m = 0.87$ was 10137 (Figure 3, 2nd year); much lower than when using $m = 0.5$, and better along all other statistical indexes (Figure 3) for the estimative. However, for comparison purposes over the years, the same m value (e.g., $m = 0.5$) could be presented, to maintain the same model. The ability to vary m value is one advantage of the Excel spreadsheet.

Figure 1. Soybean grain mean yield produced in four consecutive years as affected by application rates of each fertilizer, triple superphosphate (REF) or partially acidulated rock phosphate (PROD). Agronomic effectiveness from PROD relative to REF is expressed by the sr parameter.





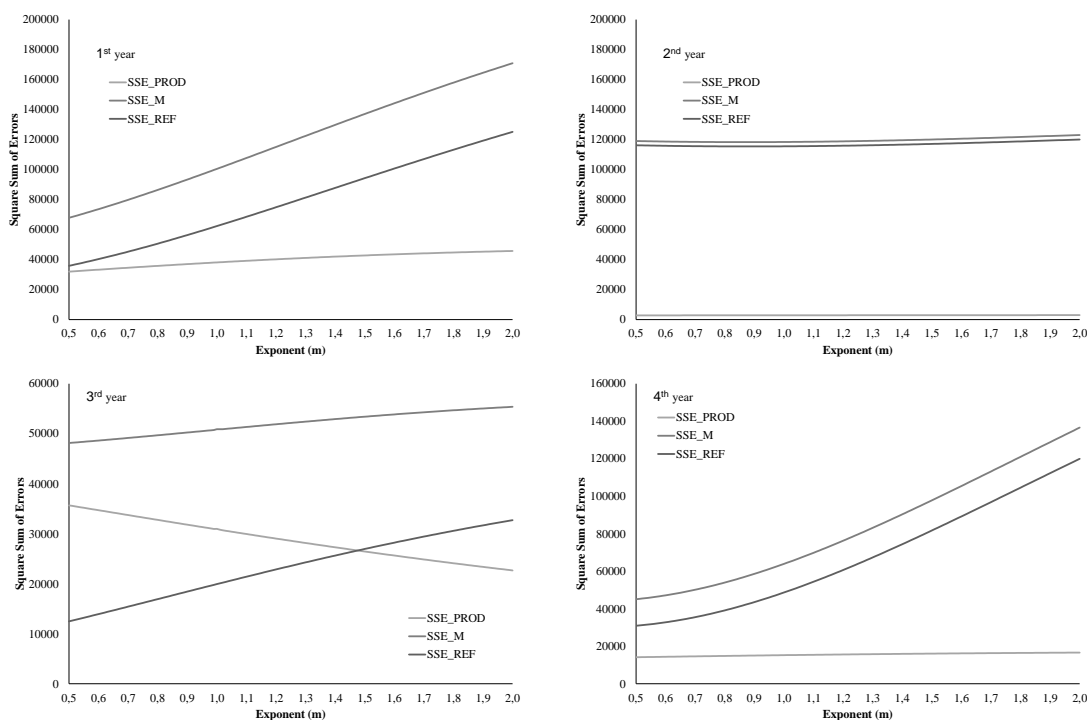
Source: Authors

The Excel spreadsheet, nevertheless, provided equivalent results to those published by Goedert *et al.* (1988) but, additionally, subsidizes the user with many graphs and statistics. Values of R^2 were slightly lower than in (Goedert *et al.*, 1988), but there is no information about SSE values or additional statistics from the end estimates from Goedert *et al.* (1988) or Colwell and Goedert (1988) to compare with those obtained by the Excel spreadsheet.

Varying m exponent causes parameters, and SSE values to change (Figure 2). The SSE tab of the Excel spreadsheet allows the user to estimate m value, which renders the lowest SSE for the model. Even though, the users may choose any m value to attend their needs. Exponent m was limited from 0.5 to 2. However lower values of m can be added manually, using m values < 0.5 cause the estimated curves to form a sharp angle shape. Graphs of that nature resemble those presented by Bai *et al.* (2013). Values of m from 0.5 to 1 are preferred for using the substitution rate method, mainly when data from PROD and REF reach the same maximum level. The work of Ron and Loewy (2015), as an example, could provide good data for using the method with m values in this range. Increasing the m exponent, curves will tend to a linear shape. Values of from $1 < m < 2$ cause a downward curve shape on the higher doses. Although possible, the use of m values from 1 to 2 is not recommended, as the error of the estimates tends to increase. The quadratic model ($m = 2$), in the work of Xia and Yan (2011), indicated optimal rates of fertilization for rice and wheat in response to fertilizer rates. In this situation ($m = 2$) the substitution rate method will not

work. The use of m values from 1 to 2 depends on the materials being tested and the purpose of the analysis. The work of Fontes *et al.* (2010) brings a range of data, where a fixed m value would not work. Varying m , therefore, would give flexibility to apply the substitution rate method in a broad number of situations. The choice of a determined m value will depend on the materials being tested, and the expected behavior.

Figure 2. Sum of square errors (SSE) due to varying the m exponent from 0.5 to 2, with increments of $(\gamma, \text{equation } 5) = 0.01$, using excel solver. SSE_PROD = values of SSE for the products; SSE_M = optimized SSE for both REF and PROD; SSE_REF = values of SSE for the reference.

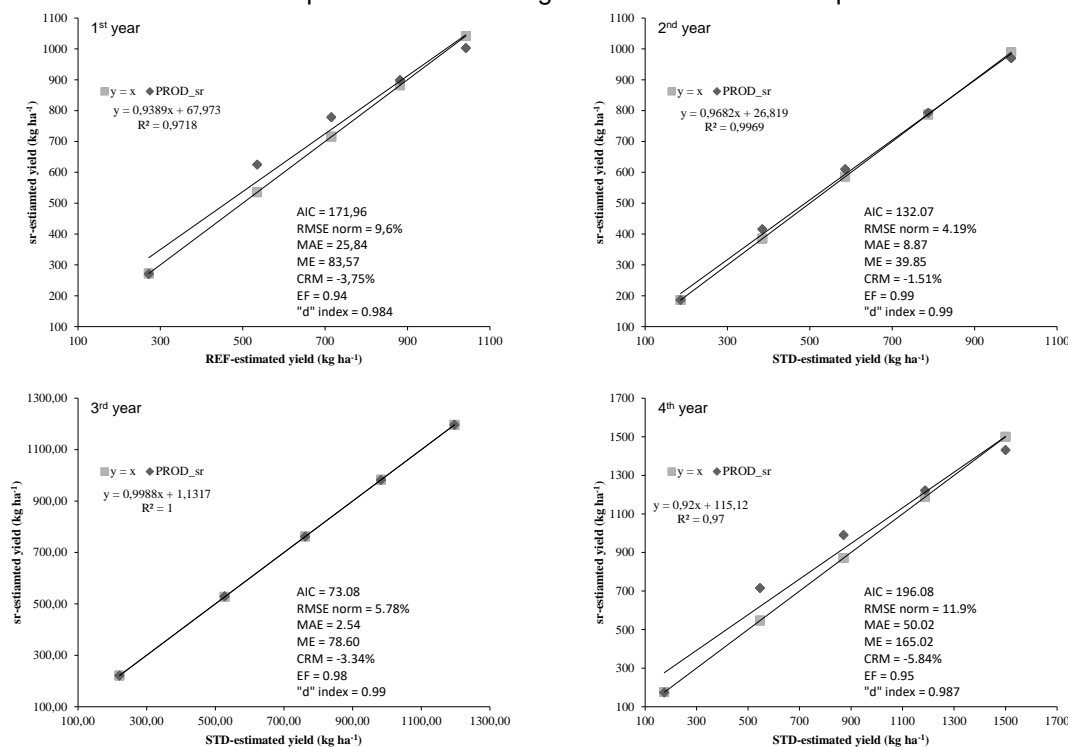


Source: Authors

The first equation estimated to describe REF data, for each year, was compared using the Excel spreadsheet, with the unified equation estimated using sr values. By plotting the y axis of each equation (estimated yield) against each other, straight lines were produced (Figure 3). These straight lines were compared to an ideal 1:1 line indicating differences among an equation estimated from original data and the unified equation. Graphs are presented on the “1 x 1 line” tab on Excel spreadsheet, and show if the estimated equations are acceptable, according to the statistical indexes. These indexes are calculated

automatically by an Excel macro after “SR calculation” button is pressed for sr adjust on the “output” tab. Statistical values placed inside graphics, however, are not automatic. The user will need to change values manually.

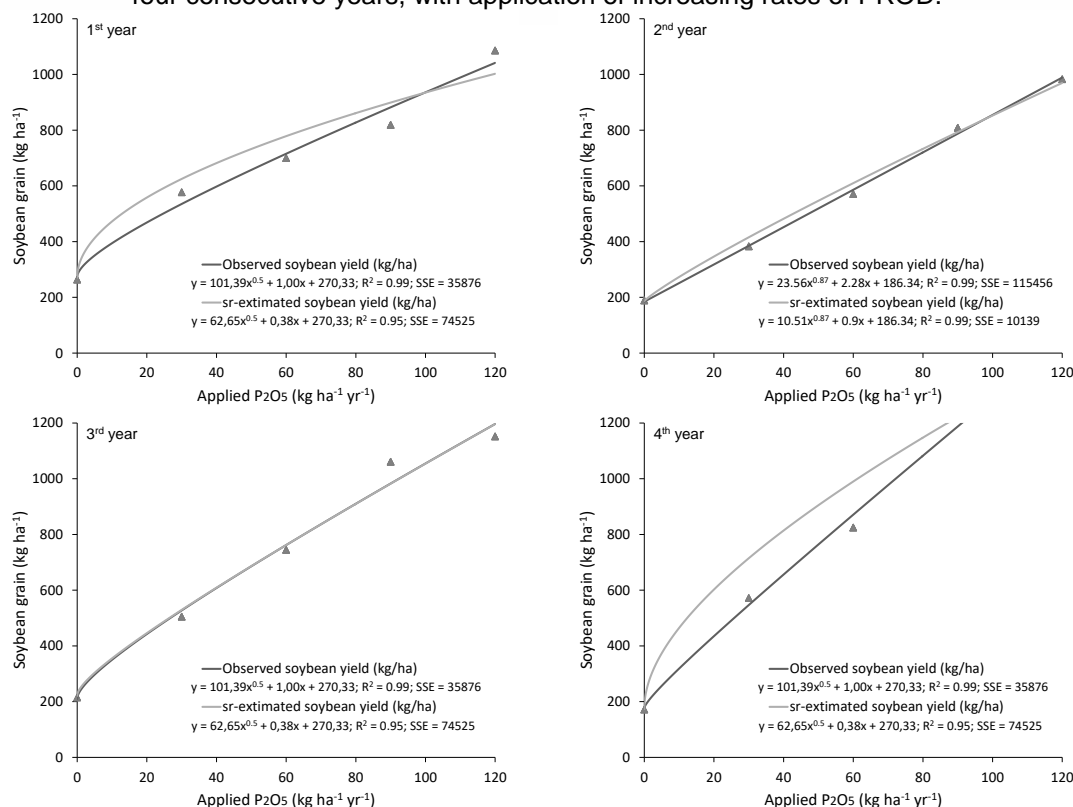
Figure 3. Soybean grain mean yield produced in four consecutive years, with application of increasing rates of partially acidulated rock phosphate (PROD). Comparisons of the REF estimated equation versus data generated from unified equation.



Source: Authors

In a reverse analysis, plotting the estimated equation for the PROD (equation 9), produced using the original data and the unified equation adjusted by the sr value for the PROD (equation 15; Figure 4), yielded a graph showing how much change the original equation endured during the procedure to reach the unified equation. These results can be found at the “predicted” tab in the Excel spreadsheet. Estimated equations for the first, second, and fourth year underwent substantial changes during the search for a unified equation. These changes are associated errors during the procedure to fit the unified equation. A great part of this error was generated from forcing the PROD y-intercept to be equal to the REF y-intercept. The error is not proportional to the y-intercept shift as it was normalized by SSE during the procedure.

Figure 4. Comparison of two predicted response curves, derived from the original partially acidulated rock phosphate (PROD) data, and from the unified equation adjusted by the substitution rate sr parameter to fit PROD data. Data of soybean grain mean yield produced in four consecutive years, with application of increasing rates of PROD.



Source: Authors

While statistical indexes show reliable and robust results within the dataset, the successful use of Excel spreadsheet, though, will depend on the user needs and experimental design, following model assumptions. Another platform would provide easier data input and changes in the experiment design, with saving capabilities, better interface, faster data processing, and a system for producing organized reports.

4 CONCLUSION

Given the difficulties associated with the iterative calculations required by the substitution rate method, we developed a user-friendly Excel spreadsheet, made available for download, to facilitate the application and dissemination of this method. We believe our study encourages critical thinking when comparing data such as fertilizer effectiveness, as well as other topics involving similar response

curves. The proposed tool not only provides an accessible approach to comparing fertilizers but also offers flexibility for adjustments and the inclusion of more sophisticated models, expanding its potential applications.

The results of this research can significantly contribute to both academia and society. For researchers and students, the spreadsheet serves as a practical and educational tool, promoting the understanding and application of quantitative methods in agronomic experiments. For technicians and farmers, it supports more informed decision-making by considering the overall behavior of response curves rather than isolated points, which can lead to more efficient use of agricultural inputs and more sustainable management practices.

As a limitation, we highlight that the spreadsheet was developed based on specific and simplified models, which may not adequately represent all types of biological responses. Therefore, we suggest that future studies explore the incorporation of additional nonlinear models, as well as the use of more robust programming languages, such as R or Python, to enhance the analytical capabilities of the tool.

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