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Statistics

Bayesian approach to the zinc extraction curve of soil with sewage sludge

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Abstract:

Zinc uptake is essential for crop development; thus, knowledge about soil zinc availability is fundamental for fertilization in periods of higher crop demand. A nonlinear first-order kinetic model has been employed to evaluate zinc availability. Studies usually employ few observations; however, inference in nonlinear models is only valid for sufficiently large samples. An alternative is the Bayesian method, where inferences are made in terms of probability, which is effective even with small samples. The aim of this study was to use Bayesian methodology to evaluate the fitness of a nonlinear first-order kinetic model to describe zinc extraction from soil with sewage sludge using seven different extraction solutions. The analysed data were obtained from an experiment using a completely randomized design and three replicates. Fifteen zinc extractions were evaluated for each extraction solution. Posterior distributions of a study that evaluated the nonlinear first-order kinetic model were used as prior distributions in the present study. Using the full conditionals, samples of posterior marginal distributions were generated using the Gibbs sampler and Metropolis-Hastings algorithms and implemented in R. The Bayesian method allowed the use of posterior distributions of another study that evaluated the model used as prior distributions for parameters
in the present study. The posterior full conditional distributions for the parameters
were normal distributions and gamma distributions, respectively. The Bayesian method was efficient for the study of the first-order kinetic model to describe zinc extraction from soil with sewage sludge using seven extraction solutions.

Keywords: micronutrient, nonlinear model, Bayesian inference.

Introduction

The fate of sewage sludge generated in treatment plants is a large problem for sanitation companies. Due to its high organic matter and nutrient contents, the use of sewage sludge in agriculture has been observed to be beneficial to the supply of macro and micronutrients to plants (Carvalho, Ribeirinho, Andrade, Grutzmacher, & Pires, 2015; Silva & Andrade Pinto, 2010). Micronutrient uptake is essential for crop growth and development, and the lack of a given micronutrient may cause significant decreases in crop yield. Micronutrient availability in periods of higher plant demand is essential to avoid limitations to crop yield (Crusciol, Carmeis Filho, Fernandes, & Alvarez, 2016). Marré et al. (2015) evaluated micronutrient accumulation in coffee fruits with different maturation cycles and observed that the maturation cycle should be considered for correct soil fertilization. Crusciol et al. (2016) investigated different plant parts of several rice cultivars and observed different micronutrient uptake rates and accumulation and higher yields for cultivars that present higher micronutrient uptake.

Micronutrients, including zinc (Zn), are required by plants at very low concentrations; they are essential for plant growth and reproduction and are as important as macronutrients for plant nutrition. Micronutrients also have a role in harvest yield and quality. Plants take up elements that are essential for humans and animals (Kirkby & Römheld, 2007).

Experts in plant nutrition have been interested in the study of micronutrients due to their importance in crop production. Orioli Júnior et al. (2008) and Prado, Romualdo, Rozane, Vidal, and Marcelo (2008b) compared the effect of different Zn application methods on the nutrition of wheat and maize. The following treatments were tested: Zn incorporated in soil and applied to furrows, seed treatment, foliar spraying, and control. Orioli Júnior et al. (2008) observed that localized Zn application produced higher Zn concentrations and foliar application in higher Zn accumulation in wheat shoot dry matter. Prado et al. (2008b) observed that Zn application generated an increased height and dry matter yield in maize. Prado, Romualdo, and Rozane (2008a) evaluated the effect of application of two zinc sources—zinc sulfate and zinc oxide—on sorghum nutrition and early growth. Zn doses of 0, 14.3, 28.6, 57.2, and 114.4 g kg^{-1} seed were tested. Application of 14.3 g Zn kg^{-1} seed as zinc oxide was adequate for sorghum early growth. Leal et al. (2007) evaluated the effect of different Zn doses applied to maize seeds on plant nutrition and dry matter yield. Shoot and root Zn concentrations linearly increased with an increase in Zn doses, without causing plant toxicity.

Conversely, the detrimental effect of Zn application was observed by Yagi et al. (2006), who evaluated the effect of Zn application to seeds on germination, nutrition and early development of sorghum cultivars. The authors observed that the control treatment presented higher root and total dry matter, mean daily germination and germination speed. The lower root dry matter production was attributed to possible Zn toxicity and affected the total dry matter as it affects nutrient uptake. Chaves, Mesquita, Araujo, and França (2010) evaluated the effect of high Zn concentrations on early development of Jatropha curcas and observed decreased root, stem and leaf dry matter with increasing Zn doses.

Menezes, Dias, Neves, and Silva (2010) noted that Brazilian soils present low Zn content and highlighted the importance of evaluating the soil Zn content and availability to obtain higher crop yields. Extraction solutions have been employed in a laboratory to simplify analyses, increase their accuracy, and determine the soil content of various chemical elements (Bortolon & Gianello, 2010). Different extraction solutions have been employed to determine the soil availability of Zn and other micronutrients to plants (Araújo & Nascimento, 2005; Bortolon & Gianello, 2010; Menezes et al., 2010; Rodrigues, Barros, Neves, Alvarez, & Novais, 2012), and sequential extractions have shown temporal variations in soil chemical fractions, which enable the evaluation of different elements (Oliveira, Amaral Sobrinho, & Mazur, 2003; Souza, Muniz, Marchi, & Guilherme, 2010).

The nonlinear first-order kinetic model, which is also referred to as the Stanford and Smith model, is extensively employed to describe soil nitrogen (Oliveira, Silva, Muniz, & Savian, 2013; Pereira, Muniz, Sáfadi, & Silva, 2009; Pereira, Muniz, & Silva, 2005) and carbon mineralization (Andrade, Silva, Pires, & Coscione, 2013; Andrade, Bibar, Coscione, Pires, & Soares, 2015; Andrade, Andreazza, & Camargo, 2016; Barreto et al., 2010; Fernandes et al., 2011; Nunes, Rodrigues, Barreto, Rodrigues, & Monroe, 2016; Paula, Matos, Matos, Pereira, & Andrade, 2013; Silva, Furtado, Fernandes, & Muniz, 2019a; Silva, Silveira, Furtado, & Muniz, 2019b; Zhou et al., 2012) and potassium release (Zeviani, Silva, Oliveira, & Muniz, 2012). This model may also be used to evaluate the soil Zn concentration relative to the number of performed extractions (Souza et al., 2010). Studies typically use few observations; however, inference in nonlinear regression models is only valid for sufficiently large samples (Martins Filho, Silva, Carneiro, & Muniz, 2008). An alternative is the Bayesian method, which enables the use of small samples and incorporation of data from previous studies and provides a probability distribution for the parameters and a direct interpretation for the credible interval (Gelman et al., 2014; Machado, Muniz, Sáfadi, & Savian, 2012).

The Bayesian methodology is based on the Bayes Theorem, whose development is based on conditional probability. According to Bolstad and Curran (2016), Bayes theorem can be written in the form of proportionality as:

$$P(B_j|A) \propto P(A|B_j)P(B_j) \tag{1}$$

where: is the a prior probability for the events , j = 1, 2,..., p, is the likelihood, and is the a posterior probability of event .

In this study, the Bayesian method was used to evaluate the nonlinear first-order kinetic model to describe zinc extraction from soil with sewage sludge using seven different extraction solutions. Posterior distributions obtained in a study that evaluated the nonlinear first-order kinetic model (Pereira et al., 2009) were used as prior distributions in the present study. In addition, the credible intervals of the model parameters were estimated.

Material and methods

The analysed data were extracted from Souza et al. (2010); the data are the results expressed as means from an experiment that evaluated fifteen sequential zinc extractions from soil with sewage sludge using seven different extraction solutions, with a completely randomized experimental design and three replicates.

The experiment was performed in a laboratory. A soil classified as Kandiudox (according to the Brazilian Soil Classification System) was evaluated from an experiment performed in Jaguariúna, São Paulo State, Brazil. The soil presented the following characteristics: 25.5 g kg^{-1} organic matter (Walkley-Black method); 450 g kg^{-1} clay; P (Mehlich I) = 3.5 mg dm-3; K+ = 1.51 mmolc dm^{-3}; titratable acidity (by titration with 0.5 mol L^{-1} calcium acetate at pH 7.0) (H^+ Al^{3+}) = 35 mmolc dm^{-3}; pHH2O = 5.5; Ca^{2+}, Mg^{2+} and Al^{3+} (1 mol L^{-1} KCl) = 27.5, 8.5, and 1 mmolc dm^{-3}, respectively.

Sewage sludge was collected at the Sewage Treatment Plant of the city of Franca, São Paulo State. The sewage sludge was applied to the soil once a year for five consecutive years, at the following doses per year: 24.11 t ha^{-1} dry weight, 26.03 t ha^{-1} dry weight, 30.13 t ha^{-1} dry weight, 35.45 t ha^{-1} dry weight and 34.80 t ha^{-1} dry weight, for a cumulative total of 150.53 t ha^{-1}. The total Zn concentration in the soil with sewage sludge was 71.74 mg kg^{-1}.

Seven extraction solutions were used for the sequential extraction of trace-elements from the soil samples, of which four were composed of low-molecular-weight organic acids (0.1 molc L^{-1}): i) modified organic acid solution (MOAS); ii) simplified organic acid solution (SOAS); iii) lactic acid; iv) acetic acid; and three extraction solutions used in routine analyses; v) Mehlich I; vi) ammonium acetate (NH4OAc); and vii) diethylenetriaminepentaacetic acid (DTPA).

Soil zinc accumulation relative to the number of extractions was described using a nonlinear first-order kinetic model (Souza et al., 2010):

$$C_i = C_l[1 - exp(-kt_i)] + \varepsilon_i \tag{2}$$

where: the response variable Ci is the accumulated zinc extracted (mg kg^{-1}) in extraction ti; Cl is the amount of zinc extracted until equilibrium (mg kg^{-1}); k is the extraction rate, i.e., constant k indicates the extraction speed; independent variable ti is the number of extractions; and is the error with a normal distribution, mean zero and precision .

The likelihood is given by (Pereira et al., 2009) $P(y|C_l,k,\tau) \propto exp\left\{-\frac{\tau}{2}\sum_{i=1}^{n}\{y_i - C_l[1 - exp(-kt_i)]\}^2\right\}$

Since parameter Cl indicates the amount of zinc extracted to equilibrium, this parameter is expected to have a higher probability around a central value and as it moves away from this central value, the probability decreases. In a study on nitrogen mineralization in soil, Pereira et al. (2009) evaluated the first-order kinetic model using the Bayesian approach obtaining as posterior distributions for parameter Cl the normal distribution, and this distribution describes the expected behaviour for the parameter. Thus, this distribution was used as a prior distribution in the present study, that is,

$$P(C_l|\mu_c,\sigma_c^2) \propto exp\left\{-\frac{1}{2\sigma_c^2}(C_l - \mu_c)^2\right\} \tag{4}$$

The parameter represents precision, so it assumes only positive values. Pereira et al. (2009) obtained for this parameter the gamma distribution, and this distribution considers the expected behaviour for the parameter. Therefore, for parameter , the gamma distribution was used as a prior, that is,

$$P(\tau|\alpha_e,\beta_e) \propto \tau^{\alpha_e - 1} exp\{-\tau\beta_e\} \tag{5}$$

It is expected that the estimated values for the extraction rate parameter k will be between 0 and 1, thus it was assumed as a prior distribution for this parameter the beta distribution, that is,

$$P(k|\alpha,\beta) \propto k^{\alpha-1}(1-k)^{\beta-1} \tag{6}$$

The hyperparameters , , , of the prior distributions can be specified based on the researcher's knowledge and other studies on the phenomenon. For the present study, hyperparameters were specified based on the estimated values considering the frequentist analysis by Souza et al. (2010).

According to Bayes' Theorem (2), the joint posterior distribution is obtained by multiplying the likelihood (3) by the prior distributions (4), (5) and (6). To infer any model parameter, its marginal posterior distribution needs to be obtained. The joint posterior distribution should be integrated relative to all other model parameters. Integration of the joint posterior distribution can be complicated and requires the use of the Gibbs sampler and Metropolis-Hastings algorithms (Gelman et al., 2014).

Full conditional posterior distributions were obtained from the joint posterior distribution. Using the full conditionals, samples of the marginal posterior distributions (chain) were generated using the Gibbs sampler and Metropolis-Hastings algorithms, which were implemented in R. Chain convergence was assessed using the Raftery and Lewis (1992) and Geweke (1992) criteria, which are available in the Bayesian Output Analysis (boa) package for R.

Results and discussion

Inferences about each parameter of the nonlinear first-order kinetic model were made using the marginal distributions for each parameter. According to Bayes' Theorem (2), the joint posterior distribution is obtained by multiplying the likelihood (3) by the prior distributions (4), (5) and (6). The posterior full conditional distributions (7), (8) and (9) were obtained from the model's joint posterior distribution. For the parameters , posterior distributions from a study of soil nitrogen mineralization were employed as prior distributions. Equation (7) and equation (9) show that the posterior full conditional distributions were normal distributions and gamma distributions, respectively, and depend on the prior hyperparameters. As these distributions were known, Gibbs sampling was applied. For the parameter k, the posterior full conditional distribution (8) was not known, therefore, the Metropolis-Hastings algorithm was employed, from which the approximations of the marginal distributions were obtained.

$$C_l|k,\tau,\mu_c,\sigma_c^2 \sim N\left(\frac{\tau\sum_{i=1}^{n} y_i[1-exp(-kt_i)]+\frac{\mu_c}{\sigma_c^2}}{\tau\sum_{i=1}^{n}[1-exp(-kt_i)]^2+\frac{1}{\sigma_c^2}}, \frac{1}{\tau\sum_{i=1}^{n}[1-exp(-kt_i)]^2+\frac{1}{\sigma_c^2}}\right) \quad (7)$$

$$p(k|C_l,\tau,\alpha,\beta) \propto k^{\alpha-1}(1-k)^{\beta-1}exp\left\{-\frac{\tau}{2}\sum_{i=1}^{n}\{y_i - C_l[1-exp(-kt_i)]\}^2\right\} \quad (8)$$

$$\tau|C_l,k,\alpha_e,\beta_e \sim G\left(\frac{n}{2}+\alpha_e, \frac{\sum_{i=1}^{n}\{y_i - C_l[1-exp(-kt_i)]\}^2+2\beta_e}{2}\right) \quad (9)$$

The results of the chain convergence analysis for the first-order kinetic model, which was fitted to the data on zinc extraction with the seven extraction solutions, are presented in Table 1. The criterion proposed by Geweke (1992) indicates the convergence of the posterior mean and presents $p > 0.05$ for all parameters for all extraction solutions, with no evidence against chain convergence. According to the Raftery and Lewis (1992) criterion, the dependence factor (DF) was always less than five, and the decision rule showed that the sampled chains reached convergence.

TABLE 1.
Dependence factor (DF) of the Raftery and Lewis criterion and p-value of the Geweke criterion.

Extraction solution	Parameter	DF	Geweke p-value
	C_1	0.9906	0.8114
Mehlich I	k	1.0109	0.5410
	τ	1.0109	0.4731
	C_1	1.0755	0.4511
NH_4OAc	k	1.1676	0.4932
	τ	0.9906	0.4484
	C_1	1.0117	0.9118
DTPA	k	1.0109	0.3519
	τ	1.0224	0.8459
	C_1	0.9906	0.3946
MOAS	k	1.0109	0.0745
	τ	0.9906	0.4501
	C_1	0.9703	0.9865
SOAS	k	0.9906	0.4990
	τ	0.9703	0.7365
	C_1	0.9703	0.6971
Acetic acid	k	0.9703	0.4650
	τ	1.0533	0.5977
	C_1	1.0320	0.0845
Lactic acid	k	0.9813	0.1739
	τ	1.0109	0.8425

The posterior means and respective credible intervals for each parameter of the first-order kinetic model for the seven extraction solutions are presented in Table 2. The analysis of the data obtained for the sequential Zn extractions from soil with sewage sludge showed that all model parameters were significant because no credible intervals with 95% probability included zero. The nonlinear first-order kinetic model fitted using the Bayesian method was adequate to describe the data. The estimates obtained for the model parameters using a Bayesian approach were coherent with the estimates obtained by Souza et al. (2010) using the classical approach. An advantage of the Bayesian method is obtaining a credible interval (highest posterior density), which is the probability interval (1 - α)% that contains the most likely values for the parameter (Guedes, Rossi, Martins, Janeiro, & Carneiro, 2014; Martins Filho et al., 2008).

TABLE 2.
Posterior mean for the parameters and highest posterior density (HPD); (LL: lower limit and UL: upper limit).

Extraction solution	Parameter	Posterior mean	HPD 95% LL	HPD 95% UL
	C_1	36.2520	35.4314	36.9987
Mehlich I	k	0.9382	0.8580	0.9982
	τ	0.5096	0.1787	0.8923
	C_1	10.9212	9.2158	12.6657
NH_4OAc	k	0.1254	0.0877	0.1636
	τ	3.2442	1.1876	5.4576
	C_1	21.7316	20.9246	22.5406
DTPA	k	0.8932	0.7642	0.9948
	τ	0.5259	0.1895	0.9114
	C_1	31.1650	30.1250	32.1784
MOAS	k	0.4687	0.3888	0.5544
	τ	0.5888	0.2269	1.0072
	C_1	31.7904	30.8301	32.7242
SOAS	k	0.4075	0.3539	0.4658
	τ	0.7362	0.2765	1.2463
	C_1	27.1902	26.4479	27.9740
Acetic acid	k	0.3564	0.3142	0.3988
	τ	1.4602	0.5686	2.5114
	C_1	35.0520	33.9295	36.3727
Lactic acid	k	0.4610	0.3831	0.5515
	τ	0.3952	0.1577	0.6841

The credible intervals showed that the amount of accumulated Zn (parameter Cl) extracted from soil with sewage sludge using the tested extraction solutions followed the descending order Mehlich I = lactic acid > MOAS = SOAS > acetic acid > DTPA > NH4Oac (Table 2). This finding shows agreement with Araújo and Nascimento (2005), who obtained a greater Zn recovery with Mehlich I than that with DTPA from soil with sewage sludge. Menezes et al. (2010) obtained similar results for soil fertilized with macro and micronutrients, with or without liming.

Different micronutrient accumulations and uptake rates, including those of Zn, were obtained by Crusciol et al. (2016) and Marré et al. (2015) for different plant parts of several rice cultivars and coffee fruits with different maturation cycles, respectively. The different extraction solutions yielded different amounts of accumulated Zn (parameter Cl) and different uptake rates (parameter k), which demonstrates different forms of removal and accumulation and indicates that they can be used to simulate Zn uptake and accumulation in different plant parts (Table 2 and Figure 1). MOAS has the closest composition to the maize rhizosphere (Koo, Chang, Crowley, & Page 2006). Based on the credible intervals for parameter Cl and k (Table 2), MOAS presented the same accumulated Zn amount and accumulation rate as SOAS, which is similar in its predictive efficiency of Zn in soil with sewage sludge.

The parameter Zn sequential extraction rate, k (Table 2), was similar for DTPA and Mehlich I and higher than that for the remaining extraction solutions, based on the credible interval with 95% probability. This finding is consistent with Souza et al. (2010), who observed that although extraction using Mehlich I was as fast as DTPA, accumulated Zn (parameter Cl) was higher for Mehlich I than for DTPA. The parameter for Mehlich I and DTPA was the only parameter that presented a left-asymmetric marginal distribution (Figure

1). In future studies, a prior asymmetric distribution can be considered for this parameter (Savian, Muniz, Sáfadi, & Silva 2009). For the remaining extraction solutions, a symmetric posterior marginal distribution was observed for the parameter k (Figure 1)

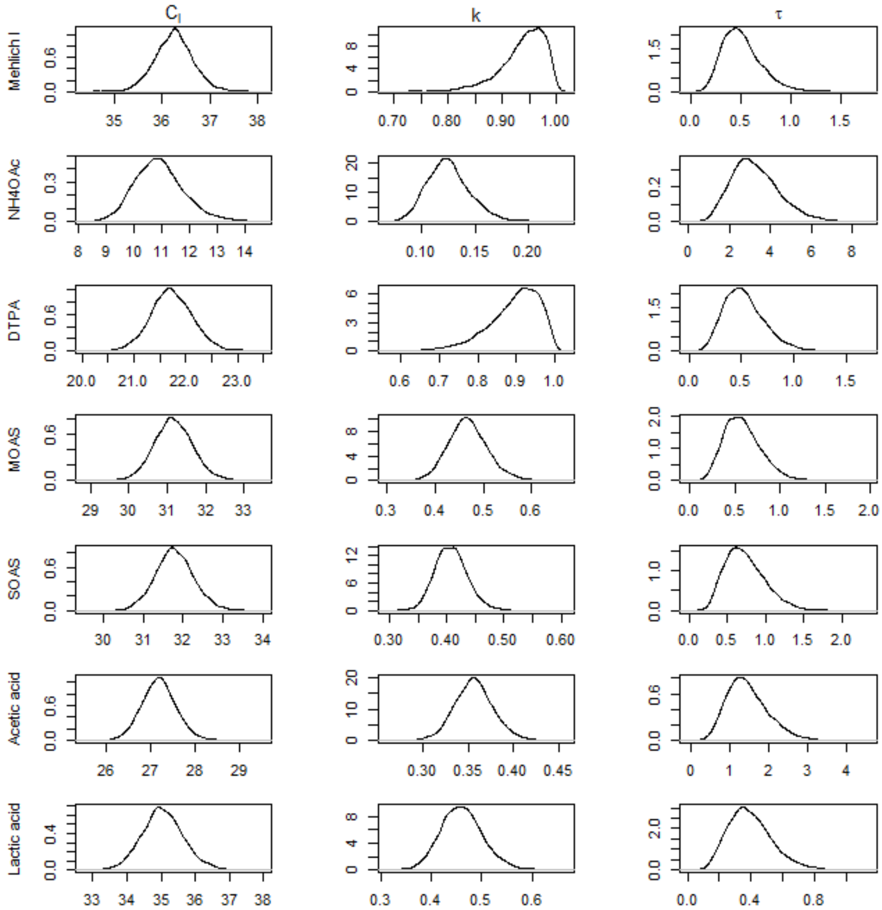

FIGURE 1.
Marginal distribution probability density functions for the model parameters (Cl, accumulated zinc; k, extraction rate; and precision).

Conclusion

The Bayesian method was efficient for the study of the first-order kinetic model to describe zinc extraction from soil with sewage sludge using seven different extraction solutions. The Bayesian method allowed the use of posterior distributions of a study that evaluated the first-order kinetic model as prior distribution for parameters (amount of accumulated zinc) and (precision) in the present study. The full conditional posterior distributions for the parameters were normal and gamma distributions, respectively. For the extraction rate parameter k for DTPA and Mehlich I, a prior asymmetric distribution may be employed in future studies.

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