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Estimation of parameters in complex ^{15}N tracing models by Monte Carlo sampling

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Abstract

The most widely used method to quantify gross N transformation rates in soils is based on ^{15}N dilution and enrichment principles. To identify rate parameters, ^{15}N-tracing experiments are analysed by models that are linked to algorithms that try to minimize the misfit between modelled and observed data. In currently available ^{15}N-tracing models optimization algorithms are based on the Levenberg–Marquardt method that is suitable for the determination of small number of parameters. Therefore, these models are restricted to a few processes. Methods based on Monte Carlo sampling have the potential to overcome restrictions on parameter numbers but have not been tested for application in ^{15}N-tracing models. Here, for the first time, we use a Markov chain Monte Carlo (MCMC) method with a tracing model to simultaneously determine the probability density functions (PDFs) of the whole set of parameters for a previously published data set [Müller, C., Stevens, R.J., Laughlin, R.J., 2004. A ^{15}N tracing model to analyse N transformations in old grassland soil. Soil Biology & Biochemistry 36, 619–632]. We show that the MCMC method can simultaneously determine PDFs of more than 8 parameters and demonstrate for the first time that it is possible to optimize models where transformations are described by Michaelis–Menten kinetics. Setting the NH_4^+ oxidation rate to Michaelis–Menten kinetics reduced the misfit by 19%. Together with monitoring diagnostics for parameter convergence, the MCMC method is a very efficient and robust technique to determine PDFs for parameters in ^{15}N-tracing models that contain large number of N transformations and complex process descriptions.

Keywords: ^{15}N tracing; Model; N transformations; Metropolis algorithm; Monte Carlo sampling; Markov chain; Michaelis–Menten kinetics

1. Introduction

Techniques based on the principle of ^{15}N isotope enrichment and dilution are widely used to quantify nitrogen (N) transformation rates in terrestrial and aquatic ecosystems (Blackburn, 1979; Stark, 2000). In tracing experiments one or more soil N pools are enriched with ^{15}N and the N concentrations and enrichments are determined in the labelled but also in various product pools over a period of time. The calculation of gross rates is based on models that describe their interactions with individual soil N pools. In their pioneering work, Kirkham and Bartholomew (1954, 1955) considered an organic N pool and one mineral N pool and developed analytical solutions for the mineralization and immobilization process in soil. With the progress in analytical methods since the 1950s, we have now techniques available that can differentiate the pools of organic N and mineral N into compound-specific N species. This led to the development of more detailed ^{15}N tracing models (Myrold and Tiedje, 1986; Mary et al., 1998; Müller et al., 2004). Current ^{15}N-tracing models are based on a set of differential equations that are solved by numerical techniques (e.g. Runge–Kutta algorithm) (Mary et al., 1998). Non-linear optimization routines are used to find sets of kinetic parameters that minimize the misfit between modelled data and a set of

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observed data. The estimation of parameters in those models is usually carried out with algorithms based on the Levenberg–Marquardt method. However, this technique is only suitable for small number of parameters (usually not more than 6 parameters) (Aster et al., 2005) and therefore restricts the development of more complex models. In current ^{15}N-tracing models this problem is solved in two ways: (1) the optimizations are only carried out between two adjacent observations points in time (Mary et al., 1998) so that N transformations with small rates can be ignored or (2) optimizations are carried out over the entire experimental period but in more than one step (Müller et al., 2004). Both approaches have their draw backs because they may ignore transformation rates that are only apparent in longer time sequences (Müller et al., 2005) or may misinterpret ^{15}N-tracing data (Luxhøi et al., 2005). Another disadvantage of current ^{15}N-tracing models that follows from the restriction on parameter numbers is that N transformations are usually described by either zero- or first-order kinetics but not Michaelis–Menten kinetics, which would be conceptually the best kinetics to use but doubles the number of parameters (Myrold and Tiedje, 1986).

Complex ^{15}N-tracing models have recently been published that include nitrite species (Müller et al., 2006) and gaseous N species (Stange and Döhling, 2005) but the currently applied optimization techniques are unable to estimate all parameters in these models simultaneously. Therefore, further progress in ^{15}N-tracing techniques can only be expected once we are able to estimate large number of parameters via robust optimization techniques. The most promising methods that can simultaneously estimate large number of parameters are based on Bayesian data analysis (Gelman et al., 2003). In particular, methods that perform a guided random walk in the model parameter space via Monte Carlo (MC) sampling are considered to be the most efficient techniques to collate parameter sets and their probability density function (PDF) of large-scale problems (Tarantola, 2005). MC sampling techniques have been developed for applications in nuclear physics (Metropolis and Ulam, 1949; Metropolis et al., 1953) and are recently applied successfully to estimate large number of parameters in ecosystem models (Braswell et al., 2005; Knorr and Kattge, 2005; Xu et al., 2006). In this paper, we show for the first time that a Markov chain Monte Carlo (MCMC) method that uses the Metropolis algorithm (MA; Metropolis et al., 1953) is suitable to simultaneously collate parameter sets representing the PDF of all parameters of complex ^{15}N-tracing models. These sets of PDFs are then used to derive optimized parameter values, their error covariances and parameter deviations from Gaussian distribution. Furthermore, we demonstrate that this technique is able to optimize parameters of N transformations that are based on Michaelis–Menten kinetics. We will first describe the algorithm and then use the new method with experimental data and the model (ModelB) described by Müller et al. (2004).

2. Materials and methods

2.1. MC sampling

The aim of an optimization algorithm is to find the so-called global minimum. Fig. 1 illustrates a misfit function, $f(\mathbf{m})$, for a theoretical 2-parameter model. There are two combinations in the parameter space where the misfit function has a minimum: one local and one global minimum. Optimization algorithms should be able to avoid or move in and out of the local minimum in search

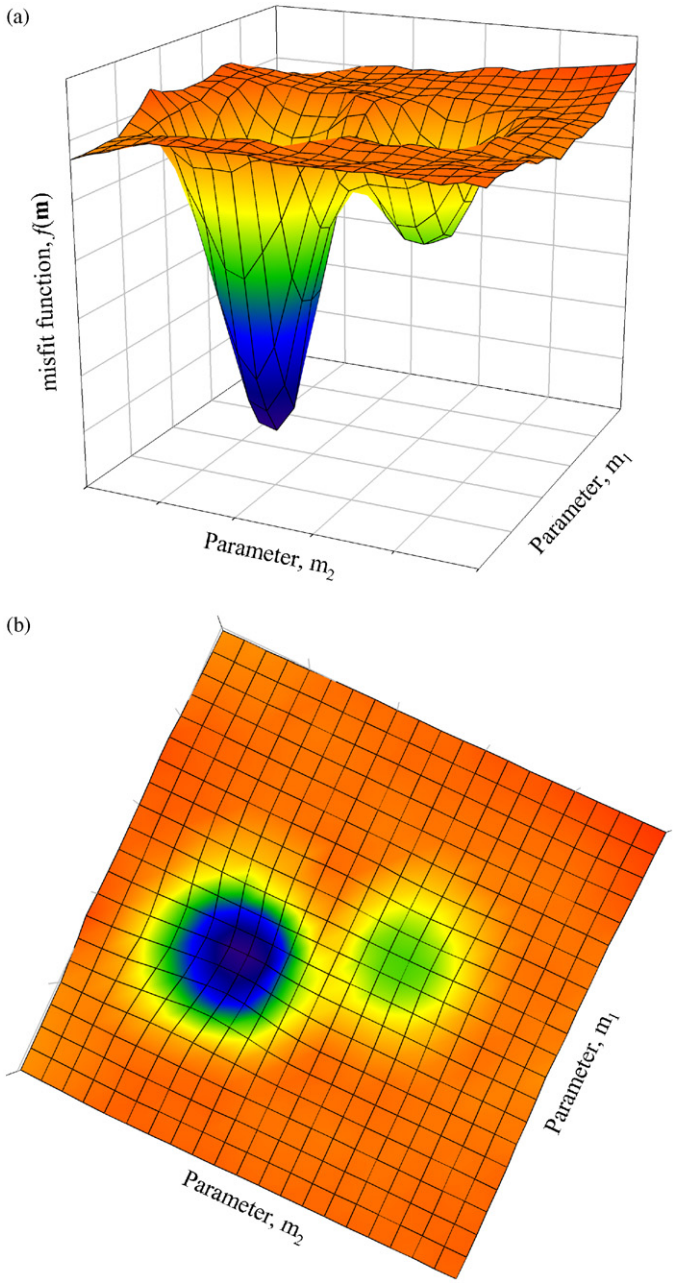

Fig. 1. Model space of a misfit function, $f(\mathbf{m})$, of a theoretical two-parameter model, (a) and (b) represent the view from the side and from above respectively.