Geoderma 235–236 (2014) 323–328

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Sequestering carbon and improving soil fertility; Validation of an improved method for estimating CO_2 flux

Renaldo Belfon [a,*], Isaac Bekele [a], Gaius Eudoxie [a], Paul Voroney [b], Gregory Gouveia [a]

[a] Department of Food Production, University of the West Indies, St. Augustine, Trinidad and Tobago
[b] School of Environmental Sciences, University of Guelph, Ontario, Canada

ARTICLE INFO

Article history:
Received 17 January 2014
Received in revised form 24 July 2014
Accepted 28 July 2014
Available online 9 August 2014

Keywords:
Climate change
Tropical soils
Carbon dynamics
Interpolation
Cross validation

ABSTRACT

Carbon dioxide flux to the atmosphere is the major pathway whereby carbon is lost from agricultural soils. Linear interpolation has traditionally been used to estimate soil CO_2 flux in lab-based studies but the resulting curves are not representative of biological systems. The objective of this study was to examine the effectiveness of linear, natural cubic spline and constrained cubic spline interpolation models for estimating CO_2 flux from contrasting soils under different management regimes. Cross-validation techniques were employed to examine the predictive accuracy, overshoot/undershoot behavior, smoothness and deviation of cumulative CO_2 flux estimates of each approach. The predictive accuracy of the interpolation models differed with soil type and between amended and unamended soils. Predictive accuracy also decreased with increased interval length though being sensitive to the nature of the region being estimated. Linear interpolation accurately predicted most measured data points and had a low spread of potential cumulative CO_2 flux values (between 154% and −54%) but produced non-smooth curves. Natural cubic spline interpolation produced relatively smooth curves but had low predictive accuracy and high variability in potential cumulative CO_2 flux values (between 528% and −617%). Constrained cubic spline interpolation produced the smoothest curves while its predictive accuracy and spread of potential cumulative CO_2 flux (between 175% and −53%) was comparable to that of linear interpolation. These results demonstrate that the constrained cubic spline interpolation technique offers improvements over linear interpolation for estimating soil CO_2 flux.

1. Introduction

Cultivation of agricultural soils is linked to reduced soil organic carbon (SOC) content and increased atmospheric CO_2 levels, which are threats to global food and climate security. Agricultural soils have the potential to sequester between 0.4 Pg and 0.8 Pg of carbon annually through cropland management and this approach may be a more feasible method of climate change mitigation than geo-engineering approaches (Lal, 2004; Peng et al., 2013). The application of organic amendments to the soil is one of the most direct methods of improving SOC content and the return of plant residues into the soil has been promoted as a recommended management practice due to the ready availability of residues and attendant benefits to soil health (Jarecki and Lal, 2003).

Monitoring changes in SOC stocks is critical to examining the effectiveness of management interventions but this is often difficult when using standard direct measurements of soil carbon content due to the slow rate at which this parameter responds to changes in soil inputs and its high spatial variability. Quantifying cumulative CO_2 flux from the soil may provide information at shorter time-scales and concerns about spatial variability may be addressed by adequate replication during gas flux sampling (Davidson et al., 2002). Carbon loss assessment can be done under the assumption that most CO_2 fluxes are due to decomposition of soil organic matter constituents by heterotrophic microorganisms while the remaining material becomes stabilized soil organic matter (Jenkinson and Rayner, 1977). However, the effectiveness of this approach is dependent on the selection of a sampling regime which is able to capture all critical phases of CO_2 flux stemming from microbial respiratory activity (Gabriel, 2010; Gomez-Casanovas et al., 2013).

Laboratory-scale incubations in closed systems allow the examination of short-term soil carbon dynamics under controlled conditions. These are more manageable than field experiments and usually require a lower sampling frequency because environmental conditions like temperature are not as variable as in the field (Parkin and Venterea, 2010). Since continuous measurements of soil respiration is often unfeasible, linear interpolation of periodic measurements of CO_2 flux followed by numerical integration is used to estimate cumulative CO_2 flux. However, the curves generated from linear interpolation are discontinuous at node points and this is not representative of dynamic

* Corresponding author.
E-mail addresses: r.belfon@hotmail.com (R. Belfon), isaac.bekele@sta.uwi.edu (I. Bekele), gaius.eudoxie@sta.uwi.edu (G. Eudoxie), pvoroney@uoguelph.ca (P. Voroney), gregory.gouveia@sta.uwi.edu (G. Gouveia).

http://dx.doi.org/10.1016/j.geoderma.2014.07.027

biological systems (Greeff, 2003; Janson, 2012). The shortcomings of linear interpolation in relation to smoothness becomes more apparent over longer sampling intervals which are typical in the latter stages of incubations (Flavel and Murphy, 2006; Parkin and Kaspar, 2004). This suggests that smooth interpolation models may be more appropriate for the estimation of CO_2 fluxes but there is currently a dearth of information on the efficacy of other approaches under laboratory conditions (Gomez-Casanovas et al., 2013).

Cubic polynomials are the lowest degree polynomials which ensure C^2 continuity and may be better suited for estimating CO_2 flux than linear methods due to their smooth nature. Natural cubic spline interpolation is the most commonly used piecewise interpolation technique and is performed by fitting unique cubic polynomials between each interval, giving equal weighting to subsequent polynomials at nodes (Embree, 2009). This model is less susceptible to oscillation for dense data clusters and overshooting/undershooting between large intervals than are comparable global interpolation methods where a single polynomial is used to fit all data points (Hagan and West, 2006). However, piecewise natural cubic spline interpolation is not exempted from this behavior and undershooting in regions with low flux values is of particular concern as this may produce sub-zero estimates of flux rate which erroneously implies that the soil is accruing carbon without additional inputs (Adams, 2001; Waggoner, 1997).

Constraints can be applied to interpolation models to modify their behavior but little research has been conducted on optimizing interpolation models for estimating CO_2 flux over time. The constrained cubic spline technique developed by Kruger (2003) to model the flow of fluids retains the smooth curves characteristic of cubic spline methods while concomitantly eliminating oscillation and overshooting/undershooting behavior. This is achieved by utilizing piecewise polynomials in a manner similar to natural cubic spline interpolation, save that greater weighting is given to the second polynomial at each node, and this results in curve shape being influenced more by the latter polynomial (Greeff, 2003). This interpolation procedure may be appropriate for estimating CO_2 flux but validation studies using empirical data are required to assess its suitability across a range of soils with differing CO_2 flux profiles.

A range of intrinsic and extrinsic factors must be considered when selecting an interpolation approach to model CO_2 flux. Thus, the objective of this study was to examine the effectiveness of linear, natural cubic spline and constrained cubic spline interpolation for estimating CO_2 flux from contrasting soils under different management regimes.

2. Materials and methods

2.1. Soils and amendment properties

The interpolation techniques were evaluated using data obtained from an incubation study examining the decomposition rate of organic amendments in contrasting soils. The Frederick soil (very-fine, mixed, Vertic Tropaquolls) was collected from a site near the Caroni swamp, Trinidad and Tobago (10°55′69″N 61°43′72″W) and is used for sugar cane and forage-grass cultivation while the Piarco soil (clayey, kaolinitic, Aquoxic Tropudults) was sampled from an agricultural plot near Port-of Spain, TT (10°36′17″N 61°18′57″W) and is currently used for intensive vegetable production. The Frederick soil was clayey textured (62.5% clay and 36.7% silt), acidic (pH 4.2), contained 2.4% total C and 0.29% total N with no detectable inorganic carbon while the Piarco soil contained 25% clay with 47.5% silt, was moderately acidic (pH 5.4), contained 1.04% total C and 0.12% total N with no detectable inorganic carbon. Corn (*Zea mays*) stalks were collected soon after harvest and were stored indoors under ambient conditions for four months prior to the start of the incubation study. Corn stalks contained 36.7% carbon and 1.2% nitrogen. Soil and plant material were transported to the School of Environmental Sciences, University of Guelph, Ontario, Canada without biocidal treatment where the incubation study was conducted.

2.2. CO_2 flux measurement

The incubation was conducted in a controlled room at 24 °C using 750 mL Mason jars (internal diameter 7.58 cm, 17.4 cm depth) fitted with alkali traps modified after Mulvaney et al. (1997) as incubation vessels. The experiment used a 2 (soil) × 2 (amendment) completely randomized factorial design with seven replicates giving a total of twenty eight experimental units. The equivalent of 110 g air dried Piarco and Frederick soil was added to incubation vessels and pre-incubated at 40% water holding capacity for 15 d to allow microbial activity to stabilize (Bartlett and James, 1980). Corn stalks (ground to <2 mm) were incorporated into the soils at a rate equivalent to 25 Mg C/ha. Thereafter, the soils were maintained at 50% water holding capacity by intermittently re-moistening with DI water. The incubation was stopped after 80 d when CO_2 fluxes from amended soils had decreased to the level of unamended soils. CO_2 flux was measured in duplicate by sealing alkali traps containing 10 mL 0.3 M NaOH into randomly selected incubation vessels for between 3 and 24 h, dependent on predicted flux rate. The traps were then removed, excess $BaCl_2$ was added to precipitate carbonates and unreacted NaOH was back-titrated with standard 0.1 M HCl to a phenolphthalein endpoint (Anderson, 1982). Three empty incubation vessels were included as references to facilitate calculation of CO_2 flux according to the formula of Stotzky (1965).

2.3. Evaluation of interpolation techniques

2.3.1. Study I

This study examined predictive accuracy of each interpolation model on data from amended and unamended soils using an approach adapted from Adams and Deventer (1994) as this re-sampling method is more reliable than methods based on common statistical tests (Arlot and Celisse, 2010; Braga-Neto and Dougherty, 2004). The initial data sets consisted of 15 (n) CO_2 flux values with measurement intervals that ranged from 1 to 20 d over the 80 day-period. Predictive accuracy of the interpolation models was assessed using leave-one-out cross validation (LOOCV), where individual data points were sequentially removed from each data set and the absolute error between newly estimated values and those in the initial data set was recorded. The Pearson correlation coefficient between interval length stemming from the deletion of measured data points and absolute error was also assessed at $P < 0.05$ using Minitab v15 (Minitab Inc., State College, PA). The smoothness of interpolated curves in the initial data sets was also assessed. Many attempts have been made to devise a mathematically sound interpretation of curve smoothness that matches intuitive expectations including calculation of strain energy and relative differences from linear curves (Adams, 2001; Kruger, 2003). Curves that have derivatives that are continuous at all lower orders are considered “mathematically smooth” with respect to those orders. Linear curves i.e. straight lines are instinctively considered non-smooth and the absolute value of the second derivatives of CO_2 flux values was used to compare the smoothness of interpolated curves as the aforementioned curves only possess first derivatives. For comparison between interpolation models, curves with a smaller degree of bending between measured data points and which by extension had smaller non-zero second derivative values were considered smoother. This approach gave an estimation of the smoothness of interpolated curves while discerning these from curves which were straight lines.

2.3.2. Study II

This study used more exhaustive cross validation techniques to verify the results of LOOCV in the previous study. Soil respiration data from the corn stalk amended Frederick soil was selected for this study from among the available data sets as it possessed a range of curve shapes