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Near infrared reflectance spectroscopy: A tool to characterize the composition of different types of exogenous organic matter and their behaviour in soil

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ABSTRACT

In addition to total organic carbon and nitrogen, potential organic carbon mineralization under controlled laboratory conditions and indicators such as the indicator of remaining organic carbon in soil (I_{ROC}), based on Van Soest biochemical fractionation and short-term carbon mineralization in soil, are used to predict the evolution of exogenous organic matter (EOM) after its application to soils. The purpose of this study was to develop near infrared reflectance spectroscopy (NIRS) calibration models that could predict these characteristics in a large dataset including 300 EOMs representative of the broad range of such materials applied to cultivated soils (plant materials, animal manures, composts, sludges, etc.). The NIRS predictions of total organic matter and total organic carbon were satisfactory ($R^2_P = 0.80$ and 0.85, ratio of performance to deviation, $RPD_P = 2.2$ and 2.6, respectively), and prediction of the Van Soest soluble, cellulose and holocellulose fractions were acceptable ($R^2_P = 0.82$, 0.73 and 0.70, $RPD_P = 2.3$, 1.9 and 1.8, respectively) with coefficients of variation close to those of the reference methods. The NIRS prediction of carbon mineralization during incubation was satisfactory and indeed better regarding the short-term results of mineralization ($R^2_P = 0.78$ and 0.78, and $RPD_P = 2.1$ and 2.0 for 3 and 7 days of incubation, respectively). The I_{ROC} indicator was predicted with fairly good accuracy ($R^2_P = 0.79$, $RPD_P = 2.2$). Variables related to the long-term C mineralization of EOM in soil were not predicted accurately, except for I_{ROC} which was based on analytical and well-identified characteristics, probably because of the increasing interactions and complexity of the factors governing EOM mineralization in soil as a function of incubation time. This study demonstrated the possibility of developing NIRS predictive models for EOM characteristics in heterogeneous datasets of EOMs. However, specific NIRS predictive models still remain necessary for sludges, organo-mineral fertilizers and liquid manures.

1. Introduction

A decline in soil organic matter content has been identified as one of the major threats to soil by the Commission of the European Communities (2006). Exogenous organic matter (EOM) is an important and potentially growing source of material that could be applied to cultivated soils to improve their fertility and increase their organic matter content, thus also potentially contributing to the prevention of global warming through carbon sequestration (Marmo et al., 2004). Exogenous organic matter includes all organic matter arising from external sources such as urban areas, municipalities, agriculture, forestry and industry. It also comprises crop residues as they may have amending properties as urban, industrial or animal EOMs and can be characterized using the same methods (Marmo et al., 2004). Tools to predict the fate of EOM in soil would enable better account to be taken of their contribution to global environmental balances.

Various characteristics of EOM have been used to predict its transformation in soils. Van Soest biochemical fractions (Van Soest, 1963; Van Soest and Wine, 1967) and the potential mineralization of total organic carbon (TOC) contained in EOM (EOM-TOC) during soil incubation under controlled laboratory conditions have been standardized (AFNOR, 2009a,b) and are useful tools to predict the fate of EOM in soil (Francou et al., 2008; Henriksen and Breland,

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1999; Thuriès et al., 2002; Trinsoutrot et al., 2000). The most stable part of EOM remaining in soil over the long-term can be estimated from incubation data by extrapolating the kinetics of EOM-TOC mineralization or fitting a stable pool of EOM-TOC decomposition models (Lashermes et al., 2009; Sleutel et al., 2005; Thuriès et al., 2001). It can also be estimated with the indicator of remaining organic C in soil (I_{ROC}, Lashermes et al., 2009) calculated as a function of soluble, cellulose- and lignin + cutin-like fractions of Van Soest fractionation (SOL, CEL and LIC, respectively), and the proportion of EOM-TOC that is mineralized after three days of incubation in soil (C_{3d}). The equation used to calculate I_{ROC} was based on a partial least square (PLS) regression between the analytical characteristics of EOM and the EOM-TOC remaining in soil over the long-term extrapolated from the kinetics of C mineralization during long-term incubations (more than 156 days). In both cases (fitting of mineralization kinetics or calculation of the I_{ROC} indicator) the estimation of remaining organic C requires quite costly and time-consuming analytical methods.

Near infrared reflectance spectroscopy (NIRS) measures the reflectance of samples in the spectral range between 800 and 2500 nm. The quantification of analytical characteristics based on NIRS requires multivariate statistical methods, referred to as chemometric methods, to fit the spectral response to sample properties in order to build predictive models. Once calibration has been developed, NIRS is a rapid, inexpensive and non-destructive method for sample characterization which does not require any consumables. It has already been used to determine the total C and nitrogen (N) contents of soils (Barthès et al., 2006), to assess the elemental and biochemical composition of plant materials (Stenberg et al., 2004; Stuth et al., 2003; Thuriès et al., 2005), composted materials (Albrecht et al., 2009; Michel et al., 2006; Vergnoux et al., 2009) and animal manures (Malley et al., 2002; Reeves and Van Kessel, 2002; Sørensen et al., 2007), to predict the C and N mineralization of plant materials (Borgen et al., 2010; Bruun et al., 2005; Shepherd et al., 2005) or the mineralization of soil organic matter (Thomsen et al., 2009). However, NIRS predictive models for the composition and long-term degradability of EOM in soils have generally been built using relatively homogenous EOM sets that include either plant materials or animal manures or composts etc., and rarely with heterogeneous EOM sets.

The objectives of this study were to evaluate the potential of NIRS: (1) to determine organic C and total N contents and Van Soest biochemical fractions in a sample set of 300 EOMs representing the broad diversity and heterogeneity of the EOMs applied in agriculture, and (2) to predict the proportion of EOM-TOC remaining in soil in the long-term after EOM applications, either by predicting the stable pool of a decomposition model fitted to the kinetics of EOM-TOC mineralization during laboratory incubations or by predicting the I_{ROC} indicator.

2. Materials and methods

2.1. EOM dataset

The dataset included 300 EOM samples collected and analysed in the context of different research programmes (Lashermes et al., 2009) and covering a broad range of fresh and transformed organic materials applied in agriculture. These included 32% of urban composts (17% of municipal solid waste composts, 7% of co-composts of sludge and green wastes, 7% of biowaste composts, 1% of green waste composts), 10% of composted animal manures, 16% of non-composted sludges, 14% of farmyard manures, 10% of plant materials, 6% of anaerobically-digested wastes, 4% of liquid manures, 3% of organic and organo-mineral fertilizers, 2% of non-composted urban wastes and 3% of screening refuse and organic amendments. The 124 composts included in the dataset were selected from a larger database of 270 composts on basis of the representativeness of their NIR spectra (see Section 2.4.1) in the planes of a principal component analysis (PCA) using the standardized Mahalanobis distance H between paired samples. This procedure was performed using the SELECT function of WinISI software version 1.63 (Foss NIRSystems, Infrasoft International, State College, PA, USA) (Shenk and Westerhaus, 1991). During the SELECT procedure, the algorithm identifies and selects spectra by discarding their most closely neighbouring spectra. This process is repeated until the desired number of samples is reached.

2.2. Chemical and biochemical characterization of EOMs

All EOM samples were oven-dried at 40 °C and finely ground (<1 mm) before analysis. Total organic matter (TOM) content was determined by loss on ignition at 480 °C, total organic C (TOC) content by dry combustion using an Elemental Analyser after the dissolution of carbonates with hydrochloric acid (AFNOR, 1995), and total N (totN) content also by dry combustion (AFNOR, 1998). Mineral N (NH_4^+ and NO_3^-) contents were determined on dry EOM after KCl extraction by spectrophotometry on a continuous flow analyser (AFNOR, 1996, 1997). The organic N (orgN) content was calculated as the difference between total N and mineral N. The biochemical composition of EOM was determined using the Van Soest method (Van Soest, 1963; Van Soest and Wine, 1967) as modified under the French standard XP U 44-162 (AFNOR, 2009a). The soluble (SOL), hemicellulose-like (HEM) cellulose-like (CEL) and lignin + cutin-like (LIC) fractions were separated. One-gram-samples of ground EOM were mixed with 2 g calcinated sand and extracted with 100 mL hot water for 30 min and then neutral detergent for 60 min (extraction of the SOL fraction, NDF residue), hot acid detergent for 60 min (extraction of the HEM fraction, ADF residue) and 180 min in cold, 72% sulphuric acid (extraction of the CEL fraction, ADL residue). The residual material (ADL) corresponded to the LIC fraction. After each extraction step, the OM content was determined in the residues by loss on ignition at 480 °C. All biochemical fractions were expressed as a percentage of TOM according to the following equations: SOL = 100 − NDF, HEM = NDF − ADF, CEL = ADF − ADL, and LIC = ADL. The holocellulose fraction (HOL) was calculated as HOL = HEM + CEL.

The C mineralization of EOM (expressed as a percentage of TOC) was measured during 91-day incubations of soil + EOM mixtures in hermetically sealed jars under controlled conditions at 28 °C with a soil moisture level corresponding to 75%–100% of the soil water holding capacity. Because the incubations were being run in the context of various research programmes, different cultivated soils taken from temperate areas were used. It was assumed that the effect of soil type on the EOM-TOC mineralization would be negligible when compared with the impact of EOM quality (Coppens, 2005). The C-CO_2 was trapped in 10 mL 0.5 M NaOH which was periodically replaced, and then determined using colorimetry (AFNOR, 2009b).

2.3. Stable organic C in EOMs

The indicator of remaining organic carbon (I_{ROC}) estimates the stable pool of EOM-TOC potentially remaining in soil over the long-term after application. It is calculated using the SOL, CEL and LIC fractions of Van Soest fractionation and the proportion of EOM-TOC mineralized after 3 days of incubation (C_{3d}), according to the formula:

$$I_{ROC} = 44.5 + 0.5\ \mathrm{SOL} - 0.2\ \mathrm{CEL} + 0.7\ \mathrm{LIC} - 2.3C_{3d} \quad (1)$$

It is expressed as a percentage of TOC. This indicator was based on extrapolating long-term C mineralization kinetics during incubation for more than 156 days (Lashermes et al., 2009).