Use of NIRS to predict organic matter characteristics and RothC model pools of exogenous organic matter

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Introduction

Soil organic matter decrease has been identified as one of the major threat towards soils by the European commission. Exogenous Organic Matters (EOM) of residual origin, deriving from agricultural, urban or industrial activities are important and potentially increasing sources of EOMs. The use of EOM in croplands can contribute to increase soil organic matter content and soil fertility along with the recycling of their organic fraction.
The fate of EOM in soil is routinely assessed by EOM characterisations according to laboratory methods standardized in France: (i) biochemical fractionation by successive solubilization in different reagents (Van Soest method, AFNOR 2005a), and (ii) measure of potential C mineralization during 91-days laboratory incubations (AFNOR 2005b). Those methods lead to the calculation of an Indicator of Residual Organic Carbon (I_{ROC}, Lashermes et al, 2009) corresponding to the proportion of residual C of EOM incorporated into soil organic matter.
Prediction using Near Infra-red Reflectance Spectroscopy (NIRS) are of great interest for EOM management. The previous standardized methods are rather time consuming, costly and generating pollutant wastes and NIRS has been shown to be suitable to predict C and N content, biochemical data or C and N mineralization patterns of plant materials (Bruun et al, 2005, Thuriès et al 2005, Henriksen et al, 2007), or of composted materials (Vergnoux et al., 2009).
To evaluate the long term potential C sequestration in croplands after EOM application, multi-compartments C dynamic models such as RothC model are useful tools. Those models are poorly parameterized for the use of EOM. The distribution of EOM C among initial DPM (decomposable) and RPM (Resistant) pools in RothC has been previously determined by fitting either field or laboratory C mineralization data.
The aim of this study was to assess the potential of NIRS to predict chemical, biochemical characteristics, IROC indicator and Roth C pools of a wide range of 458 EOMs, including complex OMs like composts.

Materials and methods

EOM dataset
The panel included 458 EOMs from different research programs, covering a wide range of organic materials applied on cultivated soils. It includes 50% of urban composts (18% of municipal solid wastes composts, 18 % of green wastes and sludge composts, 10% of biowaste composts, 10% of green waste composts), 10 % of composted animal manures, 10% of sewage sludges, 9% of farmyard manures, 7 % of plant materials, 4% of anaerobically digested wastes, 2% of liquid manures, 2% of organic and organo-mineral fertilizers and 2% of other products.
Chemical and biochemical characterisation of EOMs
EOMs were air dried and finely ground before analysis. Organic C and total N content were determined using elementary analysis (AFNOR). Total organic matter was determined by loss on ignition at 480°C. Biochemical composition was determined using the Van Soest's method

(Van Soest & Wine, 1969) according to the French standard NFU 44-162 (AFNOR 2005a), the biochemical fractions separated were the soluble OM in neutral detergent (SOL), hemicelluloses-like (HEM), cellulose-like (CEL), lignin and cutin-like (LIC) fractions. The C mineralization of EOM was measured during incubations of soil-EOM mixtures in controlled conditions at 28 °C with soil moisture corresponding to 75% to 100% of the soil water holding capacity. EOMs were incubated into hermetically closed jars, C-CO_2 was trapped into 10 ml of 0.5 M NaOH periodically replaced and colorimetrically determined.

Indicator of Residual Organic C (I_{ROC}) and Roth C model pools calculation

The Indicator of Residual Organic Carbon (I_{ROC}) was calculated based on the SOL, CEL and LIC fractions and the proportion of organic C mineralised after 3 days of incubation according to the formula $I_{ROC} = 44.5 + 0.5\ SOL - 0.2\ CEL + 0.7\ LIC - 2.3\ C_{3d}$ (Lashermes et al 2009). EOM organic matter were distributed into initial pools of the RothC model DPM (decomposable pool), and RPM (resistant pool) and HUM (humified pool) by fitting with the C mineralization kinetics using least squares criterion on a Scilab (Digiteo) version of the model.

NIR analysis

NIR spectra were performed in reflectance with a Foss NIRSystem 6500 apparatus from 400 to 2500 nm with one datapoint every 2 nm. For calibrations, only the interval 1100 – 2500 nm were used. EOM dried at 40 °C and finely ground (< 1 mm) were packed on a 5 cm circular cup, two replicates of acquisition were performed for all products with independent cup fillings and spectra of the two replicates were averaged. Spectra were transformed using WinISI software version 1.63 (Foss, Infrasoft international) mathematical pre-treatment applied were standard normal variate and detrend, second derivative calculated on 5 datapoints and smoothing (Savitzky and Golay smoothing) on five data points. Calibrations were calculated using the WinISI modified Partial Least Squares (mPLS) with cross validation calculated on 100 blocs. Statistics to evaluate goodness of fits included coefficient of determination R^2, standard error of calibration (SEC), Standard Error of Cross Validation (SECV), ratio SD (Standard Deviation) to SECV (RPD ratio) and coefficient of variation CV = 100* SECV/mean of measured data indicating the % of errors of the models. To evaluate the quality of calibrations, a validation set of about 25 % of the overall set of EOMs were separated from the calibration set. The statistics for validation included Standard error of prediction (SEP), R^2 and coefficient of variation CV = 100 * SEP / mean of measured data. A precursory Principal Component Analysis (PCA) was performed and the EOM presenting a Mahalanobis distance H > 3 were considered as spectral outliers and removed from the dataset. A total of 19 outliers, mostly sludges, were removed. The final dataset contained 439 EOMs with 332 EOMs for calibration and 107 EOMs for validation.

Results and discussion

The calibrations of organic C, OM and total N were satisfactory considering the heterogeneity of the dataset, with $R^2 > 0.88$ and RPD > 2.6. For these characteristics, predicted results on the validation subset were also fairly satisfactory.

Biochemical fractions were quite well adjusted except for the HEM fraction which is known to have high uncertainty. R^2 of the other biochemical fraction were > 0.85 with CV of 15.4, 16.6 and 17.3% for SOL, CEL and LIC, respectively. The predictions of validation set for the biochemical fractions had less good R^2 than calibration set with only the CEL fraction having a $R^2 > 0.8$. However, the CV of predictions were fairly similar to the CV of calibrations. The accuracy of prediction of the biochemical fraction were lower than predictions reported in other studies (e.g. Thuries at al., 2005, Vergnoux et al., 2009) but our dataset was composed of highly heterogeneous EOM analysed in different laboratories. Furthermore, the variability

of the calibrations approached the repeatability of the experimental method (i.e. intra + inter-laboratory variance) (AFNOR 2005a).

Table 1. Statistical results for calibration, cross validation and prediction of chemical and biochemical characteristics, proportions f EOM organic C mineralised after 3 and 91 days of incubation (C_{3d} and C_{91d}), Indicator of Residual Organic C (I_{ROC}) and RothC model initial pool (DPM)

	Calibration								**Validation**				
	n	**Mean**	**SD**	**SEC**	**R^2**	**SECV**	**CV (%)**	**RPD**	**n**	**Mean**	**SEP**	**R^2**	**CV (%)**
organic C (%DM)	302	29.4	9.4	3.2	0.88	3.6	12.3	2.6	107	31.0	4.7	0.72	15.0
OM (% DM)	298	56.4	18.9	5.6	0.91	6.6	11.7	2.9	107	60.8	6.3	0.87	10.4
total N (%DM)	267	1.82	1.11	0.29	0.93	0.36	19.8	3.1	84	2.05	0.32	0.84	15.8
SOL (% OM)	300	38.3	14.6	5.2	0.87	5.9	15.4	2.5	105	34.1	7.7	0.61	22.5
HEM (% OM)	275	9.9	5.7	3.2	0.69	3.4	34.6	1.7	105	12.3	4.0	0.60	32.9
CEL (% OM)	288	26.1	12.1	4.1	0.88	4.3	16.6	2.8	105	26.8	4.5	0.81	16.7
LIC (% OM)	292	23.5	10.4	3.5	0.89	4.1	17.3	2.5	105	26.1	4.8	0.69	18.3
C_{3d} (% added C)	293	5.1	4.3	1.6	0.86	2.0	38.2	2.2	104	2.9	1.6	0.73	56.0
C_{91d} (% added C)	291	24.5	13.9	6.6	0.77	7.1	29.2	2.0	103	19.1	7.8	0.59	41.0
I_{ROC} (% TOC)	282	62.2	15.2	5.4	0.87	5.8	9.3	2.6	103	67.9	5.7	0.79	8.4
DPM (% TOC)	282	19.9	16.2	6.3	0.85	6.8	33.9	2.4	103	10.8	6.5	0.67	60.2

The direct predictions by NIR of the C mineralised after 3 and 91 days of incubation give fairly good results, in the same order than those obtained by Bruun et al (2005). Predictions were better for C_{3d} than for C_{91d} (R^2 = 0.86 and 0.77 and RPD = 2.2 and 2.0, respectively). However, the CV was higher for C_{3d} (38.2%) than for C_{91d} (29.2%).

The I_{ROC} indicator was fairly well directly predicted by NIRS (table 1, Fig. 1). This indicator being calculated from a linear combination of the fractions SOL, CEL, LIC and Cm3 which have their own experimental errors, the statistics of calibration obtained (R^2 =0.87, errors = 9.3 % and RPD = 2.6) thus appeared to be relatively low. The calibration of I_{ROC} was stable according to the fairly good statistics of validation (R^2 = 0.79 and low CV = 8.4 %). The I_{ROC} indicator predicted by combination of the predicted values with NIRS of the SOL, CEL, LIC fractions and Cm3 was slightly better than the I_{ROC} directly predicted by NIRS (R^2 = 0.86 and CV = 8.4%, for the calibration set and R^2 = 0.81 and CV = 7% for validation set, detailed results not shown).

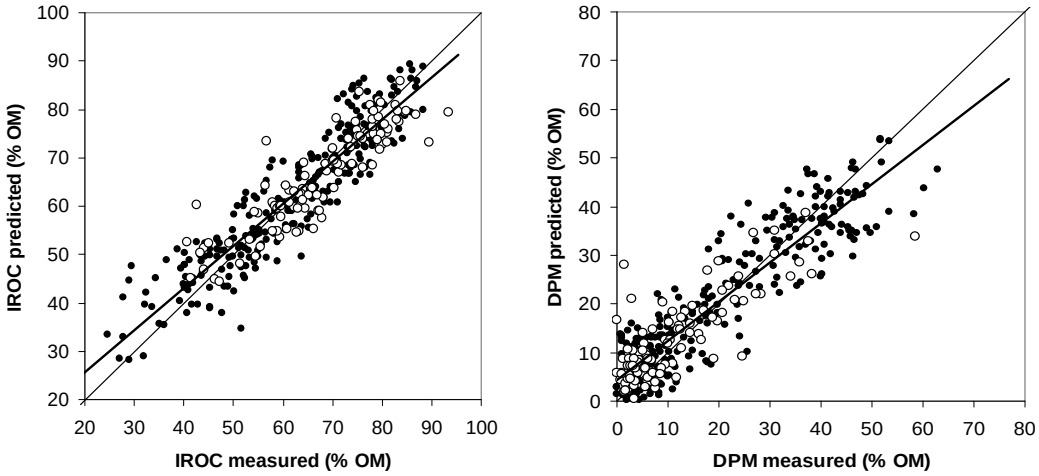

Figure. 1. Measured values of the IROC indicator (i.e. calculated from SOL, CEL and LIC biochemical fraction and Cm3) and fitted values of the DPM pools of the model RothC (i.e. fitted values to C mineralization kinetics of EOM during laboratory incubations) VS predicted values with NIR spectra. Black circles: calibration set, white circles: validation set.

The splitting of EOM carbon into the RothC model initial pools DPM (decomposable pool) RPM (resistant pool) and HUM (humified pool) were obtained by fitting RothC model to the kinetics of C mineralization during 91 days. The NIRS predictions of DPM pools were promising (table 1, Fig. 1) with quite good R^2 (0.85) and RPD (2.4) of calibration. However CV of the calibration model was important: 33.9% for the calibration set and 60.2% for the validation set which seems to be due to a limited number of outlying individuals as visible graphically (Fig 1.). The calibrations of the others RothC initial pools RPM and HUM were not satisfactory. The splitting of EOM into the RPM and HUM pools may be influenced by a possible under-estimation of EOM carbon degradation during laboratory incubations. However, a good correlation was found between DPMs fitted to laboratory based and field based data. The HUM compartment seems to be useless to fit the model to field data. Thus, the predictions of the DPM pool with NIRS could make it possible to predict the initial separation of EOM in the entry pools DPM and RPM of the RothC model.

Conclusion

NIRS calibrations make it possible to predict several chemical, biochemical characteristics of a wide panel of EOMs with acceptable accuracy. Although the calibration can certainly be improved by homogenising the dataset, it seems important to have global predictive equation valuable for a large range of products. The direct predictions of the I_{ROC} indicator showed the great predictive potential of NIRS for actual EOM management. Future works will focus on acquiring additional field data to validate the relations between RothC pool fitted to laboratory data and RothC pools fitted to field data in order to accurately simulate long-term EOM carbon dynamics in field condition.

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