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Methane production and fertilizing value of organic waste: organic matter characterization for a better prediction of valorization pathways

Julie Jimenez[1], Han Lei[1], Jean-Philippe Steyer[1], Sabine Houot[2], Dominique Patureau[1]

[1]LBE INRA, UR0050, 102 Avenue des Etangs, Narbonne, F-11100, France

[2] UMR ECOSYS, INRA, AgroParisTech, Université Paris-Saclay, 78 850 Thiverval-Grignon, France

E-mail: julie.jimenez@ inra.fr

Abstract

Organic wastes are potential sources of both energy as well as crop production fertilizers. Correlations and models, involving organic matter characterization, have been previously described by several authors although there is still a lack in knowledge on the potential of simultaneous predictions of methane and organic fertilizer quality to optimize the wastes treatments. A methodology combining chemical accessibility and fluorescence spectroscopy was used to characterise 82 different organic wastes. Characterization data were compared with the biochemical methane potential (BMP), and with the biodegradable organic carbon obtained by soil incubation (C_bio). High correlations values were observed (R^2 of 0.818 for BMP and 0.845 for C_bio). Model coefficients highlighted the differences and similarities between anaerobic and aerobic soil biodegradation, suggesting that anaerobic recalcitrant molecules could enhance soil fertility. This is a first step in the development of a tool for optimizing both types of valorisation according to agrosystem needs and constraints.

Key words biodegradability, methane production, soil, fluorescence, accessibility

List of abbreviations

Abbreviation	Definition	Units
ADM1	Anaerobic Digestion Model N°1	
BMP	Biochemical Methane Potential	$NmlCH_4.gVS^{-1}$
C_bio	Biodegradable organic Carbon in soil incubation	%TOC
COD	Chemical Oxygen Demand	gO_2. g DS^{-1}
DS	Dried Solids	% fresh matter
FFMSW	Fermentescible Fraction of Municipal Solid Wastes	
HCA	Hierarchical Clustering Analysis	
IROC	Indicator of Residual Organic Carbon	% TOC
NIRS	Near InfraRed Spectroscopy	
NEOM	Non Extractible Organic Matter	%COD
OM	Organic Matter	
OR	Organic Residues	
PCA	Principal Component Analysis	
PEOM	Poorly Extractible Organic Matter	%COD
PLS	Partial Least Square regression	
$P_f(i)$	Fluorescence percentage of a zone i	%
R^2	Correlation coefficient from PLS	
REOM	Readily Extractible Organic Matter	%COD
RMSE	Root Mean Square Error	Unit of the predicted variable
RMSEP	Root Mean Square Error of prediction	Unit of the predicted variable
Q^2	Percent of variation of Y predicted by model in cross-validation	
SEOM	Slowly Extractible Organic Matter	%COD
S(i)	Area of a zone i from fluorescence spectra	Nm^2
SPOM	Soluble from Particular extractible Organic Matter	%COD
TOC	Total Organic Carbon	mg C. g DS^{-1}
$V_f(i)$	Normalized fluorescence volume of a zone i	U.A.
$V_{f\_raw}(i)$	Raw fluorescence volume of a zone i	U.A.
VS	Volatile Solids	% DS

23

Introduction

The aim of environmental biorefinery is to establish a complete valorisation of organic wastes, which should turn into valuable organic resources. Indeed, process treatments involved in biorefinery include anaerobic digestion, fermentation, aerobic digestion, composting, thermal conversion, etc… The choice of these treatments depends on the characteristics of the organic residues (OR) and on the targeted services (i.e. energy production, high added value molecules or organic fertilizers).

In this study, focus was put on two main services: (i) the production of methane from anaerobic digestion of OR, which could potentially be subsequently used for electricity or heat production and (ii) the use of OR as organic fertilizer on cropped soils whether treated or not, thanks to their content in nutrients and organic carbon.

In both cases, the potential interest is related to the biodegradation potential of the organic matter during anaerobic digestion (the higher the biodegradation potential, the greater the methane production) or during aerobic soil incubation (the lower the biodegradation potential, the greater its value as an organic soil amendment).

Until present, the quality of digestate for agronomic valorisation has been poor. Management and prediction of anaerobic digestion for methane production would allow for digestate quality control and the availability of this knowledge would improve the optimisation of anaerobic digestion for both targeted services. The main issue to achieve this goal would be to identify relevant actuators for controlling both potentials. These two potentials depend on the chemical characterization of OR as well as its chemical and biodegradability/stability (Angelidaki et al., 2004; Lashermes et al., 2009; Peltre et al., 2014 ;Godin et al., 2015).

Indeed, during the past two decades, several authors observed significant correlations between certain indicators based on the chemical composition of OR and the studied potentials (Buffiere et al., 2006; Gunaseelaan et al., 2007 and 2009; Lashermes et al., 2009; Lesteur et

al., 2011; Thomsen et al., 2014; Peltre et al., 2014; Thomsen et al., 2014; Godin et al., 2015; Bekiaris et al. 2015 a and b; Kafle et al., 2016; Fitamo et al., 2017). These correlations were used for predicting biological incubation tests which can be resource and time consuming (Godin et al., 2015).

Usually, the anaerobic biodegradation potential of an OR is assessed by performing a Biochemical Methane Potential test (BMP) (Angelidaki et al., 2004). During this test, the methane production related to anaerobic biodegradation is measured for at least 30 days (depending on the OR) on a mixture of OR with an anaerobic inoculum under optimal conditions (35°C, addition of metals and nutrients, appropriate substrate : inoculum ratio and bicarbonate buffer). At the end of the incubation period, the cumulated production is assumed to be the methane potential production of the OR. A similar biological incubation test is widely used to assess the aerobic organic carbon degradation of OR during soil incubation under controlled conditions of moisture and temperature, over at least 91 days (Lashermes et al., 2009). A number of authors have applied a chemical characterisation of OR for BMP and soil carbon mineralization prediction. For aerobic biodegradation, an indicator of residual organic carbon (IROC) has been developed by Lashermes et al. (2009) and has been standardized as mentioned by Peltre et al. (2011). It was based on fiber fractionation (Van Soest, 1963) and on the organic carbon fraction mineralized after 3 days of incubation. It has been applied to predict the evolution of soil OM after repeated applications of various organic residues in long-term field experiments (Peltre et al., 2012). Van Soest fractionation has also been successfully used for BMP prediction of lignocellulosic residues (Buffiere et al., 2006; Gunaseelaan et al., 2007 and 2009; Thomsen et al., 2014; Kafle et al., 2016). However, it cannot be applicable to all OR as demonstrated by Mottet et al., (2010) who applied a Van Soest fractionation to wastewater treatment sludge for BMP prediction. Bayard et al. (2015) applied similar approach on agricultural and forest residues. Although the BMP and some

lignocellulosic characterics of substrates were correlated, its prediction was low. Furthermore, some of the results obtained concerning the impact of cellulose and hemicellulose on BMP were contradictory (Thomsen et al., 2014). In the case of OR containing a mixture of all the biochemical groups and a low fiber content, the first "Soluble" Van Soest fraction represented more than 80% of VS (Mottet et al., 2010; Jimenez et al., 2015) and gathered a large diversity of molecules that could not characterize the biodegradability. According to Lashermes et al. (2009), Van Soest fractionation was not sufficient for the prediction of the IROC on a large panel of residues. The addition of the organic carbon fraction mineralized after 3 days of incubation can be associated to the readily biodegradable fraction which is generally high in animal waste excluding litter and wastewater sludge.

Another common methodology for predicting BMP and carbon mineralisation on soil is Near InfraRed Spectroscopy (NIRS). The use of the NIRS to quantify BMP (Lesteur et al., 2011; Godin et al., 2015; Fitamo et al., 2017) has been successfully investigated, and subsequently led to its commercial use at a later stage. A similar study was applied to the IROC (Peltre et al., 2011). A few outliers were observed and mainly associated to wastewater sludge, liquid manure and organo-mineral fertilisers. However, the NIRS method provides limited qualitative information about chemical composition of OR due to overlapping overtones and combination bands (Bekiaris et al., 2015b). This tool, therefore, does not facilitate a more mechanistic interpretation.

More recently, a Fourier transform mid-infrared photoacoustic spectroscopy technique (FTIR-PAS) was applied to predict BMP on plant biomass (Bekiaris et al., 2015a) and the mineralisable fraction of carbon in soils from several OR (Bekiaris et al., 2015b). This technique allowed for (i) the influence of sample particle size and absorption of dark and opaque samples to be ignored and (ii) for more information to be produced on the composition of OM than with NIRS (Bekiaris et al., 2015 a and b). In these two different

studies, although the authors demonstrated the impact of the composition of OR on biodegradability prediction, they did not confront the results from both studies. Nonetheless, differences and similarities did appear, as for example the ability of certain carboxylic acids to produce both a negative effect on BMP on one hand, and a positive impact on mineralisable soil carbon.

Few studies have dealt with anaerobic versus aerobic biodegradability correlations (Bayard et al., 2015; Maynaud et al., 2017). However, no studies have yet focussed on the impact that OM characterisation may have on both biodegradation pathways, and on the differences and similarities between these impacts, in particular for BMP and soil incubation tests. Despite the fact that some authors applied similar characterization tools for BMP test predictions in one hand and soil carbon mineralization test on another hand, not a single study has yet addressed the simultaneous prediction of both potentials.

Moreover, biodegradability of OR not only depends on the quantity of OM but it also relies on the accessibility and complexity of the OM (Jimenez et al., 2015). Given the complex organisation of certain organic residues, the term "accessibility" defines the potential access to the molecules by microorganisms responsible for their degradation. It can depend on the physical characteristics of the OR (particle size, porosity of the OR), on the distribution of the organic fraction within the OR matrices in relation with the process duration, the hydrolytic activity or the applied pre-treatment. Molecules with a weight below 1000 Da can pass through the cell wall (Aquino, et al., 2008). Finally, once the OM becomes accessible, it can be more or less easily biodegradable by microorganisms, depending on its chemical nature or complexity. Cardeña et al. (2017) demonstrated that ozonation enhanced the accessibility of certain microalgae which have structural and physical barrier to biodegradation, allowing, at the end, their biodegradability. Furthermore, both complexity and accessibility have not yet been considered together in any existing indicator. The chemical nature of extracted organic

fractions have been observed to vary during treatments such as composting, which thus explains the change in biodegradability of given organic fractions (Peltre et al., 2012). One study did successfully predict the biodegradability of sewage sludge under anaerobic conditions by considering both accessibility and complexity (Jimenez et al., 2014). The methodology developed was based on the combination of a sequential chemical extraction to assess accessibility and fluorescence spectroscopy to assess the complexity of each extracted organic fraction. Since, this sequential extraction methodology has been updated for applications over a wider spectrum of OR (Jimenez et al., 2015). Maynaud et al. (2017) used this combined approach in order to characterize solid and composted digestates. The authors also performed anaerobic and aerobic tests without inoculum in order to characterize the stability of the studied digestates. One main conclusion based on a statistical study highlighted the strong potential of this methodology to predict digestate biodegradability. According to the present literature review, the improvement of mechanistic knowledge and optimisation of anaerobic digestion valorisation pathways are still limited by the lack of studies dealing with the comparison between aerobic and anaerobic predictions from OM characterisation. The updated methodology (Jimenez et al., 2015) has therefore been applied to predict both anaerobic biodegradability thanks to BMP measurements and aerobic carbon biodegradation in soil. The main objectives of this study are (i) to predict both energy production and soil organic carbon potential using a combination of accessibility and complexity characterisation performed on the same OR, (ii) to use the OM characterization to analyse the similarities and differences between anaerobic biodegradability and soil organic carbon mineralization and thus (iii) to identify OM characterization actuators in order to optimize anaerobic digestion for methane production and organic amendments quality requirements.

Material and methods

To assess the accessibility (i.e. sequential chemical extractions) and complexity (i.e. fluorescence spectroscopy) of OM, eighty two OR were characterised with the recently developed methodology. They were also incubated under anaerobic conditions during BMP and 44 of them were incubated under aerobic conditions with crop soil. These incubation tests led to the evaluation of the methane potential and potential residual organic carbon. Statistical relations were investigated between the characterisation and the degradation kinetics parameters.

a. Sample set

Eighty two samples were used for anaerobic incubation. The samples covered a large range of types of OM. Indeed, the OR considered were: 2 biowastes (e.g. food waste); 3 Fermentable Fractions of Municipal Solid Wastes (FFMSW) ; 3 green wastes, 4 initial composting mixtures (2 sludge-green waste mixtures and 2 digested sludge-green waste mixtures), 22 composts (9 from sludge, 6 from digested sludge, 2 from biowaste digestates, 2 from FFMSW digestates and 3 from manure digestates),1 potting mix (e.g. commercial medium for plant growth), 3 types of manure, 6 secondary wastewater sludge and 38 digestates obtained after anaerobic digestion of sludge (11), manure (13), territorial waste mixtures (8), FFMSW (3) and crop residues (3).

From these 82 samples used for anaerobic incubation, 44 samples were used for aerobic incubation tests: these include 21 digestates (5 from sludge, 7 from manure, 3 from territorial wastes, 3 from crop residues and 3 from FFMSW), 8 composts (4 from sludge digestates, 1 from manure digestate and 3 from sludge), 4 urban wastewater treatment sludge, 3 FFMSW, 3 manures, 2 green wastes, 2 initial composting mixtures (digested sludge and green waste mixtures) and 1 potting mix. In addition, 3 samples were used for aerobic incubation only (i.e. 1 soil, 1 territorial waste, 1 crop residue digestate).

b. Physico-chemical characterization

The Dried Solids (DS) were analysed by gravimetry after 24h at 105°C and the Volatile Solids (VS) were analysed by gravimetry after 2h at 550°C. The VS was obtained by subtraction of the mineral matter obtained after 550°C and of the DS.

The Chemical Oxygen Demand (COD) was measured in duplicate using Aqualytic® kits (0-1500 mg $O_2.L^{-1}$). Units were in $mgO_2.L^{-1}$ for the liquid phases and $mgO_2.gDS^{-1}$ for the solid and total phases. Indeed, the analysis of the freeze-dried and grinded (1mm) sample was performed on a solution of $1gDS.L^{-1}$.

The Total Organic Carbon (TOC) was performed on grinded freeze-dried samples by catalytic combustion at 900°C using a TOC-V-SSM-500A Shimadzu device. The units were in $mgC.gDS^{-1}$.

c. Chemical fractionation

The application of a recently published method (Jimenez et al., 2015) was extended to a wider range of organic residues. This methodology, based on chemical extractions that indicate the chemical accessibility of organic residues, is a modified version of the protocol in (Jimenez et al., 2014). The main modification consists in the addition of a sulfuric acid extraction step from the Van Soest protocol (Van Soest, 1963) for determining the carbohydrates (i.e. cellulose and hemicellulose). Sequential extractions (30 mL of each extractant) were performed on 0.5-1 g of freeze-dried and grinded (1mm) samples. Each extraction stage was followed by a centrifugation step (18600g, 20 minutes, 4°C) and a 0.45µm filtration step. The resulting fractions were:

(1) Extractable Soluble from Particulate Organic Matter (SPOM) (milli-Q water solution containing 10 mM of $CaCl_2$, 15 min × 4, 30°C, 300 rpm), which represents the most accessible fraction and essentially contains water-soluble proteins and sugars.

198 (2) Readily Extractable Organic Matter (REOM) (NaOH 10 mM, 15 min × 4, 30°C, 300
199 rpm), which represents an accessible fraction of mainly proteins and lipids.

200 (3) Slowly Extractable Organic Matter (SEOM) (NaOH 0.1 M, 4 h × 4, 30°C, 300 rpm),
201 which mainly contains humic-like and fulvic-like acids and complex proteins (i.e. glycolated
202 proteins) as well as certain lignocellulosic compounds which can be soluble under strongly
203 basic conditions.

204 (4) Poorly Extractable Organic Matter (PEOM) (25 mL H_2SO_4, 72%, 3 h × 2, 30°C, 300
205 rpm), which targets holocelluloses (i.e. hemicellulose and cellulose).

206 (5) Non-Extractable Organic Matter (NEOM), which contains lignin-like compounds and
207 non-extractable humic-like acids (i.e. humin).

208 Results are expressed in COD ($gO_2.gDS^{-1}$).

209 d. 3D fluorescence spectroscopy

210 The acquisition of 3D fluorescence spectra was performed on the extracted fractions, allowing
211 for OM complexity to be qualified (Jimenez et al., 2014 and 2015). The complexity of OM
212 could be assessed through the proportions of fluorescence volumes of the most recalcitrant
213 molecules such as humic-like substances, fulvic-like acids, lipofuscin-like (i.e. a
214 lignocellulosic marker) as well as amino acids and less complex molecules (Muller et al.,
215 2014).

216 The fluorescence spectrometer was a Perkin Elmer LS55. Excitation wavelengths varied
217 between 200 and 600 nm with a 10 nm incrementation. Based on the work of Jimenez et al.
218 (2014) and Muller et al. (2014), spectra were decomposed into seven zones, each associated to
219 a particular biochemical family. The simplest molecules (i.e. amino acid fluorescence) are
220 located in zones 1 to 3 while the more complex molecules are located in zones 4 to 7. The

proportion of fluorescence for a given zone "i" $P_f(i)$ was calculated using the fluorescence zone volumes V_f (i) according to Equations 1 and 2:

$$V_f(i)(U.A./mg.COD.L^{-1}) = \frac{V_{f\_raw}(i)}{COD_{sample}} \times 1 \Big/ \frac{S(i)}{\sum_{i=1}^{7} S(i)} \quad \text{Equation 1}$$

$$P_f(i)(\%) = \frac{V_f(i)}{\sum_{i=1}^{7} V_f(i)} \times 100 \quad \text{Equation 2}$$

with:

$V_f(i)$ (U.A. $mg.O_2.L^{-1}$): the normalized volume of the zone i,

$V_{f\_raw}(i)$ (U.A. $mg.O_2.L^{-1}$): the raw volume of the zone i, COD_{sample} (mg $O_2.L^{-1}$) : the COD concentration of the sample,

$S(i)$ (nm^2): the area of a zone i,

$P_f(i)$ (%) : the fluorescence proportion of a zone i.

e. Biodegradation tests

Biochemical Methane Production (BMP) tests

The BMP values were obtained using an innovative and rapid FlashBMP® method developed by Ondalys (Lesteur et al., 2011) and commercialized by Buchi. This method is based on Near InfraRed Spectroscopy (NIRS) applied to more than 600 types of OR (agro-industrial waste, green waste, energy crops, municipal solid waste, sludge and digestates) for which classical BMP tests were performed according to Angelidaki et al. (2004). Samples were freeze-dried and grinded to 1 mm before NIRS acquisition. Spectra were measured using a BUCHI NIRFlex N-500 (Buchi, Switzerland), with add-on vials, allowing for immediate analysis. Results are expressed in mL $CH_4.gVS^{-1}$.

242 **Soil incubation tests**

243 Freeze-dried and 1 mm grinded organic residues were incubated with 100 g of cropped soil,
244 (substrate: soil ratio between 0.002 and 0.01 g TOC product/g TOC dried soils) in
245 hermetically closed bottles (1L) during, at least 91 days under moisture and temperature
246 controlled conditions. For unlimited microbial growth conditions, mineral nitrogen was
247 added. Incubation of the soil without the addition of OR was also performed so as to take into
248 account the mineralization of soil organic carbon. The soil was provided by a control
249 treatment sampled during the QualiAgro field experiment (Ile de France, France) which began
250 in 1998 to study the effects of various organic fertilizers (Houot et al., 2002). Soil moisture
251 content was adjusted to a water content equivalent to 75 to 100% of the soil water holding
252 capacity. Carbon mineralization was monitored using a 20 mL trap solution of NaOH (0.5N)
253 for CO_2 which was periodically replaced during the incubations. The CO_2 was analysed by
254 titration of the remaining NaOH with HCl (1 M) or measured by gas chromatography (Perkin
255 Elmer CLARUS 480) following the acidification of the NaOH trap solution with HCl (1M) in
256 hermetic jars. Cumulated mineralized carbon was obtained as a percentage of initial TOC.
257 The mineralised TOC was identified as C_bio and results were expressed in $gC.gC^{-1}$.
258
259 **Statistical analysis**

260 In order to determine the correlations between biodegradability and indicators from OM
261 characterization, principal component analysis (PCA), hierarchical clustering analysis (HCA)
262 and partial least square (PLS) regressions were performed using SIMCA software from
263 UMETRICS.
264 In its simplest form, a linear model specifies the (linear) relationship between a dependent
265 (response) variable *Y*, and a set of X predictor variables, the *X*'s. The dataset was split into two
266 subsets: one for the calibration step (3/4 of the data) and one for the validation step (1/4 of the

data). Indeed, for the validation of the model set up to be robust, the dataset used for calibration should not be the same as the dataset used for validation. In order to cover and validate the whole range of data values, (i) the dataset was sorted by increasing the Y-variable values and (ii) one out of four data points were selected for the validation step, as in Jimenez et al. (2014).

The parameters from the PLS models used to assess model robustness are the following:

- Correlation coefficient R^2
- Root Mean Square Error (RMSE), used as an accuracy measurement of differences between predicted values and measured model values.
- RMSEP is the RMSE for the prediction of validation samples
- Q^2: percentage of variation of Y predicted by the PLS model according to cross-validation. This parameter indicates how well the model predicts the data. A large Q^2 (>0.5) indicates good predictivity. Moreover, it is a compromise between root mean square error and R^2. Q^2 also represents the criteria for the choice of the component number. In others words, when the cumulated Q^2 reaches its maximum value, the corresponding component is selected.

Results and discussion

- Anaerobic biodegradability prediction

Based on the methodology of Jimenez et al. (2015), the 82 samples were first characterized (fractionation and 3D fluorescence) and BMP measurements were performed. Samples covered a large range of OM quality. Indeed, BMP values ranged from 31 to 394 Nml $CH_4.gVS^{-1}$. The characterization data (X variables) were compared to the BMP data (Y variable).

On one hand, PLS regression was applied using 33 explicative variables (X variables) composed of $P_f(i)$ (i= 1 to 7), the fluorescence percentage of each zone and the COD percentage of each fraction (e.g. SPOM, REOM, SEOM, PEOM, NEOM). This model is identified as Model n°1. As suggested by Thomsen et al. (2014), the sum of the five fractions was equal to 1. The residual non extactible OM (e.g. NEOM) was included in the PLS to remove misinterpretations of regression coefficients weight due to relative nature of compositional data. On another hand, Model n°2 was built using 5 explicative variables composed of the five fractions. Out of the 82 observations, 56 were used to set up a first calibration for both models. The validation samples were selected according to the increasing BMP values. One sample out of four was used for validation (i.e. a total of 26 samples for validation).

Table 1 presents the quality parameters of the evaluated PLS models. Results clearly point out that Model n°1 has the best prediction potential (i.e. Q^2 =0.689 for Model 1 and 0.250 for model 2), highest correlation coefficient (i.e. R^2 = 0.818 for Model 1 and 0.410 for Model 2) and a low RMSE value. The most significant and positive variables in Model 2 were the accessible SPOM and REOM fractions. However, the lack of description in the quality fraction did not allow for certain OR and OR digestates to be distinguished. Indeed, although some digestates had high SPOM, they also contained non-biodegradable material that was not considered by fractionation only. Consequently Model n°1 was selected. The quality of this model is illustrated in Figure 1. The distribution of experimental Y-variables versus predicted Y-variables was similar to the line of perfect fit (y=x) for BMP values. This result points to the closeness between the model and experimental data. Three components were sufficient enough to explain 61% of the X-variables (i.e. characterisation data) and 82% of the Y-variables (i.e. BMP data). The Root Mean Square Error (RMSE) was 34 Nml $CH_4.gVS^{-1}$ and the Root Mean Square Error of Prediction (RMSEP) was 66 Nml $CH_4.gVS^{-1}$. These results could allow for an accurate prediction of the methane potential, with values ranging between 31 and 394 mL $CH_4.gVS^{-1}$.

According to the PLS scores and loading results (figures 2a, 2b, 2c), the BMP values were positively correlated to the fluorescence zones 1 to 3 (i.e. protein-like compounds) and to the SPOM fraction (i.e. the most accessible fraction). They were negatively correlated to the SEOM fraction and to the complex fluorescence zones (4 to 7) from all fractions. Therefore, the first component was essentially characterised by the complexity of the OR (figure 2b), the second component was characterised by the SPOM fraction, while the third one was negatively correlated to the SEOM (figure 2c) and positively correlated to the SPOM. Finally, these second and third components were rather related to the OR accessibility.

Table 2 highlights the impact of the most significant X-variables affecting the prediction of Y-variables derived from the calculation of the weight of each variable. Positive and significant variables comprised the SPOM fraction and the fluorescence zone 3 related to protein-like molecules from all organic fractions. Bayard et al. (2015) observed similar results with good correlations between BMP values and water soluble COD applied on biowastes, residual municipal solid waste and their digestates. Moreover, with the use of principal component analysis, Maynaud et al. (2017), pointed out that SPOM and fluorescence zones 1 to 3 were correlated with BMP values of digestates.

Conversely, the negative and significant variables were associated to the SEOM fraction (i.e. the moderately accessible fraction) and to the complex fluorescence zones 4 and 6 from REOM, related to complex molecules such as humic-like and fulvic-like acids. Bayard et al. (2015) also demonstrated that the humic substance index (i.e. obtained using a similar NaOH extraction as for SEOM followed by an acid precipitation to recover fulvic acids) had a negative impact on BMP values of biowastes and their digestates.

This result implies that the combination of accessibility and fluorescence-derived complexity could allow for the prediction of organic residue biodegradability under anaerobic conditions.

A Hierarchical Clustering Analysis (HCA) was performed simultaneously with the PLS. This analysis highlighted 6 observation groups, as illustrated by the scores plot in Figure 2a. According to this analysis, the highest BMP values are positively correlated to the fluorescence zones 1 to 3 (i.e. protein-like) and to the SPOM fraction (i.e. the most accessible fraction). They are associated with Group n°4 samples that are mainly composed of sludge, biowaste and vegetables (e.g. potatoes). Conversely, the lowest BMP values are negatively correlated to the complex fluorescence zones (4 to 7). They are associated with Groups n°1 and 2, according to their content in accessible fractions and are essentially composed of well stabilized manure/territorial digestates and biowaste/FFMSW composts, digestate composts and potting mix. These results are consistent: the more the OR are complex and poorly accessible, the lower the biodegradability. In terms of BMP, intermediate groups could be formed: Group 5 mainly contains digestates with high SEOM fractions (sludge and manure) while Group 6 is mainly composed of FFMSW, manure and lignocellulose-like compounds with higher BMP than the digestate groups. Group 3, comprising two samples (sludge compost and initial mixture between green waste and digestate sludge), is close to the rich SEOM Group n°5. Jimenez et al. (2015) demonstrated that this characterisation, based on the two concepts of accessibility and complexity, could help to categorise organic residues. Indeed, this study confirms that the anaerobic biodegradability of a large panel of OR can be concurrently categorized and predicted thanks to this methodology.

- Prediction of organic carbon biodegradability

As for BMP prediction, the correlation between OR characteristics and aerobic mineralisation results was investigated thanks to a PLS regression using the same 33 explicative variables as for BMP (i.e. Model n°3), and using the 5 fractions (i.e. Model n°4). A first calibration model was set-up for 31 observations and 16 samples were used for validation, in the same manner as for BMP prediction.

The Y-variable was the aerobic carbon biodegradability (C_bio) fraction of TOC measured during soil incubation tests. The dataset was obtained from a huge diversity of organic residues with a high range of biodegradability (from 7 to 46 % TOC).

From table 1, results implied that the Model n°3 had the best prediction quality (Q^2 =0.745 for Model 3 and 0.456 for Model 4), a high correlation coefficient (R^2 = 0.845 for Model 3 and 0.632 for Model 4) and a low RMSE value. The most significant variables in Model 4 include the accessible fraction REOM (positively correlated) and NEOM (negatively correlated). Despite the promising prediction potential of Model 4, the poor quality description of the fraction did not allow for certain OR (i.e. sludge and manure) and their respective digestates to be distinguished as for BMP prediction. Consequently, Model n°3 was selected for C_bio prediction.

As illustrated by Figure 3, the plot of measured values versus predicted values points to the ability of this model to predict biodegradable organic carbon (i.e. closest to the perfect fit line). Two components were required to explain 53% of X-variables. The RMSE accounted for 5.1% of TOC while the RMSEP accounted for 7.3% of TOC.

The scores and loadings of the PLS model are plotted in Figure 4. According to this plot, the first component is defined by the fluorescence-derived complexity, while the second component is defined by the accessibility axis. Indeed, as for BMP prediction, C_bio was positively impacted by the most accessible fraction SPOM and by the simplest fluorescence zones represented by the protein-like in SPOM and REOM. Conversely, the least accessible fraction NEOM was negatively related to the organic carbon mineralisation. This is contrary to the BMP model for which NEOM was not significant. However, again as for BMP prediction, the most complex fluorescence zones of the 3D fluorescence spectra of SPOM and REOM represented by humic-like, fulvic-like acids and lignocellulose-like molecules also had a strong negative impact on carbon mineralization.

The HCA comprised 6 groups of observations, as presented by the scores in Figure 4. Group n°1 was mainly composed of sludge and sludge digestate and characterised by the highest C_bio values. Sludge samples were characterised by a large REOM fraction and the simplest fluorescence zones from REOM and SPOM while, similarly to BMP prediction, sludge digestates were rather characterised by a large SEOM fraction. Nevertheless, sludge digestate was part of a separate group in BMP prediction and not part of the same group as for C_bio (i.e. the most biodegradable samples). This confirms that, depending on their OM characteristics, aerobic and anaerobic biodegradation potentials cannot be similar for all substrates. Some digestates could be more biodegradable under aerobic soil incubation than in anaerobic BMP tests. In contrast, similarly to the soil and to the potting mix, Group n°4 contained the poorest biodegradable OR. They were characterised by a high NEOM fraction and complex fractions of SPOM. This latter characteristic was also observed in the group characterised by low BMP values (i.e. potting mix, close to stabilized composts).

Other groups were categorised as intermediate according to their nature. Indeed, Group n°2 was composed of FFMSW, initial composting mixtures of green waste and sludge, and vegetables, which represented a mixture of compounds that were rich in either protein-like fractions, or lignocellulose-like fractions. Group n°3 was composed of digestates from territorial OR or from crop residues. They were associated to a large PEOM fraction and to complex fluorescence zones in this fraction. Groups n° 5 and 6 contained manure digestates, wooden structures and composts in the lower part (rather associated with a high NEOM fraction and manure, i.e. a lignin-like content), and FFMSW digestates and green waste in the upper part (mainly associated with a large PEOM fraction, i.e. a cellulose and hemicellulose content). All these samples were also characterised by complex fluorescence zones from PEOM fraction.

As for the BMP prediction model, Table 2 highlights the impact of the most significant X-variables on the Y-variable prediction and confirms all the previous observations. Concerning the prediction of C_bio, the most significant positive variables were PEOM, SPOM, REOM and SEOM with fluorescence zones 1 to 3 (i.e. protein-like) from SPOM and REOM and fluorescence zones 5 and 6 from SEOM. The most significant negative variables were NEOM and certain complex fluorescence zones from SPOM and REOM.

- Anaerobic versus soil aerobic biodegradability: impact of OM quality

In Table 2, the weight of the model variables revealed existing similarities and differences between anaerobic biodegradability and aerobic soil incubation. Both types of biodegradability were positively impacted by the SPOM fraction and the simplest fluorescence zones.

However, contrary to the BMP value prediction, SEOM showed a positive influence on aerobic biodegradability, namely its fluorescence zones 5 and 6. Indeed, the SEOM fraction and its fluorescence zone 6 were related to humic-like substances, which are mostly found in digestates. This fraction and the associated molecules which tend to be recalcitrant under anaerobic conditions showed a positive influence in soil incubation conditions. This is consistent with the nature of the molecules which can affect the production of humus. Consequently, combining anaerobic digestion (by optimising the anaerobic recalcitrant SEOM-like production) with the digestate landspreading could entail a higher organic fertilizing value. Digestate characterisation results from a statistical analysis of nuclear magnetic resonance data (Tambone et al., 2010), showed how anaerobic digestion is capable of preserving recalcitrant molecules (i.e. lignin-like, steroids or complex lipids) known as humus precursors.

The PEOM and NEOM fractions presented a significant impact on C_bio predictions while these same fractions had no significant effect on BMP. This is consistent with the results obtained by Lashermes et al. (2009) involving a positive impact of the cellulose fraction and a negative impact of the lignin fraction, both being obtained by Van Soest fractionation.

Moreover, even though the most biodegradable samples contain a large fraction of SPOM and a high content of protein-like fluorescence zones, aerobic biodegradation appears to be further advanced than anaerobic biodegradation. In both cases, the characterisation protocol was sufficiently detailed for both mineralization potentials to be predicted. In addition, the differences between both pathways could lead to a balance between methane and organic amendment production. For example, sludge digestates and certain manure digestates that are rich in the moderately accessible SEOM fraction, presented high C_bio values. These are more appropriate for fertility purposes while NEOM-rich digestate composts and complex molecules with low C_bio values should be more appropriate for long-term organic amendment.

Characterisation data used in common for both models (e.g. BMP and aerobic soil biodegradation) have been used to investigate the correlations between the BMP and C_bio variables. Figure 5 illustrates the resulting correlation. C_bio and BMP were positively and significantly correlated, with a Pearson coefficient of R= 0.787. In addition, a linear regression between BMP and C_bio data was established with the following equation: BMP = 474.98 x C_bio + 15.462, with a correlation coefficient of $R^2 = 0.619$, meaning that only 62% of the samples variance is explained by the linear regression.

In some cases, two samples had similar BMP values but very different and lower C_bio values (for example this could be the case for green waste and sludge; potting mix and territorial digestate). Despite the fact that, in many cases, the biodegradable state of OM is

462 generally stable under both anaerobic and aerobic conditions, the structural and functional
463 diversity of soil microbial communities tend to enhance OM degradation under aerobic
464 conditions.

465 In the literature, many authors have tried to correlate BMP test values with rapid aerobic test
466 results (i.e. respirometry). They observed reliable and positive correlations between these two
467 tests that were performed on the same types of organic residues. Cossu et al. (2008) and
468 Scaglia et al., (2010) found such correlations on MSW landfill (R^2>0.80 and 0.89
469 respectively); positive correlations between BMP and Biological Oxygen Demand tests were
470 also observed by Liu et al. (2015) with agricultural and forest residues (R^2>0.94) and Bayard
471 et al. (2015) with biowaste and digested biowaste (R^2 = 0.81). Maynaud et al. (2017) also
472 demonstrated a good correlation between anaerobic biodegradability and aerobic
473 biodegradability obtained on solid and composted digestates without inoculum addition (R^2 =
474 0.8). In the present work, aerobic biodegradability is achieved by soil incubation. This main
475 difference with other studies reported from the literature suggests that aerobic inoculum from
476 soil was completely different in terms of diversity and biodegradation ability.

477 As previously mentioned, the organic carbon stability and potential efficiency of increasing
478 soil OM were usually estimated with the IROC calculated as a function of the fractions
479 provided by the Van Soest methodology and a 3-day carbon mineralisation test (C3d)
480 (Lashermes et al., 2009). According to the authors, the models built with the Van Soest
481 fractionation variables were not sufficiently robust and accurate to predict the IROC whereas
482 the addition of the C3d favoured a better prediction. The C3d variable was the most
483 significant variable of the IROC model, positively correlated with biodegradable TOC and
484 associated with the most readily biodegradable OR (i.e. sludge, liquid manure, animal wastes
485 without litter). Besides, the soluble fraction used for the IROC calculation is positively
486 correlated to the residual TOC obtained at the end of the incubation (Lashermes et al., 2009).

This soluble fraction is very large for a lot of protein-like OR (i.e. sludge, liquid manure, some animal wastes, digestates) according to Lashermes et al. (2009), Mottet et al. (2010), Peltre et al. (2011), and Jimenez et al. (2015). Despite its accessible chemical feature, this fraction can contain both biodegradable and non-biodegradable molecules (Peltre et al., 2011). Prediction of biodegradable TOC still needs to be improved due to a lack in complexity information. Moreover, in contrast to the fractionation procedure applied in this study, the humic-like fraction was absent in the Van Soest fractionation. Indeed, thanks to the SEOM fraction and 3D fluorescence spectroscopy, it is possible to identify and include humification in organic waste characterisation. According to the type of sample, the SEOM fraction contains mainly complex protein-like molecules or/and humic-like substances (Jimenez et al., 2015). Also, the fluorescence signal of this fraction reveals the degree of complexity which can then be associated to its biodegradability. As PLS models have proved, the SEOM fraction represents a key variable for both soil carbon mineralization and BMP predictions. Humification, being a key process in organic carbon stabilisation, could account for a more efficient capacity in increasing soil organic carbon stocks after spreading. Unlike the IROC indicator, this methodology has the capacity to better take into account the chemical nature of the extracted fractions and their evolution during treatment for the prediction of the potential efficiency of increasing soil organic matter after residue application. The same OM fractionation combined with 3D-fluorescence spectroscopy has enabled the prediction of both methane production and mineralisable soil carbon: these input variables could be used in future investigations to combine dynamic models of carbon fate in conditions ranging from anaerobic digestion to soils. Results have shown how anaerobic digestion and soil incubation can be complementary regarding OM biodegradability for methane production and OM stability for soil amendment purposes. Depending on the soil constraints, this approach is a first step in optimising the whole processing chain from anaerobic digestion to soils.

Indeed, the main issue for this kind of modelling is the difference between the considered input/output variables of the models (ADM1, Batstone et al., 2002; Garnier et al., 2003; Sole-Mauri et al., 2007; Oudart et al. 2012; Zhang et al. 2012; Denès 2015). The next step should be to use these fractions as common variables in mechanistic models in order to simulate OM accessibility throughout the whole processing chain of OR until soil utilisation.

Conclusions

Chemical accessibility and fluorescence spectroscopy have proved to predict both methane potentials and soil mineralized carbon, implying that the methodology can be used for aerobic and anaerobic decomposition models if plant-wide modelling is considered. Moreover, humic–like acids fraction and its associated fluorescence zone appeared to be recalcitrant for BMP but positive for C_bio prediction. These differences could be used as actuators since these recalcitrant molecules can be precursors of humus production, thus promoting the choice of digestate spreading. It is the first step towards improving the quality control of OR for their valorisation to be most profitable.

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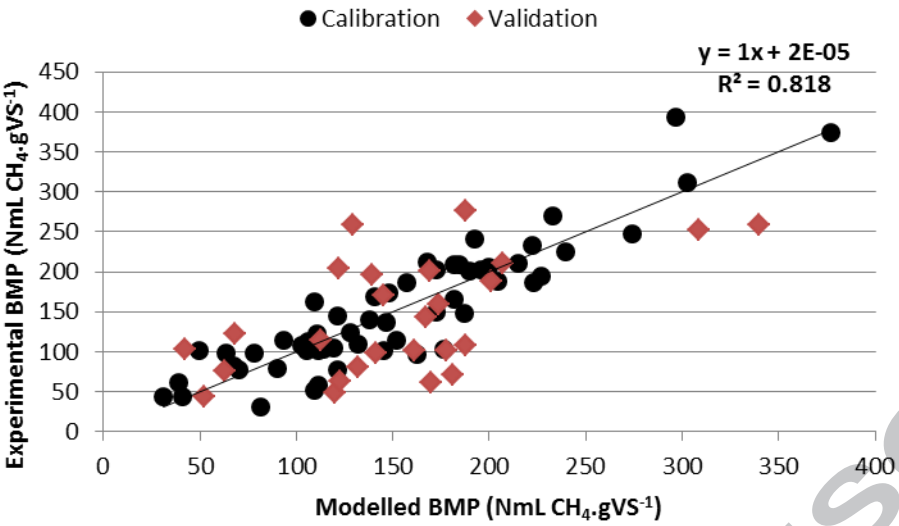

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653 Figure 1: Observed versus predicted BMP value obtained with the PLS model n°1 *(black dots: calibration data and red dots:*

654 *validation data)*

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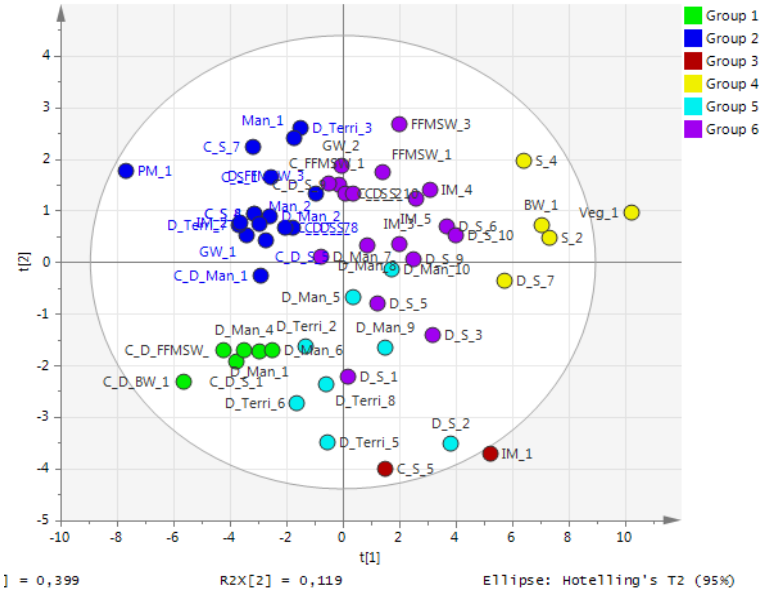
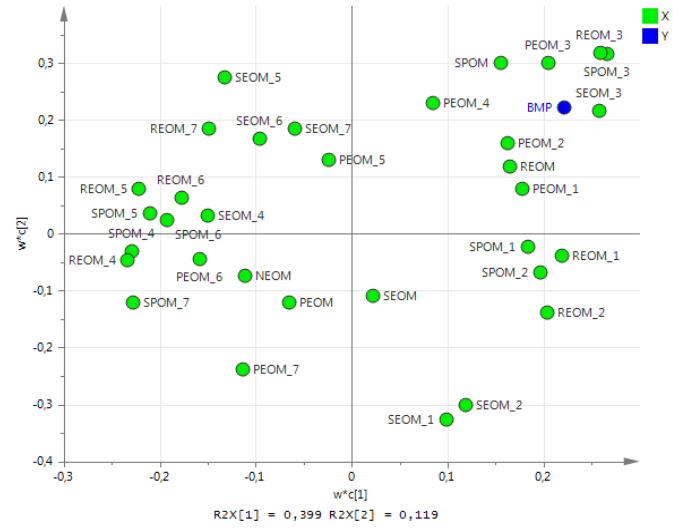
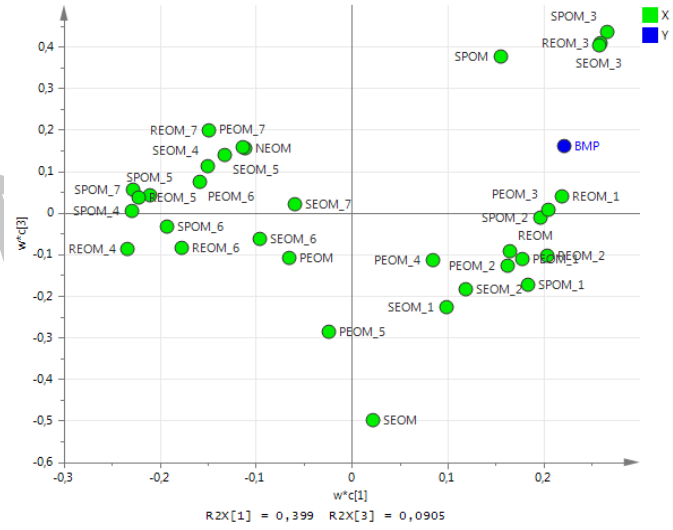


(a)



(b)



(c)

Figure 2: Scores obtained on calibration data and HCA analysis (a) and loadings plots (b) and (c) for BMP prediction model n°1

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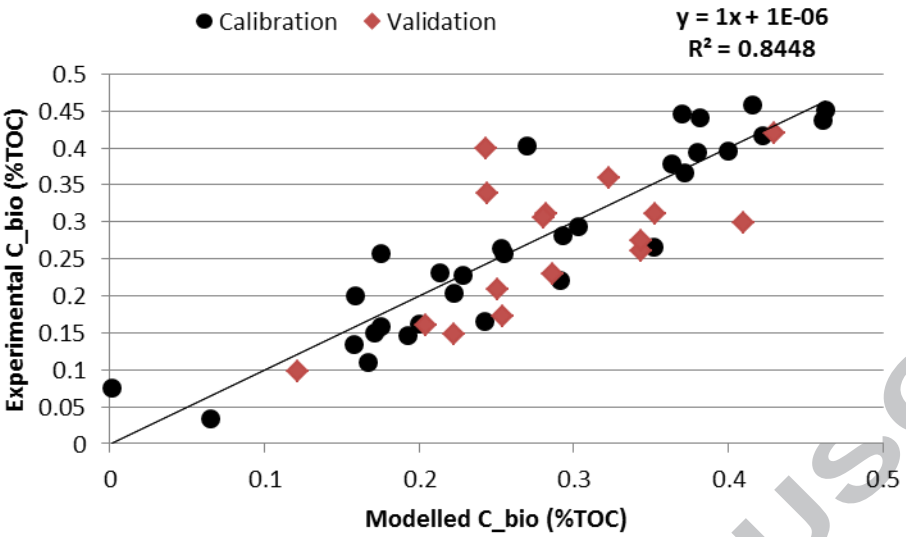

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665 Figure 3: Observed versus predicted Cbio value obtained with the PLS model n°3 (*black dots: calibration data and red dots:*

666 *validation data*)

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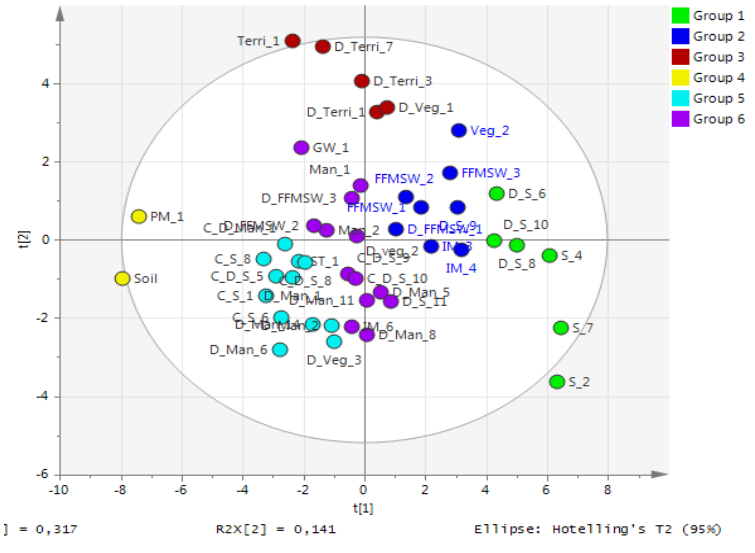
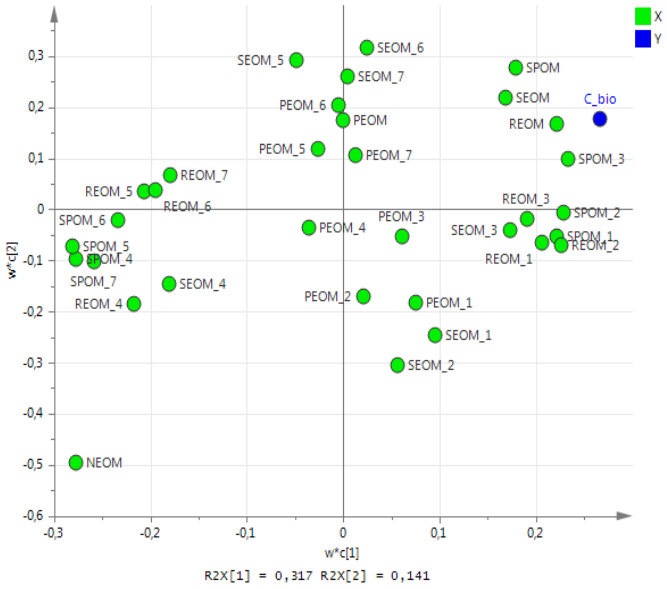


670 (a)



671 (b)

672 Figure 4: Scores (a) and loadings (b) related to the C_{bio} variable prediction applied on all the data

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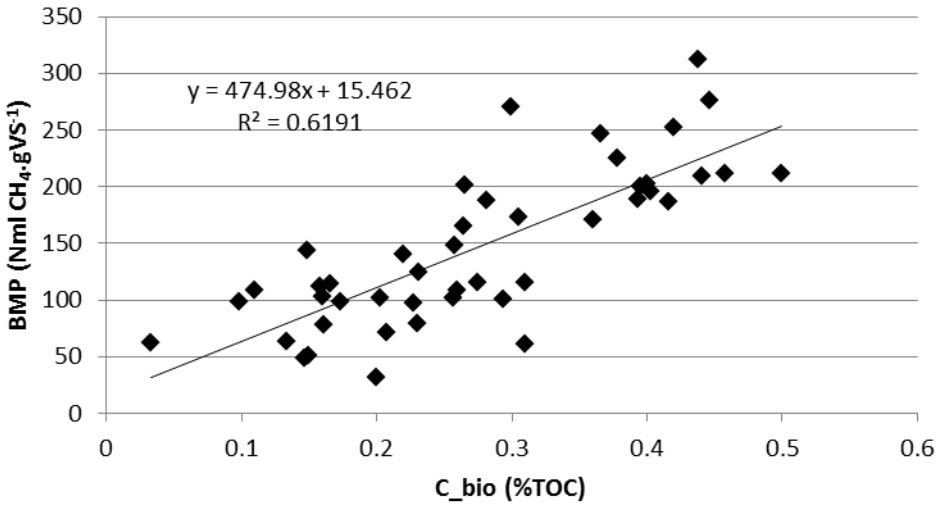

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678 Figure 5: Correlation between BMP experimental values and C_bio experimental values

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680

681 Table 1: Quality parameters of the PLS models for BMP and C_bio prediction

Y-Variables	X-variables	Model	Number of Component	RMSE	RMSEP	R^2X	R^2Y	R^2Y (calibration+validation)	Q^2
BMP ($NmlCH_4.gVS^{-1}$)	33 (fractions and fluorescence data)	1	3	33.950	65.788	0.608	0.818	0.637	0.689
BMP ($NmlCH_4.gVS^{-1}$)	5 (fractions)	2	2	60.542	61.599	0.583	0.41	0.366	0.250
C_bio (%COT)	33 (fractions and fluorescence data)	3	2	0.051	0.073	0.528	0.845	0.738	0.745
C_bio (%COT)	5 (fractions)	4	2	0.078	0.098	0.58	0.632	0.549	0.456

682

683

Table 2: Significant positive and negative impacts of the X-variables on Y-variables prediction obtained from coefficients weight and variable importance for projection plots

X-Variables\Y-Variables	BMP	C_{bio}
SPOM	**+++**	**+**
Fluorescence Zones 1-3	**+++**	**++**
Fluorescence Zones 4-7	0	**- -**
REOM	0	+
Fluorescence Zones 1-3	**+++**	**+**
Fluorescence Zones 4-7	-	**- -**
SEOM	**- -**	+
Fluorescence Zones 1-3	**+++**	0
Fluorescence Zones 4-7	0	+
PEOM	0	**++**
Fluorescence Zones 1-3	++	0
Fluorescence Zones 4-7	0	0
NEOM	0	**---**

Legend:
+: positive impact; -: negative impact
+++/---: extremely sensitive (weight >0.15); ++/--: very sensitive (0.1<weight<0.15); +/-: sensitive (0.05<weight<0.1); 0: not sensitive;

691 **Highlights**

692 •Fractionation and fluorescence data allowed the best prediction of biodegradability.

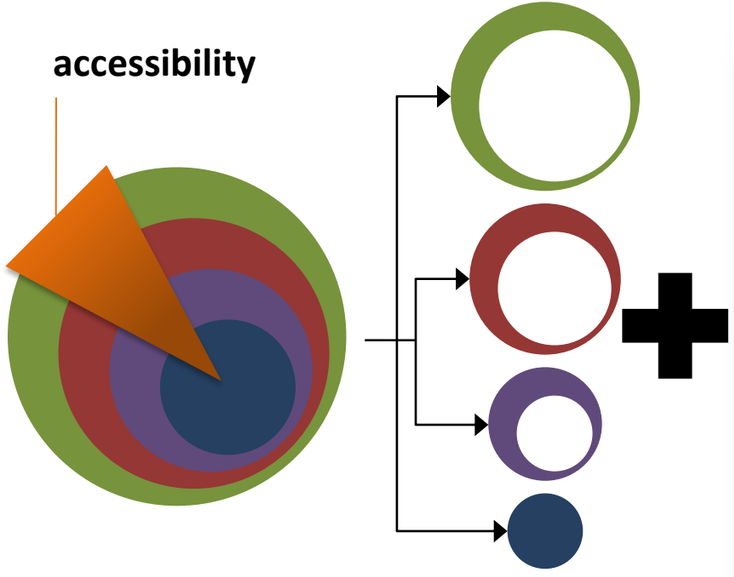
693 •Differences and similarities are observed on the variables impact on predictions.

694 •Humic-like fraction has a negative impact on BMP but not on soil mineralized carbon.

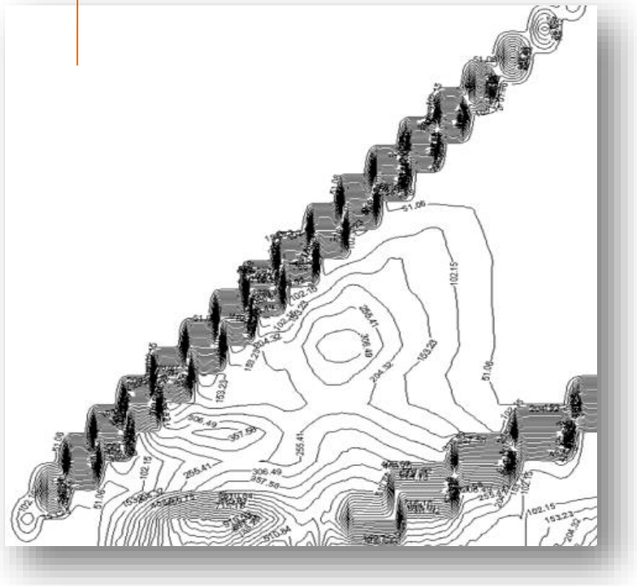
695 •Actuators identification can be found to control valorization ways.

696

accessibility



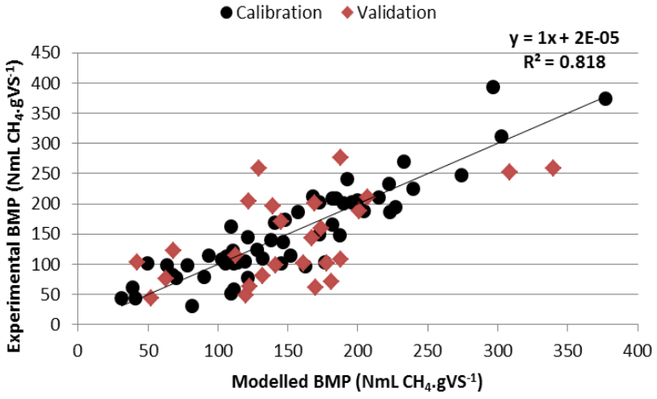
complexity

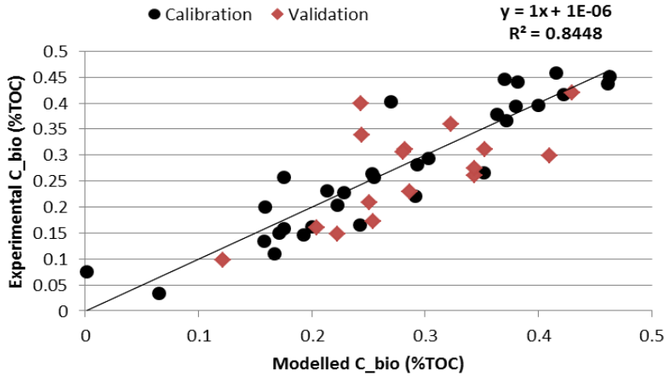


Anaerobic

Aerobic

Methane potential





Soil amendment potential