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Liste des abréviations

AFNOR	Association Française de Normalisation	
AIC	Critère d'information d'Akaike	Akaike information criterion
Al	Aluminium	Aluminium
ANK	Ankarafantsika	Ankarafantsika
BMP	Potentiel Methanogène Biochimique	Biochemical Methane Potential
BOV FUM	Fumier de bovin	Dairy manure
BOV LIS	Lisier de bovin	Dairy slurry
C/N ou C-to-N	Rapport carbone sur azote	carbone to nitrogen ratio
C _{182j} -C _{182d}	Carbone minéralisé à 182 jours	Mineralized carbon at 182 days
C ₂ H ₂	Acétylène	Acetylene
C _{3j} -C _{3d}	Carbone minéralisé à 3 jours	Mineralized carbon at 3 days
CAL	Etalonnage	Calibration
CCM-Co	Compost de fumier de volaille-Co	Compost of chicken manure-Co
CCM-Rep	Compost de fumier de volaille-Repro	Compost of chicken manure-Repro
Cd	Cadmium	Cadmium
CDV SP	Compost de déchets verts	Composted green waste-SP
CDV&B	Compost de déchets verts et de boues	Composted green waste with sewage sludge
CEC	Capacité d'Echange Cationique	Cationic Exchange Capacity
CEE	Communauté Economique Européenne	European Economic Community
CEL	Fraction cellulose	Cellulose-like fraction
Cend-Ash	Cendres	Ashes
CFV	Compost de fumier de volaille	Composted chicken manure
CFW-M	Compost d'ordures ménagères-M	Composted fermentable waste-M
CFW-U	Compost d'ordures ménagères-U	Composted fermentable waste-U
CGW-LP	Compost de déchets verts-LP	Composted green waste-LP
CGW-SP	Compost de déchets verts-SP	Composted green waste-SP
CGWSS	Compost de déchets verts et de boues	Composted green waste with sewage sludge
CH ₄	Méthane	Methane
CoA	Compost de fumier de bovin et de bagasse	Composted dairy manure with bagasse
COD ou DOC	Carbon Organic Dissouts	Dissolved Organic Carbon
COLI	Les Colimaçons	Les Colimaçons
Corg ou orgC	Carbone organique	Organic carbon
CPS Co	Compost de lisier de porc	Compost of pig slurry

CPSc-SJ	Compost de lisier de porc centrifugé	Compost of centrifuged pig slurry
Cr	Chrome	Chromium
Cu	Cuivre	Copper
CV	Coefficient de variation	
DEA	Activité enzymatique dénitrifiante	Denitrifying Enzyme Activity
distance (H)	distance de Mahalanobis	Mahalanobis distance
DM-Bb	Lisier de bovin de Madagascar-Bp	Madagascar Dairy manure-Bb
DM-Bp	Lisier de bovin de Madagascar-Bp	Madagascar Dairy manure-Bp
DM-Run	Lisier de bovin de la Réunion	Réunion Dairy manure
DS-LiB	Lisier de bovin de Madagascar-LiB	Madagascar Dairy slurry-LiB
DS-Run	Lisier de bovin de la Réunion	Réunion Dairy slurry
DV-GW	Déchets verts	Green Waste
ECUM-SCUM	Ecumes de sucrerie	Sugar scum (lime)
ETM-TE	Eléments Trace Métallique	Trace Elements
FSW	Déchets de poissonnerie	Fishery waste
GM-Mdg	Fumier de caprin de Madagascar	Madagascar Goat manure
GM-Run	Fumier de caprin de la Réunion	Réunion Goat manure
GWh	Giga Watt heure	Giga Watt heure
HCEL	fraction hémicellulose	Hemicellulose-like fraction
IS	Force ionique	Ionic Strenght
ISMO ou I_{ROC}	Indice de Stabilité de la Matière Organique	Index of Remaining Organic Carbon
K_2O	Potassium total	Total potassium
k'_L	Constante de mineralisation du compartiment labile	Mineralization rate of the very labile compartment
k_R	Constante de mineralisation du compartiment résistant	Mineralization rate of the resistant compartment
k_{remin}	Constante de re-minéralisation de la fraction N-immobilisée	Re-mineralization rate of the immobilized N-fraction
k_v	Constante de volatilisation de la fraction N	Volatilization rate of N fraction
LIC	Fraction lignine et cutine	Lignin&cutin-like fraction
logCd	Cd apporté par la MOEx	Added Cd from the MOEx
logCr	Cr apporté par la MOEx	Added Cr from the MOEx
logCu	Cu apporté par la MOEx	Added Cu from the MOEx
logNi	Ni apporté par la MOEx	Added Ni from the MOEx
logOM	OM apporté par la MOEx	Added OM from the MOEx
logP	P apporté par la MOEx	Added P from the MOEx
logPb	Pb apporté par la MOEx	Added Pb from the MOEx
logZn	Zn apporté par la MOEx	Added Zn from the MOEx
LPS-A	Terreau d'ordures ménagères-A	Potting soil from landfill-A

LPS-I	Terreau d'ordures ménagères-I	Potting soil from landfill-I
LPS-T	Terreau d'ordures ménagères-T	Potting soil from landfill-T
LZN	Lazaina	Lazaina
MARE	La Mare	La Mare
MB ou w.w.	Matière Brute	Wet weight
Méthode PLS - PLS method	Méthode des moindres carrés partiels	Partial Least Square Method
MJ	Méga joules	Mega joules
MLR	Regression linéaire multiple	Multiple Linear Regression
MO - OM	Matière Organique	Organic Matter
MOEx-EOM	Matières Organiques Exogènes	Exogeneous Organic Matter
MOS-SOM	Matières Organiques du Sol	soil organic matter
MS ou dw ou dm	Matières sèches	dry weight ou dry matter
MSC		Multiplicative Scatter Correction
MV	Matière Volatile	Volatile Matter
N ₂	Diazote	Dinitrogen
N ₂ O	Oxyde nitreux	Nitrous oxide
NH ₃	Ammoniac	Ammoniac
NH ₄ ⁺	Ammonium	Ammonium
Ni	Nickel	Nickel
NO	Oxyde nitrique	Nitric oxide
NO ₂ ⁻	Nitrite	Nitrite
NO ₃ ⁻	Nitrate	Nitrate
Norg ou orgN	Azote organique	Organic nitrogen
NPK	Engrais mineral	Mineral fertilizer
O ₂	Oxygène	Oxygen
OCDE - OECD	Organisation de coopération et de développement économiques	Organization for Economic Cooperation and Development
OMW	Déchets d'huilerie	Oil mill waste
out	Outlier	Outlier
P ₂ O ₅	Phosphore total	Total phosphorus
Pb	Plomb	Lead
PC	Corrélations de la bibliographies	published correlations
pCd	Cd libre dans la solution du sol	Extractable or free Cd in soil solution
PCI-LHV	pouvoir calorifique inférieur	Lower heating value
pCr	Cr libre dans la solution du sol	Extractable or free Cr in soil solution
PCS-HHV	Pouvoir calorifique supérieur	Higher heating value
pCu	Cu libre dans la solution du sol	Extractable or free Cu in soil solution
PID-P	Fientes de volaille - P	Poultry droppings -P

PID-V	Fientes de volaille - V	Poultry droppings -V
P _{im}	Fraction immobilisée de N transformé de la MOEx	Fraction of N-transformed EOM which is immobilized
PIM-Av	Fumier de volaille - Av	Chicken manure - Av
PIM-Pon	Fumier de volaille - Pon	Chicken manure - Pon
P' _L	Taille du compartiment labile	Labile compartment size
PM	Fumier de volaille	poultry manure
PM-Mdg	Fumier de porc de Madagascar	Madagascar Pig manure
pNi	Ni libre dans la solution du sol	Extractable or free Ni in soil solution
pPb	Pb libre dans la solution du sol	Extractable or free Pb in soil solution
P _R	Taille du compartiment résistant	Resistant compartment size
PRC LIS	Lisier de porcin	Pig slurry
P _S	Taille du compartiment stable	Stable compartment size
PSc-SJ	Lisier de porc centrifugé - SJ	Centrifuged pig slurry
PS-LiP	Lisier de porc - Lip	Pig slurry
pZn	Zn libre dans la solution du sol	Extractable or free Zn in soil solution
R ²	Coefficient de détermination	Coefficient of determination
R-C=O	groupements carbonyles	
R-COOH	groupements carboxyles	
RL _{max}	Elongation racinaire maximale	Maximal root lenght
RL _{min}	Elongation racinaire minimale	Minimal root lenght
RM	Fumier de lapin	Rabbit manure
RMS		Root Mean Square
R-NH ₂	Groupelements amines	
R-OH	Groupelements phénols et/ou alcools	
RPD	Rapport de l'erreur standard sur l'écart-type	Ratio performance to deviation
R-PO ₄ H ₃	Groupelements phosphates	
RRL	Elongation racinaire relative	Relative Root Length
R-SH	Groupelements thiols	
SD	Ecart-type	Standard Deviation
SEC	Erreur type d'étalonnage	Standard error of calibration
SECV	Erreur type de validation croisée	Standard error of cross validation
SEL	Erreur type de laboratoire	Standard error of laboratory
SEP	Erreur type de prédiction	Standard error of prediction
SHW	Déchets d'abattoir	Slaughterhouse waste
SIRIS	Système d'intégration des risques par interaction de scores	System of Integration of Risk with Interaction of Scores

SNVD		Standard Normal Variate and Detrend
SOL	Fraction soluble	Soluble fraction
SPIR-NIRS STEP	Spectroscopie Proche Infrarouge boues de station d'épuration	Near Infrared Spectroscopy
TAO	Transformation des Apports Organiques	Transformation of Added Organic
TAO-Bioch	Transformation des Apports Organiques - Biochimique	Biochemical-Transformation of Added Organic
TAO-Nir	Transformation des Apports Organiques- Spectroscopie Proche Infrarouge	Near Infrared Spectroscopy- Transformation of Added Organic
TAO-Par	Transformation des Apports Organiques - Paramètres	Parameters-Transformation of Added Organic
TCO	Territoire de la Côte Ouest	
TOC	Carbone organique total	Total Organic C
totCa	Calcium total	Total calcium
totK	Potassium total	Total potassium
totMg	Magnésium total	Total magnesium
totNa	Sodium total	Total sodium
totP	Phosphore total	Total phosphorus
VAL	Validation	Validation
VGT	Compost de fumier de mouton et de café	Compost of sheep manure and coffee cake
VOL BP- PSS	Boues carnées de volaille	Poultry Slaughter Sludge
VOL FIEN	Fientes de volaille	Poultry droppings
VOL FUM	Fumier de volaille	poultry manure
VOW	Déchets organiques valorisables	Valuable organic waste
ZGH	Poudre de corne de zébu	Zebu ground horn
Zn	Zinc	Zinc

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Introduction générale

A l'aube de ce 21^{ème} siècle, un accroissement sans précédent de la population mondiale pour atteindre la barre des 8 milliards d'habitants en 2025 est constaté. A Madagascar, les statistiques prévoient près de 30 millions de malgaches en 2025 (Aduraa, 2007). Sur l'île de la Réunion jusqu'à 1 million d'habitants sont prévus à l'horizon 2025. Cette croissance démographique pose de nombreux défis notamment la production de nourriture qui devra doubler, la consommation en énergie qui va croître et la gestion des déchets qui sera quadruplée (Mougeot *et al.*, 2004). Parmi ces déchets, les effluents organiques que l'on peut qualifier de matières organiques exogènes (MOEx), qu'ils soient issus de l'élevage ou de la ville, sont caractérisés par une grande variété de nature et de composition (Chabalier *et al.*, 2006). Les MOEx incluent les résidus organiques issus des activités agricoles, urbaines et industrielles ainsi que les produits issus de leur traitement (Marmo *et al.*, 2004). L'élimination de ces résidus est source de problèmes, c'est pourquoi leur valorisation en tant que « nouvelles ressources » doit être envisagée. Que ce soit à Madagascar ou à La Réunion, des pratiques concernant la deuxième vie des effluents existent et se maintiennent de génération en génération notamment dans le cas des déchets agricoles qui sont ré-utilisés en tant qu'intrants dans les sols agricoles. En effet, ils apportent à la fois des éléments fertilisants et de la matière organique ; ils contribuent ainsi à maintenir une production agricole soutenue et durable. Toutefois, à l'instar des pays comme l'Allemagne et la France, ces mêmes effluents pourraient alimenter des unités de méthanisation en vue de la production d'énergie. L'évolution, le changement et la diversification dans les habitudes et les activités de la population ont également généré de nouveaux « déchets » qui posent aujourd'hui problème à leur détenteur car leur place dans ce cycle de ré-utilisation des MOEx n'est pas encore trouvée. A cet effet, la Directive de la CEE (75/442/CEE) encourage de promouvoir la valorisation des déchets par recyclage, réemploi, récupération ou toute autre action visant à obtenir des matières premières secondaires ou à leur utilisation comme source d'énergie. Le changement de statut des MOEx de « déchets » à « nouvelles ressources » passerait par deux voies de valorisation envisageable qui sont i) la valorisation agronomique via un retour aux sols des MOEx comme « nouveaux intrants » et ii) la valorisation énergétique via la production d'énergie par ces MOEx en tant que « biomasse nouvelle ».

La valorisation raisonnée des MOEx requiert une maîtrise de leurs caractéristiques intrinsèques et de leur devenir suivant une voie de valorisation donnée ainsi qu'une prise en compte de leurs impacts environnementaux (Chen *et al.*, 2008). Plusieurs études ont porté sur la caractérisation d'une catégorie ou d'une famille de MOEx en vue de leur valorisation

agronomique et/ou énergétique (Bernal *et al.*, 2009; Guermoud *et al.*, 2009; Kranert *et al.*, 2010) dans différents pays. En milieu tropical, il n'y a que peu ou pas d'étude qui ait fait l'objet d'une considération conjointe de la diversité des MOEx (origine agricole, agro-industrielle, urbaine) et des deux scénarios de valorisation agronomique et énergétique à la fois.

La valorisation agronomique des MOEx a été longuement pratiquée dû au fait que la matière organique est à l'origine de l'activité biologique des sols et la clé de leur fertilité (Gobat *et al.*, 2003). Toutefois, contrairement aux engrais minéraux dont les dynamiques de transformation dans les sols sont bien connues, le manque de références quant aux devenir des MOEx dans les sols et leur effet sur les productions végétales est évoqué comme un des freins à leur utilisation rationnelle en agriculture (UR Risque environnemental lié au recyclage, 2008). En effet, malgré l'existence de la normalisation française sur les amendements organiques NF XPU-041 (AFNOR, 2006) et l'existence d'une typologie à partir de 273 MOEx métropolitaines françaises selon leur capacité amendante (Lashermes *et al.*, 2009) et leur dynamique de transformation de l'azote (Lashermes *et al.*, 2010), un besoin manifeste de validation de cette typologie ou de redéfinition de ses contours en milieu tropical est ressenti. Dans certaines conditions, le recyclage agricole de MOEx peut présenter des risques environnementaux et sanitaires dont il convient également de se prémunir. On peut citer les émissions de gaz à effet de serre comme l'oxyde nitreux (N_2O) (Houghton *et al.*, 2001; Chapuis-Lardy *et al.*, 2009) et l'accumulation des éléments trace métallique (ETM) dans les sols (Doelsch *et al.*, 2006). Ces aspects sont à prendre en compte car ils entraînent une dépréciation de la valeur agronomique des MOEx.

Dû à l'épuisement des énergies fossiles : 40 ans de pétrole, 70 ans de gaz,..., 200 ans de charbon, une valorisation énergétique des MOEx semble appropriée (Ghysel *et al.*, 2010). Les MOEx peuvent être bien considérées en tant que biomasse qui est l'ensemble des matières organiques biodégradables et non fossilisées issues des plantes, animaux et microorganismes mais aussi des produits, co-produits, sous-produits et déchets issus de l'agriculture et des industries associées (Demirbas, 2009). Que ce soit une valorisation énergétique via des procédés thermochimiques comme la combustion directe ou la cogénération, ou bien via des procédés biochimiques comme la biométhanisation, la détermination du pouvoir calorifique ou du potentiel méthanogène est une étape-clé. De nombreuses références rapportent le pouvoir calorifique ou le pouvoir méthanogène de MOEx de même nature (Tillman, 1978; Callejón-Ferre *et al.*, 2011; Lesteur *et al.*, 2011; Lynch *et al.*, 2013) et sont rarement pluri-

matricielles. Pour les MOEx tropicales d'origines diverses, l'alimentation de la base de données sur ces potentiels énergétiques est indispensable.

Toutefois, pour une connaissance avancée des MOEx en milieu tropical, il est nécessaire d'une part d'avoir accès à une très large gamme de MOEx tropicales pour une bonne représentativité, et d'autre part, de recourir aux analyses de leurs caractéristiques chimiques, biochimiques ou biologiques. Ces analyses en laboratoire sont en général longues, onéreuses et posent quelquefois des problèmes de fiabilité. Une alternative à cela est l'utilisation de la spectrométrie proche infrarouge (SPIR) et de ses capacités prédictives. La SPIR permet ainsi de déterminer rapidement et à faible coût tous les paramètres liés à la matière organique pour lesquels on peut disposer d'analyses conventionnelles. Toutefois, la constitution de bases de références conditionne l'utilisation de cet outil. Norris (1964), bénéficiant des progrès de la microélectronique pour les premiers instruments d'analyse, publia des résultats précurseurs sur la caractérisation de l'humidité dans les grains et ouvrit la voie aux instruments SPIR informatisés. La composition de MOEx peut être caractérisée de manière fiable par SPIR, dans le cas des litières (ex. McLellan *et al.*, (1991)), fumiers (ex. Reeves & Van Kessel, (2000)), des composts ((Suehara *et al.*, 2001; Thuriès *et al.*, 2007; Albrecht *et al.*, 2008; Vergnoux *et al.*, 2009) ou les matières premières des fertilisants organiques (Thuriès *et al.*, 2005). On perçoit aussi l'intérêt de la SPIR pour les travaux de modélisation des cinétiques de transformation des MOEx apportées au sol en fonction de leur composition biochimique (Thuriès *et al.*, 2002; Pansu *et al.*, 2003), sur la base d'analyses biochimiques conventionnelles, et sur la base d'analyses SPIR (Thuriès *et al.*, 2005; Henriksen *et al.*, 2007; Thuriès *et al.*, 2007; Thuriès *et al.*, 2007; Kaboré *et al.*, 2012). Des études ont également porté sur la prédiction des potentiels énergétiques des MOEx notamment l'énergie brute (Bastianelli *et al.*, 2010; Everard *et al.*, 2012) et le pouvoir méthanogène ou BMP (Lesteur, 2010; Doublet *et al.*, 2013).

La SPIR, technique rapide, peu coûteuse et portable dans les Pays du Sud (Shepherd *et al.*, 2007) paraît être un très bon candidat à la caractérisation de MOEx de diverses origines. Elle peut être mise en oeuvre pour des études internationales, les appareils SPIR ou les spectres pouvant être échangés, et pallier ainsi à la grande complexité réglementaire vis-à-vis des transports des échantillons au-delà des frontières (ex. pour dosages dans un laboratoire).

On l'a évoqué, à la Réunion, le développement des activités d'élevage et l'augmentation de la population génèrent une production de MOEx variées et en quantité croissante. A Madagascar, ce sont moins les évolutions récentes des activités d'élevage que celles liées à la

ville qui peuvent poser des problèmes en termes de gestion et de choix d'usages des MOEx. Les deux pays tropicaux, voisins, ont des traits communs. Cependant, ni le niveau de vie (et donc les MOEx générées) ni les contraintes réglementaires ne sont identiques. On se propose alors de considérer ces deux 'terrains' et de tester l'outil SPIR pour aider aux choix d'usages d'une grande variété de MOEx.

Ce travail de thèse a pour objet l'élaboration d'une typologie des MOEx pour orienter judicieusement leur valorisation agronomique et/ou énergétique. Une meilleure maîtrise de l'usage des MOEx passe par (i) la connaissance de leurs caractéristiques intrinsèques mesurées au laboratoire ou prédites par la SPIR, (ii) la connaissance de leurs potentiels agronomique et énergétique et la prise en compte des impacts négatifs liés à leur ré-utilisation (iii) l'intégration de ces informations dans une méthode d'évaluation multicritère d'aide à la décision. La Figure 0.1 présente un schéma récapitulatif de notre démarche.

A la suite de cette partie introductive, une étude bibliographique sera réalisée afin de documenter les composantes essentielles aux modes d'usage des MOEx et de présenter le principe de la SPIR.

A la suite de cet exposé bibliographique, le second chapitre aura comme objectif de montrer l'intérêt et la faisabilité de SPIR pour la prédiction des caractéristiques chimiques et biochimiques de la MOEx

Lors des trois chapitres suivants, il sera question de la caractérisation des potentiels « positifs » permettant d'orienter l'usage des MOEx pour une voie agronomique ou une voie énergétique. De ce fait, une étude conjointe des données mesurées de minéralisation et des données de minéralisation prédites par le modèle de Transformation des Apports Organiques (TAO) sera conduite dans le chapitre 3. Il aura pour objet la description de la dynamique de transformation des MOEx au sol et la validation du modèle TAO pour la prédiction du potentiel agronomique des MOEx de Madagascar et de la Réunion, comme c'était le cas pour des MOEx de l'Afrique de l'Ouest (Kaboré *et al.*, 2011; Kaboré *et al.*, 2012). Puis, deux chapitres seront dédiés à la détermination des potentiels énergétiques de la MOEx. Dans le chapitre 4 sera traitée la détermination de l'énergie brute d'une MOEx ainsi que les différentes méthodes pour sa prédiction. Le chapitre 5 aura pour objectif de décrire le potentiel méthanogène des MOEx et la faisabilité de la SPIR pour la prédiction de ce potentiel méthanogène.

Les deux chapitres d'après feront écho des externalités négatives liées à la valorisation agronomique des MOEx sur les aspects d'émissions de gaz à effet de serre notamment le

N₂O et de phytotoxicité par rapport aux plantes liée à l'accumulation des ETM dans les sols. Un sixième chapitre abordera tout d'abord les émissions de N₂O faisant suite à l'épandage de MOEx aux sols. Ce chapitre a pour objectif de déterminer la dénitrification potentielle de sols amendés par les MOEx. Un septième chapitre sera consacré quant à lui à l'étude de la phytotoxicité des ETM liée à l'épandage des MOEx au sol qui sont des sources potentielles d'ETM.

Dans le but d'intégration de toutes les connaissances acquises sur les MOEx : caractéristiques intrinsèques, potentiel agronomique, potentiel énergétique, externalités négatives, un huitième chapitre traitera de l'élaboration d'une typologie de MOEx suivant une valorisation agronomique et/ou énergétique.

Les chapitres énoncés ci-dessus seront rédigés sous forme d'articles scientifiques qui sont soit acceptés pour publication soit prêts à être soumis. Enfin, les principales conclusions de ce travail seront reprises et des perspectives seront envisagées, quant à l'utilisation de la SPIR et l'orientation d'usage des MOEx.

ELABORATION D'UNE TYPOLOGIE DES MOEx TROPICALES

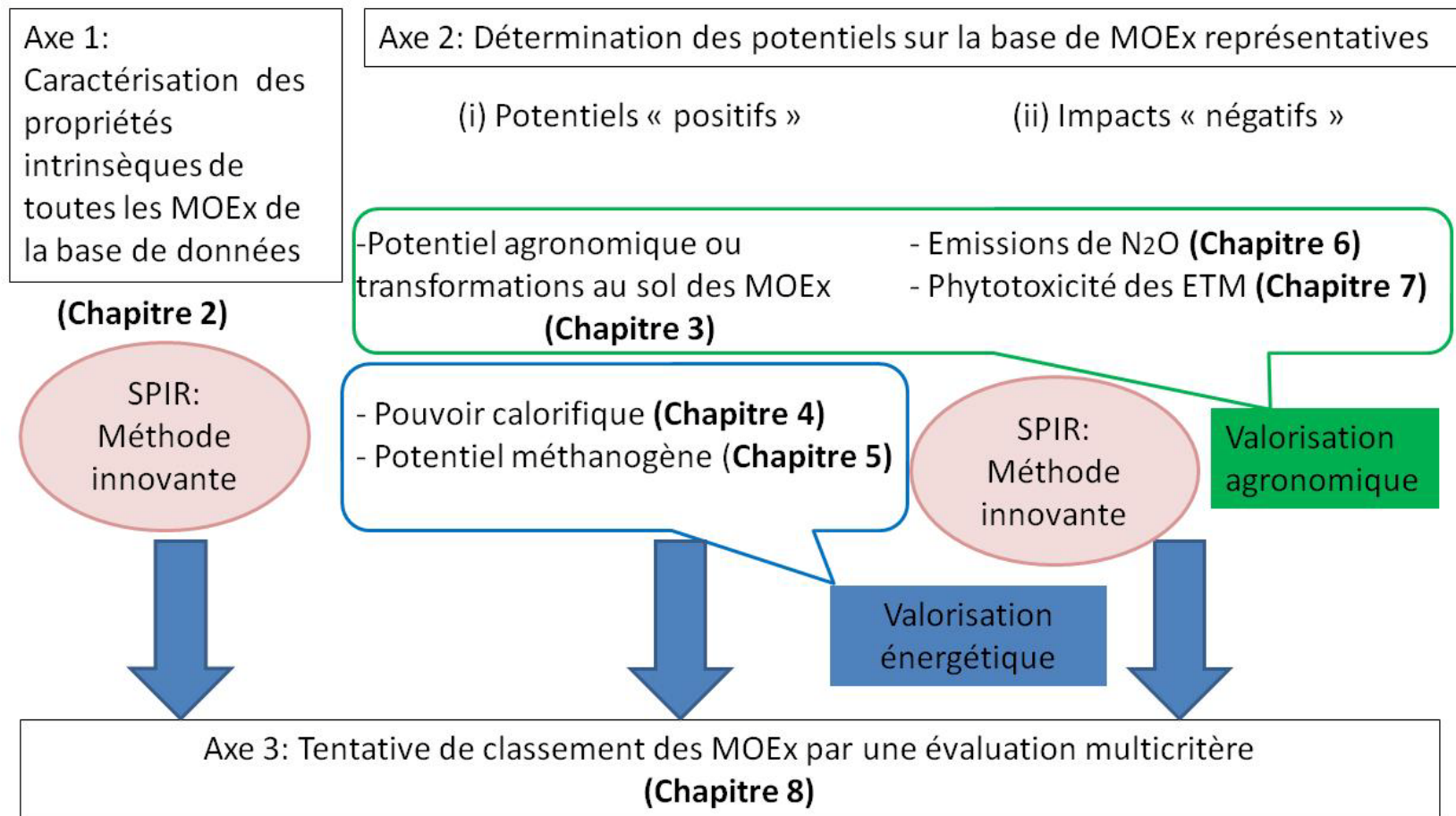


Figure 0.1 : Démarche générale adoptée pour la thèse

Chapitre 1. Synthèse bibliographique

Cette synthèse bibliographique a pour objet de reprendre les aspects théoriques liés à notre étude. Y seront abordés les points forts sur les caractérisations agronomiques et énergétiques des MOEx ainsi que les principes de la spectrométrie proche infrarouge.

1.1 Caractérisation des MOEx en vue de valorisation agronomique

1.1.1 Les caractéristiques intrinsèques

Les caractéristiques intrinsèques des MOEx sont un des principaux déterminants de leur minéralisation une fois apportées au sol (Heal *et al.*, 1997). En 1979, Swift *et al.* (1979) désignent ces caractéristiques sous le terme générique de « qualité » de la matière organique, qui est utilisé depuis dans les travaux relatifs à cette problématique (Cadish *et al.*, 1997). La description de la qualité la plus souvent utilisée est la composition chimique et biochimique. En terme de composition chimique des MOEx, les normalisations françaises NF U-044-051 (AFNOR, 2006) et NFU 42-001 (AFNOR, 1981) présentée dans le Tableau 1.1 résume les principales recommandations liées à l'usage agronomique des MOEx.

Tableau 1.1 : Catégorie de MOEx en fonction de leur action sur le sol ou sur la culture faisant référence à des normes NFU dans le cas d'une mise en marché du produit

Amendements organiques	Engrais organiques	Engrais organo-minéraux
NFU 44-051	NFU 42-001	NFU 42-001
Teneur totale en N et P_2O_5 et $K_2O < 3\%$ MB MS% $\geq 30\%$ de MB MO% $\geq 20\%$ de MB	Teneur en un des 3 éléments (N ou P_2O_5 ou K_2O) $> 3\%$ de MB	Teneur totale en N + P_2O_5 + K_2O) $> 7\%$ de MB Et Teneur en N ou P_2O_5 ou $K_2O > 3\%$ de MB

N : azote, P_2O_5 : phosphore total K_2O : potassium total, MS : matière sèche, MO : matière organique, MB : matière brute

1.1.2 Transformation des MOEx au sol

1.1.2.1 La dynamique de minéralisation de MOEx

Actuellement, les MOEx sont caractérisées au laboratoire par deux méthodes normalisées : (i) le fractionnement biochimique de la matière organique (norme XP U44-162) (AFNOR, 2009) qui permet d'estimer la capacité à induire du stockage de matière organique dans les sols à long terme et (ii) l'étude des cinétiques de minéralisation du carbone et de l'azote des MOEx au cours d'incubations en conditions contrôlées dans les sol (norme XP U44-163)(AFNOR, 2009) qui caractérisent l'effet à court et moyen termes des MOEx sur les sols. Dans notre étude, nous nous limiterons à la dynamique du carbone et de l'azote des MOEx. En effet, le contact entre le sol et les MOEx, est lié à la fois aux caractéristiques de ces matières organiques (ex : taille des résidus, surface spécifique) (Angers *et al.*, 1997; Fruit *et al.*, 1999), et à celles du sol (ex : porosité, taille des agrégats), ainsi qu'aux pratiques agricoles (ex : enfouissement, broyage, travail du sol), influence également la décomposition (Balesdent *et al.*, 2000). Cet effet peut s'exercer directement, en modifiant notamment l'accès des microorganismes au substrat (Angers *et al.*, 1997; Vanlauwe *et al.*, 1997), ou indirectement, en modifiant par exemple la disponibilité en azote (Corbeels *et al.*, 2003) ou la protection physique par les constituants du sol (Balesdent *et al.*, 2000).

En ce qui concerne le carbone, les principaux composés biochimiques déterminant la décomposition sont les composés solubles, les hémicelluloses, la cellulose, les lignines et cutines, dont les biodégradabilités sont différentes (Darwis, 1993; Derenne *et al.*, 2001). Les composés solubles et facilement accessibles sont principalement décomposés par les bactéries, alors que la cellulose et les lignines sont plutôt dégradées par des champignons (Swift *et al.*, 1979). Cependant les processus de décomposition sont complexes et impliquent pour un même substrat des populations qui se succèdent et interagissent en fonction de leur équipement enzymatique (Swift *et al.*, 1979; Schlegel, 1993).

En ce qui concerne la minéralisation nette de l'azote, le facteur principal est le rapport C/N des MOEx (Frankenberger *et al.*, 1985; Constantinides *et al.*, 1994). Dans le cas de certains types de MOEx pourtant, le rapport C/N global est un critère explicatif insuffisant. C'est le cas par exemple d'une boue et d'un compost étudiés par Ambus *et al.* (2002) ayant des rapports C/N comparables mais induisant des cinétiques de minéralisation différentes. C'est dans cette optique que l'on a cherché à expliquer ces dynamiques de MOEx à partir de l'ensemble du profil biochimique des MOEx (Houot *et al.*, 2002).

1.1.2.2 Modélisation de la transformation des MOEx

La transformation des MOEx au sol est un processus microbien complexe qui est affecté par les conditions environnementales du milieu. Malgré tout, plusieurs modèles mathématiques ont été développés comme étant des outils puissants à la simulation de cette complexité (ex. (Nicolardot *et al.*, 1994; Rodrigo *et al.*, 1997; Molina *et al.*, 1998; Pansu *et al.*, 1998; Schaffers, 2002; Pansu *et al.*, 2007). Nicolardot *et al.* (2001) and Beraud *et al.* (2005) ont simulé la minéralisation du C et de N de résidus de cultures et de composts en utilisant un modèle basé sur le rapport C/N, un critère de qualité souvent considéré comme performant pour la minéralisation des MOEx (Bruun *et al.*, 2006; Zhu, 2007) mais qui souvent est jugé comme insuffisant et inadéquat par d'autres auteurs (Linères *et al.*, 1993; Houot *et al.*, 2004). Certains auteurs (ex. (Henriksen *et al.*, 1999; Thuriès *et al.*, 2002) modélisent les dynamiques de transformations des MOEx en utilisant les résultats des analyses séquentielles de MOEx (Van Soest *et al.*, 1991). Dans notre étude, le modèle TAO (Transformation des Apports Organiques) est proposé pour la prédiction des transformations des MOEx (C et N minéralisé, N immobilisé, N réorganisé). Pour la modélisation du carbone, la structure de ce modèle (TAO-C) est définie sur la base des compartiments labile et stable des MOEx qui sont ensuite mis en relation avec les propriétés biochimiques des MOEx (Thuriès *et al.*, 2002). Pour la modélisation de la minéralisation de l'azote, TAO-N utilise 2 autres paramètres liés à la reminéralisation de N et à leur immobilisation avant d'être mis en relation avec les propriétés des EOM (Pansu *et al.*, 2003).

1.1.3 La typologie des MOEx

Par rapport à la dynamique du carbone, aucune classe de MOEx n'a été définie. Seul le calcul de l'indicateur normalisé Indice de Stabilité de la Matière Organique (ISMO) (AFNOR, 2009; Lashermes *et al.*, 2009) informe sur la proportion de matière organique persistant dans les sols sur le long terme dans le cadre de la gestion des stocks de matière organique des sols. Cet indice ISMO permet de prédire le carbone non minéralisé avec une très bonne fiabilité ($r^2=0,66$ sur 518 échantillons). La Figure 1.1 présente les plages de valeurs d'ISMO pour les différents types de matières organiques présentes dans la base de données ayant servi à son élaboration.

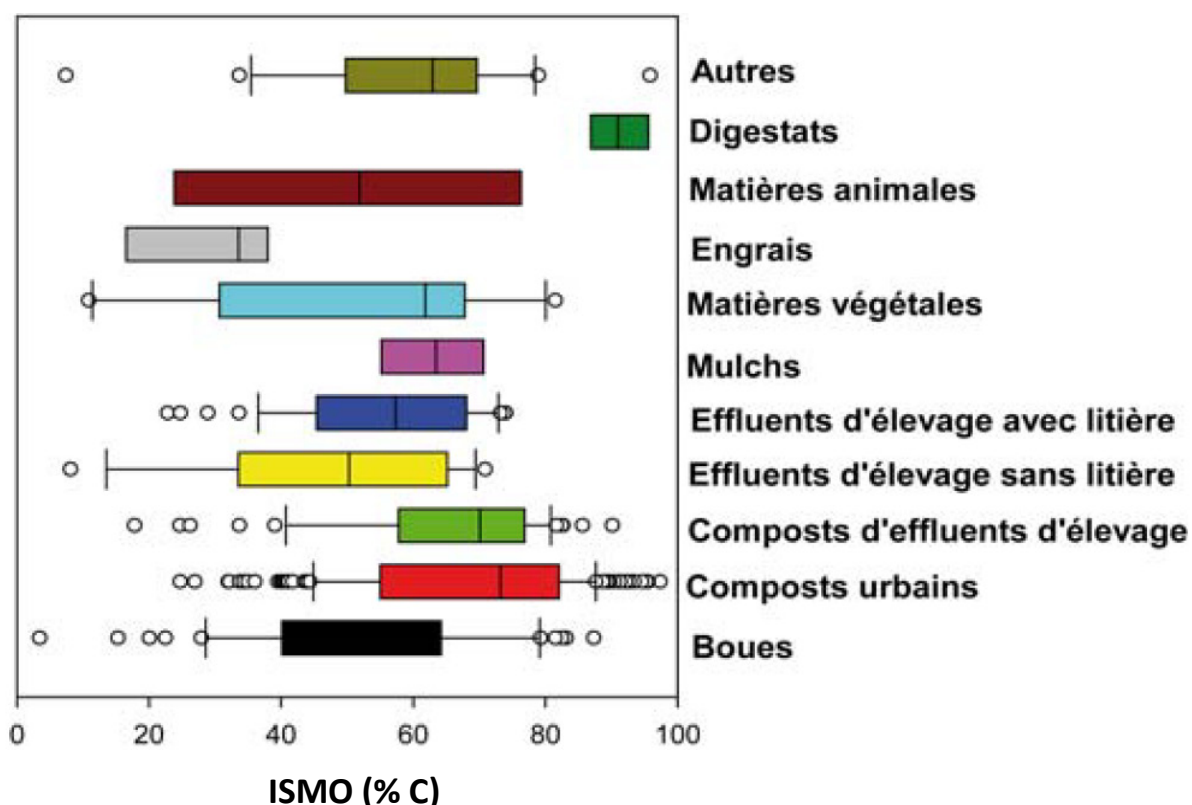


Figure 1.1 : Plage de valeurs prises par ISMO pour les différents types de matières organiques présentes dans la base de données ayant servi à son élaboration d'après Lashermes *et al.* (2009)

Vis-à-vis de l'azote, six classes de comportement agronomique ont été établies (Lashermes *et al.*, 2007; Lashermes *et al.*, 2007; Lashermes *et al.*, 2010) : classe 1 : produits ayant une minéralisation potentielle de l'azote organique très forte, classe 2 : produits ayant une minéralisation potentielle de l'azote organique forte, classe 3 : produits ayant une minéralisation potentielle de l'azote organique moyenne, classe 4 : produits ayant une minéralisation potentielle de l'azote organique moyenne à faible, classe 5 : produits ayant une minéralisation potentielle de l'azote organique faible pouvant induire des immobilisations d'azote, classe 6 : produits ayant une minéralisation potentielle de l'azote organique proche de zéro et pouvant induire des immobilisations d'azote. Cette classification permet d'aider les utilisateurs dans la compréhension des résultats de minéralisation potentielle de l'azote des produits organiques. Néanmoins les valeurs (en kg de N.t⁻¹ de MS) données au niveau des classes ne sont que des approximations. En outre, ces classes ne renseignent pas sur la dynamique des phénomènes de libération ou d'immobilisation de l'azote. Pourtant, l'aspect dynamique est essentiel pour une bonne utilisation de l'azote des produits. Seules les cinétiques de minéralisation peuvent fournir ces renseignements et leur réalisation ou leur simulation est donc toujours nécessaire. Ces classes ont été créées par classification

ascendante hiérarchique en s'appuyant sur une base de données de 273 produits qui comporte de nombreux types et non pas seulement des amendements organiques. Le traitement statistique de classification a été réalisé sur la base des données de cinétiques de minéralisation de l'azote. Par la suite, de l'ensemble des données de caractérisation des produits de chaque classe, ont été extraits les paramètres permettant de discriminer les classes les unes des autres.

1.1.4 Les impacts environnementaux de l'usage agronomique des MOEx

Si les effets bénéfiques de l'application aux sols des MOEx sont bien connus, une impasse sur les impacts négatifs de cette pratique ne peut être faite. Aussi, on se propose de décrire deux aspects pouvant déprécier l'usage agronomique des MOEx : les émissions de protoxyde d'azote ou N_2O et la phytotoxicité des ETM.

1.1.4.1 Les émissions de N_2O

Le N_2O est essentiellement produit lors de processus biologiques qui sont la dénitrification (Smith *et al.*, 1990), la nitrification (Blackmer *et al.*, 1978) et la nitrification dénitrifiante (Poth *et al.*, 1985; Wrage *et al.*, 2001). La dénitrification et la nitrification sont jusque là considérées comme les principaux processus biologiques impliqués. La nitrification est un processus requérant des conditions aérobies et dépend principalement de la disponibilité en ammonium (NH_4^+). La dénitrification quant à elle se passe en conditions anaérobies et dépend des concentrations en Carbone organique et en nitrate (NO_3^-) (ou autres oxydes d'azote) (Beauchamp, 1997). La nitrification dénitrifiante désigne la réaction d'oxydation de l'ammoniac (NH_3) en nitrite (NO_2^-) qui est ensuite réduit en oxyde nitrique (NO) puis en oxyde nitreux (N_2O) et en diazote (N_2) (Wrage *et al.*, 2001). L'importance de cette voie dans la production de N_2O n'est pas encore bien quantifiée.

La Denitrifying Enzyme Activity (DEA) est la méthode couramment utilisée pour mesurer la dénitrification potentielle (Mc Gill *et al.*, 2010). Elle consiste à mettre les échantillons dans les conditions optimales de dénitrification, notamment :

- La dénitrification se produit obligatoirement en absence d'oxygène. L' O_2 est un régulateur de la synthèse et de l'activité des enzymes réductrices dans la réaction de dénitrification (Cavigelli *et al.*, 2001).
- Les microorganismes impliqués ont aussi besoin d'un substrat carboné pour y puiser leur énergie. La disponibilité en carbone est probablement un des facteurs les plus importants influençant la dénitrification (Dinçer *et al.*, 2000). Le Carbone influence la dénitrification directement en fournissant un substrat pour la croissance microbienne

et indirectement par la consommation d'O₂ par les microbes, favorisant l'anaérobiose. D'après Zumft (1997), l'addition de carbone organique réduit la provision d'oxygène du sol en promouvant la croissance microbienne, favorisant le processus de dénitrification.

- Le nitrate comme accepteur d'électrons. Dans des conditions anaérobies où le carbone n'est pas limitant, la quantité d'enzyme produite est proportionnelle à la concentration de nitrate disponible et le taux de production de N₂O est proportionnel à la quantité d'enzyme (Tiedje *et al.*, 1989; Cavigelli *et al.*, 2001)

1.1.4.2 La phytotoxicité des ETM

Des risques de pollution des sols liés à l'épandage de MOEx peuvent exister notamment la présence de micropolluants métalliques (éléments trace métallique, ETM) dans ces MOEx constitue un facteur limitant leur utilisation en agriculture. Bien qu'ils ne soient présents qu'en faible quantité, les ETM peuvent être potentiellement toxiques. La concentration totale en ETM dans les MOEx et dans les sols suite à l'apport de MOEx n'indique que très partiellement leur toxicité. Seule l'étude de la fraction biodisponible des ETM, quantité assimilable par les organismes variant selon la spéciation des ETM, dans les différents mélanges sol-MOEx permet d'évaluer la toxicité potentielle de ces ETM.

L'interaction entre la matière organique et les ETM met en jeu le phénomène de complexation. La matière organique possède de nombreux groupements fonctionnels tels que des groupements carboxyles (R-COOH), phénols et/ou alcools (R-OH), carbonyles (R-C=O), thiols (R-SH), phosphates (R-PO₄H₃), ainsi que des groupements amines (R-NH₂) (Sarret *et al.*, 1998; Campbell *et al.*, 2006). En fonction du pH du milieu, certains groupes fonctionnels peuvent s'ioniser. La liaison métallique à la matière organique peut être vue comme un processus d'échange ionique entre H⁺ et les ions métalliques sur les groupes fonctionnels acides (Blanchard, 2000).

Les ETM ont des affinités différentes pour la matière organique. A titre d'exemple, le cuivre (Cu) est connu pour avoir une grande affinité pour la matière organique (Kabata-Pendias, 2001). Karlsson *et al.* (2006) mettent en évidence des complexes de sphère interne entre le cuivre et la matière organique dissoute. Ils suggèrent que Cu est complexé par une combinaison de groupes amines, carboxyles et carbonyles. L'affinité de Cu pour la matière organique est plus grande lorsque le pH augmente (Nierop *et al.*, 2002). Les substances humiques ont donc la propriété de complexer les métaux, toutefois, ce comportement peut conduire à la formation de complexes solubles alors que dans d'autre cas, ces complexes sont

insolubles et contribuent au maintien des métaux dans la phase solide (Varrault *et al.*, 2001). L'effet de la MO sur la mobilité des métaux est difficile à prévoir, il dépend évidemment des conditions physico-chimiques du milieu, de l'élément complexé, mais également de la nature et de la quantité de la MO présente dans le milieu

1.2 Caractérisation des MOEx en vue de valorisation énergétique

La valorisation énergétique des MOEx est envisageable suivant différentes voies : production de chaleur, production d'électricité, cogénération (chaleur et électricité), carburant automobile et injection dans le réseau de gaz naturel. Le choix entre ces diverses solutions dépend de critères à la fois économiques et techniques dans lesquels la nature et la localisation du site de production interviennent beaucoup (ATEE, 1998). Les choix de valorisations énergétiques qui sont privilégiés à La Réunion et qui pourraient être également adoptés à Madagascar concernent (i) la production de chaleur par combustion et (ii) la méthanisation. Nous nous limiterons donc à la description des potentiels liés à ces deux modes d'usage des MOEx.

1.2.1 Le pouvoir calorifique

L'utilisation des MOEx en tant que biomasse pour des productions d'énergie thermique ou électrique nécessite la détermination de son pouvoir calorifique (Cordero *et al.*, 2001; Sheng *et al.*, 2005; Erol *et al.*, 2010; Callejón-Ferre *et al.*, 2011; Yin, 2011). Le pouvoir calorifique reflète d'une façon normalisée l'énergie contenue dans un combustible (Demirbas *et al.*, 2004; Sheng *et al.*, 2005; Erol *et al.*, 2010). Il peut être exprimé en pouvoir calorifique supérieur (PCS) ou en pouvoir calorifique inférieur (PCI) (Yin, 2011). La détermination expérimentale du pouvoir calorifique est effectuée dans une bombe calorimétrique adiabatique. C'est la différence d'enthalpie entre les réactifs et les produits qui est mesurée. La mise en oeuvre de ce protocole peut être lourde dans la majorité des cas (Cordero *et al.*, 2001; Sheng *et al.*, 2005; Erol *et al.*, 2010; Callejón-Ferre *et al.*, 2011; Yin, 2011).

1.2.2 Le potentiel méthanogène

Le test Biochemical Methane Potential (BMP) (Angelidaki *et al.*, 2009) est le test actuellement le plus utilisé pour déterminer le potentiel méthane des déchets. La valeur de potentiel méthane, ou valeur BMP, est la valeur maximale de méthane produit en condition anaérobie, exprimée en $\text{Nml CH}_4 \cdot \text{g}^{-1}$ Matière Organique (MO) ou Matière Volatile (MV). La cinétique de production est également étudiée afin de déterminer la vitesse de biodégradabilité des déchets. Ces valeurs sont utilisées pour évaluer la biodégradabilité anaérobie des déchets, et permettent de dimensionner les réacteurs industriels (Buffière *et al.*, 2006), mais aussi de contrôler et d'optimiser la production. Ce test a l'avantage de pouvoir déceler les inhibitions

du métabolisme microbien, dues à la présence dans le déchet de composés inhibiteurs, tels que des antibiotiques, des métaux lourds, etc. (Hansen *et al.*, 2004; Chen *et al.*, 2008). Il met également en évidence une surcharge ou une adaptation à un type de substrat (Hansen *et al.*, 2004).

Le test BMP consiste à placer une certaine quantité de déchets en présence de micro-organismes en condition anaérobie dans un milieu tamponné et thermostaté (pH entre 6,5 et 7,2, température à 35°C ou 55°C). Plusieurs paramètres sont susceptibles de faire varier la valeur BMP mesurée sur un déchet : les plus importants sont la température (Angelidaki *et al.*, 2004), le pH (Chen *et al.*, 1996; Angelidaki *et al.*, 2004; Chen *et al.*, 2008), la taille des particules (Palmowski *et al.*, 2000; Angelidaki *et al.*, 2004) et le ratio inoculum/substrat qui a un effet sur la cinétique et le temps de latence de la réaction et non sur le BMP (Nallathambi Gunaseelan, 1995; Chen *et al.*, 1996; Raposo *et al.*, 2006).

1.3 Principes de la spectrométrie proche infra-rouge

Les analyses en laboratoire étant généralement longues, onéreuses, l'utilisation de la spectrométrie proche infrarouge (SPIR) et des capacités prédictives est recommandée. Tous les paramètres liés à la matière organique pour lesquels on peut disposer d'analyses conventionnelles peuvent être déterminées rapidement et à moindre coût par la SPIR.

La SPIR caractérise l'absorption par les molécules organiques et l'eau d'une énergie lumineuse de longueur d'onde 800-2500 nm. Ce domaine est le siège des harmoniques et des bandes de combinaison des modes de vibrations des molécules (Pasquini, 2003). Cette absorption dépend de la nature et de la concentration des molécules ; la technique (rapide et non destructive) est donc non seulement qualitative mais aussi quantitative.

Pour débiter, une sélection d'échantillons représentatifs de la population à analyser (50 et plus) doit être caractérisée selon la méthode standard de laboratoire. Les échantillons doivent couvrir toute la zone des valeurs à prédire. Il est donc important d'avoir des échantillons aux valeurs extrêmes (Leeson *et al.*, 2000). Par la suite, la collection est soumise à la SPIR pour obtenir une collection de spectres associés aux valeurs analytiques.

Afin d'obtenir une relation entre les valeurs obtenues par la méthode chimique et les valeurs spectrales, plusieurs analyses multivariées peuvent être utilisées la méthode des moindres carrés partiels (PLS, *Partial Least Square*) ou la méthode des régressions linéaires multiples (MLR, *Multiple Linear Regression*).

La précision de l'étalonnage est habituellement vérifiée par le test de validation croisée (*cross-validation*) (Terhoeven-Urselmans *et al.*, 2006). Ce modèle implique la séparation des

données en deux parties. La première partie contient n_c données employées pour construire le modèle tandis que la deuxième partie contient $n_v = n - n_c$ données pour évaluer la précision de prédiction du modèle. Il y a différentes possibilités pour séparer les échantillons (Shao, 1993). Ainsi, un modèle linéaire est établi. Les résultats sont exprimés graphiquement dans une figure où les valeurs prédites y pour l'échantillon sont comparées à leurs valeurs références (variables prédictives) x . Le coefficient de détermination (r^2) permet de déterminer la proportion de la variance dans les données prédites à la SPIR qui est attribuable à la variance des données de référence. Pour qu'un étalonnage puisse être utile à l'avenir, le coefficient r^2 doit se situer près de 1 et la droite doit croiser l'axe Y près de 0. Le Tableau 1.2 fournit de l'information pour l'interprétation du coefficient de détermination.

Tableau 1.2: Lignes directrices pour l'interprétation du coefficient de détermination (r^2) pour les sols

r^2	Interprétation
0,25 et -	Non utilisable pour un étalonnage SPIR
0,26 – 0,49	Corrélation faible : chercher les raisons
0,50 – 0,64	Précision des résultats obtenus douteuse
0,65 – 0,81	Utile pour des approximations
0,82 – 0,90	Utilisable pour la plupart des applications, incluant la recherche
0,91 – 0,96	Utilisable dans la majorité des applications, incluant le contrôle de qualité
0,97 et +	Utilisable partout

Source : Adapté de (Malley et al., 2004)

Cependant, cette valeur à elle seule ne permet pas de déterminer la qualité réelle d'un étalonnage. Il existe une certaine confusion au niveau des statistiques utilisées dans la détermination de l'erreur d'étalonnage (Malley et al., 1999). La qualité de l'évaluation du modèle linéaire est, en général, évaluée par l'erreur type d'étalonnage (SEC : *standard error of calibration*) et l'erreur type de prédiction (SEP : *standard error of prediction*). Ces statistiques représentent l'écart-type (SD : *standard deviation*) de la différence entre les valeurs Y (prédites à la SPIR) et X (références) pour la série d'étalonnage (ou *calibration*) (SEC) ou *validation* (SEP) (Equation 1.1 et Equation 1.2) (Malley et al., 2004; Pirie et al., 2005). On recherche la valeur de SEP la plus faible possible.

$$SEC = \sqrt{\frac{\sum_{j=1}^m (y_j - y'_j)^2}{m-1-q}} \quad \text{Equation 1.1}$$

Avec

y_j : concentration de référence pour l'échantillon j

y'_j : concentration de référence pour l'échantillon j

m : nombre d'échantillons du lot d'étalonnage

q : nombre de paramètres de la régression

Pour rendre les termes d'erreurs comparables entre eux, le rapport de l'erreur standard de prédiction (RPD : *Ratio performance to deviation*) est souvent employé. Le RPD (Equation 1.3) est obtenu en divisant l'écart-type des valeurs référence de la série *validation* par le SEP

$$SEP = \sqrt{\frac{\sum_{j=1}^n (y_j - y'_j)^2}{n}} \quad \text{Equation 1.2}$$

Avec

y_j : concentration de référence pour l'échantillon j

y'_j : concentration de référence pour l'échantillon j

n : nombre d'échantillons du lot de validation

Et,

$$\text{RPD} = \frac{\text{SEP}}{\text{SEP}} \quad \text{Equation 1.3}$$

Où

$$\text{SEP} = \sqrt{\frac{\sum_{j=1}^n (y_j - y'_j)^2}{n}}$$

Le Tableau 1.3 donne les lignes directrices pour l'interprétation de ce ratio.

Tableau 1.3 : Ligne directrice pour l'interprétation du ratio RPD

Valeur RPD	Classification	Application
0,0-1,9	Très faible	Non recommandé
2,0-3,0	Acceptable	Sélection non précise
3,1-4,0	Satisfaisant	Sélection
4,1-6,4	Bon	Contrôle de qualité
6,5-8,0	Très bon	Contrôle de procédé
8,1 et +	Excellent	Partout

RPD : rapport de l'erreur standard de prédiction sur l'écart-type.

Source : Adapté de Malley *et al.* (2004) et Stenberg *et al.* (2004)

Grâce à ces lignes directrices, il est possible d'évaluer la réussite et la précision d'un étalonnage dans le domaine environnemental pour des échantillons de sol, de compost, de fumier et autres. Ainsi, Malley *et al.* (2004) considèrent un étalonnage comme excellent s'il présente un $r^2 > 0,95$, un RPD > 4 . Toutefois, dans certaines applications, un RPD de 3 est jugé suffisant.

Toutefois, le RPD a également ces limites comme le montrent Bellon-Maurel *et al.* (Bellon-Maurel *et al.*, 2010). En effet, ce ratio RPD est calculé à partir des erreurs-type (SE , SE_{CV} ou SE_P) qui eux-mêmes dépendent de l'étendue des valeurs de références (set d'étalonnage ou s et de validation) et de l'écart-type (SD) qui ne décrit pas correctement une distribution asymétrique.

Une autre approche pour la comparaison des performances de la SPIR et des méthodes conventionnelles consiste à comparer l'écart-type d'étalonnage ou de prédiction obtenu par la SPIR : SE_C (standard error of calibration) ou SE_P (standard error of prediction) avec le l'erreur type de laboratoire : SEL (*Standard error of laboratory*). Selon Martens (1989) cité par Halgerson *et al.*, (2004), les modèles performants SPIR doivent avoir des SE_P (ou SE_C) inférieures à 2 fois la SEL .

Les principaux avantages et inconvénients de la méthode SPIR sont regroupés dans le Tableau 1.4

Tableau 1.4 : Avantages et inconvénients de la SPIR tirés des publications du CIRAD (2007)

Avantages	Limites
1) Rapide : quelques minutes suffisent pour recueillir le spectre d'absorption d'un échantillon, qui servira à la prédiction de sa composition. A comparer avec la très longue durée d'une analyse de composition chimique (plusieurs jours)	Prédiction des substances minérales, puisque la SPIR est basée sur l'absorption du rayonnement par les molécules organiques Prédiction des substances à l'état de traces car le signal spectral leur correspondant est trop faible.
2) Non destructive : l'échantillon est récupéré intact après analyse. Cette propriété est particulièrement importante pour des échantillons très peu abondants ou que l'on doit conserver pour des analyses ultérieures	
3) Econome en échantillon : classiquement 4 à 5 grammes suffisent. Dans certaines conditions on peut même réaliser des spectres sur des quantités extrêmement faibles.	Obtention d'un échantillon représentatif due à la réduction des quantités à analyser.
4) Peu onéreuse : le coût de passage des échantillons est très faible. Il faut simplement prévoir quelques analyses de référence au laboratoire pour vérifier que l'étalonnage reste correct au cours du temps et bien adaptée aux nouveaux échantillons.	Investissement initial dans l'appareil et la constitution des « étalonnages » pour chaque produit.

Chapitre 2. Characterization of Exogenous Organic Matter (EOM) in tropical environment: Near Infrared Spectroscopy (NIRS) to assess their chemical and biochemical composition

Avant-propos

Les MOEx en milieu tropical sont diverses et variées selon leur nature et leur origine. L'orientation d'usages de valorisation de ces MOEx exige une connaissance approfondie de leurs caractères chimiques et biochimiques pour une meilleure maîtrise de leurs propriétés intrinsèques.

En tout 2199 MOEx issues de l'élevage, de la ville, des activités agroindustrielles ont été collectées à La Réunion et à Madagascar. Certaines MOEx ont fait partie d'échantillons inventoriés puis analysés lors des programmes de recherches antérieurs et stockés dans les laboratoires, d'autres ont été collectées durant la période de nos travaux.

Pour alimenter notre base de données, on se propose de compléter/d'effectuer des dosages au laboratoire pour avoir les valeurs de référence des teneurs en matières sèches, en matières organiques, en carbone organique total, en azote organique, en phosphore total, en potassium total, en calcium total, en magnésium total, en éléments traces métalliques (cuivre, zinc, nickel, chrome, plomb, cadmium) et en fractions biochimiques (fractions solubles, fractions hémicellulose, fractions cellulose, fractions lignine et cutine) des MOEx. Ces analyses de référence étant parfois longues et sont onéreuses du fait du temps de manipulation, du prix des réactifs, de l'amortissement de l'appareil de mesure, du salaire des techniciens, ... De ce fait, un nombre limité d'échantillons ont pu être totalement renseignés. Afin de pallier à l'absence des références liées à la longue durée et aux coûts des analyses, l'acquisition des spectres des MOEx via la spectroscopie proche infrarouge suivie des méthodes chimiométriques d'étalonnage apparaît comme une solution rapide et à moindre coût.

Les objectifs de ce chapitre étaient donc de :

- Alimenter la base de données des MOEx en milieu tropical à partir d'analyses de référence acquies au laboratoire et de leurs spectres proche infrarouge ;
- Développer des modèles d'étalonnage des caractéristiques des MOEx tropicales afin de renseigner les données manquantes de notre base de données.

Les résultats obtenus à l'issue de ce chapitre seront exploités en entrée de notre tentative de classification des MOEx en milieu tropical en vue de leur valorisation agronomique et/ou énergétique.

Ce chapitre est basé sur l'article :

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Characterization of Exogenous Organic Matter (EOM) in tropical environment: Near Infrared Spectroscopy (NIRS) to assess their chemical and biochemical composition. (En préparation)

2.1 Introduction

Today, environmental policies, laws and regulation progress lead to turn organic wastes into valuable resources. The use of organic wastes materials, so called exogenous organic matter (EOM), need an extensive study of their physical, chemical and biochemical properties because they have complex structures which procured them a large functions. Only the chemical analysis of a sample in laboratory allows knowing the composition of a product. This technique represents a relatively high cost and is time consuming. Currently, there is emerging awareness of the value of near infrared spectroscopy (NIRS) as a tool for environmental and biological analyses. Near infrared spectra contain a wide variety of information that can be inferred through statistical treatments rather than physical and chemical treatments of samples. NIRS could be a valuable method for assessment of EOM characteristics. It has already been used to determine the total C and nitrogen (N) contents of poultry manure (Bastianelli *et al.*, 2010), to assess the elemental and biochemical composition of plant materials (Stenberg *et al.*, 2004; Thuriès *et al.*, 2005; Peltre *et al.*, 2011), composted materials (Albrecht *et al.*, 2008; Vergnoux *et al.*, 2009) and animal manures (Reeves *et al.*, 2000; Malley *et al.*, 2002; Malley *et al.*, 2005; Sorensen *et al.*, 2007). 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: dataset including both plant materials and animal materials.

The aim of this study is (i) to describe and to compare tropical EOM by using their chemical and biochemical characteristics and (ii) to test the ability of NIRS to predict the characteristics of tropical EOM from Réunion and Madagascar. It is the first study taking into consideration more than 2,000 heterogeneous EOM samples from south western Indian Ocean origin for building a robust NIRS calibration.

2.2 Material and methods

2.2.1 EOM dataset

The dataset included 2,199 EOM samples collected and analyzed in the context of different research programs and covering a broad range of fresh and transformed organic materials.

In term of origin of EOM, these included 1100 poultry effluents (50% of dataset), 417 bovine effluents (19% of dataset), 374 porcine effluents (17% of dataset), 198 urban effluents (9% of dataset), 66 agro-industrial effluents (3% of dataset), 22 ovine effluents (1% of dataset) and

22 other EOM (1% of dataset). 1199 EOM have been collected in Réunion and 1000 EOM came from Madagascar.

2.2.2 Chemical and biochemical characterization of EOM

All EOM were oven-dried at 40°C (Réunion EOM) or air-dried (Malagasy EOM) and finely ground (< 1mm) before analysis.

Total organic matter (TOM) content was determined by loss on ignition at 550°C according to NF V18.101 (AFNOR, 1977). The measurement uncertainty was 12%.

For Réunion EOM, total organic C (TOC) content and total organic N (orgN) content were determined by using the Dumas method as described in NF ISO 13878 (ISO 1998) and NF ISO 10694 (ISO 1995) respectively. The measurement uncertainty for TOC and orgN was 7%. For Madagascar EOM, TOC content and total N were measured using an elementary analyzer CHN (*Thermo Finnigan Flash EA1112 série*).

Phosphorus (totP) contents, potassium (totK) contents, magnesium (totMg) contents, and calcium (totCa) contents determination, samples were calcinated at 520°C, then obtained ash were solubilized in chlorhydric acid. totK, totCa and totMg were quantified by using an atomic absorption spectrometry and totP was determined by using spectrophotometry on a continuous flow analyzer. The measurements uncertainty for totP, totK, totCa and totMg were respectively 6%, 9%, 7% and 7%.

For trace element analyses, a representative EOM sub-sample was ground to 100 µm before dissolution. After calcinations at 450 °C, total dissolution was performed by acid digestion using a mixture of HF, HNO₃ and HClO₄ (ISO 14869-1). The concentrations were then determined with an inductively coupled plasma-optical emission spectrometer (ICP-OES Vista-PRO, Varian Inc.) using an axially viewed plasma system and a charge coupled device detector. For quality control, in-house reference samples and certified samples (CRM 7001 Light Sandy Soil and CRM 7004 Loam, Analytica) were used every 20 samples and each analysis was conducted in duplicate. The measurement uncertainty was 10%.

The biochemical composition of EOM was determined using the Van Soest method (Van Soest *et al.*, 1991) as modified under the French standard XP U 44-162 (AFNOR, 2009a). The soluble (SOL), hemicellulose-like (HCEL) cellulose-like (CEL) and lignin&cutin-like (LIC) fractions were separated. After each extraction step, the OM content was determined in the residues by loss on ignition at 550°C biochemical fractions were expressed as a percentage of TOM (orgSOL, orgHCEL, orgCEL and orgLIC).

Statistical analysis was performed by one-way analysis of variance (ANOVA) by using XLSTAT Software, Tukey's test allowed to compare means of a given constituent for each category.

2.2.3 NIRS analysis

2.2.3.1 Spectrum acquisition and detection of spectral outliers

For Réunion EOM, the NIR spectra were recorded on a FOSS XDS (Foss NIRSystems, Silver Spring, MD, USA) with an initial spectral range of 400 to 2498 nm with 2 nm intervals. For Malagasy EOM, the NIR spectra were recorded on an ASD (Analytical Spectral Devices) (LabSpec, ASD Inc., Boulder, CO, USA). Only the range 1100 to 2498 nm (NIR) was used subsequently because preliminary tests showed that this produced more accurate predictions than the full range (visible and NIR), possibly because the visual range is highly sensitive to moisture and variable grinding conditions (Bruun *et al.*, 2005). This was probably the case regarding our sample set as it originated from different research programs. The samples were oven-dried at 40 °C or air-dried and ground to pass a 1 mm or 2 mm screen, but without additional drying to remove residual moisture prior to NIRS analysis as this has been shown to have little effect on NIRS calibration results (Lovett *et al.*, 2005). The EOM samples were packed in 5-cm ring cups and scanned in reflectance mode. Two different spectra (each averaged from 32 scans) were recorded for each EOM on independent cup fillings, and determined in terms of absorbance (logarithm of the inverse of reflectance). Both absorbance spectra were then averaged when repeatability was considered to be good, according to the root mean square (RMS); i.e. when the RMS between two sample spectra was smaller than 2.5 times the average of all RMS calculated for each sample of the dataset. Otherwise, spectrum acquisition was repeated. The spectra were processed using Win ISI IV software (FOSS). The spectra were transformed:(1) using the standard normal variate and detrend transformation (SNVD) second derivative and smoothing calculated over five data points on both sides, which reduces baseline variation and enhances spectral features (Reeves *et al.*, 2002).

Principal component analysis (PCA) was then performed to check the spectral homogeneity of the dataset. The Mahalanobis distance (H) statistic was used to identify spectral outliers. This statistic determines the distance of a spectrum from the average spectrum and compares this distance with a critical limit according to an F-test in order to identify outliers.

2.2.3.2 NIRS standardization

Because Madagascar spectra and Réunion spectra have been acquired with different instruments, spectrum standardization was necessary. We acquired spectra of the same samples on an instrument H (host) and an instrument M (master), and then we researched a mathematical transformation between them. The spectra of the same samples recorded on two instruments H (host) and M (master) have different profiles because two spectral devices cannot have exactly similar answers (appropriate characteristics of the lamp, the detector, the ceramic, the optical alignment, etc.). Of this fact it is not *a priori* possible to use on H equations of calibration developed on M. However, the differences between the spectra of H and M are not situated at the level of the bands of absorption of products (specific of the samples) but of the general look of the spectrum (base line). These differences can be thus corrected for a simple mathematical operation by instruments standardization.

In this study, the FOSS XDS (Foss NIRSystems, Silver Spring, MD, USA) was taken as the master M and the ASD (LabSpec, ASD Inc., Boulder, CO, USA) was the host H. The standardization was performed using the WINISI IV Software (Foss).

2.2.3.3 NIRS calibration and cross-validation

Calibration was performed by partial least square (PLS) regression on transformed absorbance spectra (Geladi *et al.*, 1986) in general. When the number of samples is less than 80, the stepwise multiple linear regression procedure was chosen to select the most informative wavelengths (Shenk *et al.*, 1991).

Cross-validation by groups was used to determine the optimum number of PLS components required to calibrate the models and then calculate the predicted values on the calibration sub-set in order to assess the robustness of the models. Each group in the calibration set was predicted successively with a PLS model developed using all other groups, thus supplying an independent prediction for each group. The residuals of cross-validation predictions were pooled to calculate the standard error of cross-validation (SE_{CV}). At the end of this first cycle, samples with large residuals (i.e. a difference between prediction and measurement more than 3 times the SE value calculated using all calibration samples) and samples with a strong influence (leverage) on the model (leverage > 5 times the average leverage of all samples) were discarded as calibration outliers and cross-validation was repeated. This cycle of cross-validation and outlier removal was performed twice. The predictive accuracy and robustness of the models were then evaluated on the EOM-sub-set of validation.

2.2.3.4 Outliers, validation and extrapolation

According to the available number of references, eighty percent (80%) of the dataset were selected for calibration and the remaining samples (20%) were used for external validation. Some samples were removed from the calibration set either for being spectral outliers. The removal of spectral outliers was based on Mahalanobis distance $H > 3$ in the PCA from the average spectrum of the file. Removing these outliers avoided calibrations stretched by the leverage of few points.

2.2.3.5 Statistics

The statistical methods used to evaluate goodness of fit included the coefficient of determination and the root mean square error calculated for predicted values of the entire calibration set (R^2_C and SE_C , respectively) or during cross-validation (R^2_{CV} and SE_{CV} , respectively) after spectral and calibration outlier removal, and for predicted values of the validation set minus spectral outliers (R^2_P and SE_P , respectively). In order to compare the quality of calibrations for variables with different units and ranges, the ratio of performance to deviation for cross-validation on the calibration set (RPD_{CV}) and for the validation set (RPD_P) were calculated as the ratio between standard deviations (SD) of measured data and SE_{CV} or SE_P , respectively.

2.2.3.6 Accuracy of calibration

A value for R^2 between 0.66 and 0.81 indicated approximate quantitative predictions. Whereas value for R^2 between 0.82 and 0.90 revealed good predictions. Calibration models having a value for R^2 above 0.91 were considered to be excellent (Williams, 2003). A value for the RPD between 1.5 and 2.0 revealed a possibility to distinguish between high and low values. While a value between 2.0 and 2.5 makes approximate quantitative predictions possible. For values between 2.5 and 3.0 and above 3.0, the prediction is classified respectively as good and excellent (Saeys *et al.*, 2005). As mentioned by Bellon-Maurel *et al.* (2010) in their study, the use of this RPD had some limits and critical points because SE , SE_{CV} or SE_P , depends on the range of the reference values (calibration set and validation set) and SD does not describe correctly the spread of population in skewed populations. In order to assess the accuracy of our prediction, SE_{CV} and SE_P will be better compared with the SEL, standard error of laboratory, if this information was available.

2.3 Results

2.3.1 Analytical characteristics of EOM

Figure 2.1 to Figure 2.3 present the analytical characteristics of all EOM depending on their category. Table 2.1 presents the basic statistics for the entire dataset regarding all the reference analytical characteristics of EOM that would be further predicted using NIRS, including orgN, TOC, TOM, totP, totK, totCa, totMg, Cu, Zn, Ni, Pb, Cr, Cd, Sol, Hcel, Cel, Lic.

All determined parameters covered broad ranges of values related to the considerable diversity of EOM types and origins in the dataset. Skewness and excess kurtosis close to 0 corresponded to a normal distribution. Positive skewness indicates a distribution concentrated at low values with relatively few high values, the reverse being true for negative skewness. Positive excess kurtosis is indicative of a more acute distribution peak around the mean whereas negative excess kurtosis indicates a lower and broader distribution peak around the mean.

Table 2.2 reports the Pearson correlation of each variables category with TOC. Some variables were correlated. As expected, TOC and TOM contents were strongly correlated ($r = 0.98$), as were TOC and ash contents.

Table 2.1: Summary of analytical characteristics of the dataset on exogenous organic matters.

Variables	Units	n	Mean	SD	Min.	Max.	Skewness	Kurtosis
orgN	‰ DW	915	29.8	16.1	0.0	144.9	2.4	13.4
TOC	% DW	1063	34.3	9.2	2.0	64.2	-0.8	-0.7
TOM	% DW	1063	67.6	17.9	4.2	97.7	-1.0	0.0
tot P	‰ DW	531	15.7	14.1	0.1	158.2	3.5	27.2
tot K	‰ DW	531	31.2	38.7	0.4	300.0	4.2	21.5
tot Ca	‰ DW	449	33.6	29.9	0.2	368.0	5.1	45.8
tot Mg	‰ DW	450	9.8	6.3	0.5	36.4	1.9	4.5
Zn	ppm	264	361.8	342.2	1.0	2,221.8	2.0	4.7
Cu	ppm	264	88.1	107.5	2.8	787.6	3.5	17.1
Ni	ppm	238	19.4	25.5	0.4	247.7	5.6	41.7
Cr	ppm	238	26.2	43.9	0.5	293.5	3.6	13.9
Pb	ppm	238	97.5	364.9	0.0	3,982.0	6.8	59.3
Cd	ppm	165	0.6	0.5	0.0	3.3	2.2	6.9
Sol	%DW	350	26.3	12.9	0.1	85.5	0.7	1.3
Hcel	%DW	350	13.8	7.9	0.0	51.2	0.6	0.8
Cel	%DW	350	14.8	8.4	0.0	45.4	0.4	-0.2
Lic	%DW	350	8.4	5.6	0.1	39.4	1.3	3.5
Ash	%DW	350	36.7	20.9	2.3	98.5	0.7	0.0
Sol-org	%TOM	350	38.7	18.5	2.4	92.8	-0.2	-0.2
Hcel-org	%TOM	350	18.7	10.2	0.2	61.9	0.2	0.5
Cel-org	%TOM	350	20.0	11.2	0.2	47.7	0.0	-0.7
Lic-org	%TOM	350	13.4	10.1	0.4	86.1	2.2	12.0

Organic N: orgN, total organic C: TOC, total organic matters: TOM, total phosphorus: totP, total potassium: totK, total calcium: totCa; total magnesium: totMg, trace elements (zinc: Zn, copper: Cu, nickel: Ni, chromium: Cr, lead: Pb, cadmium: Cd), Van Soest biochemical fractions (soluble: Sol, hemicellulose-like: Hcel, cellulose-like: Cel, and lignin & cutin-like: Lic), n: number of available data for the variable considered (n = 2199 for the whole dataset), SD: standard deviation, Min: minimum value, Max: maximum value, DW: dry weight, ppm: mg.kg⁻¹.

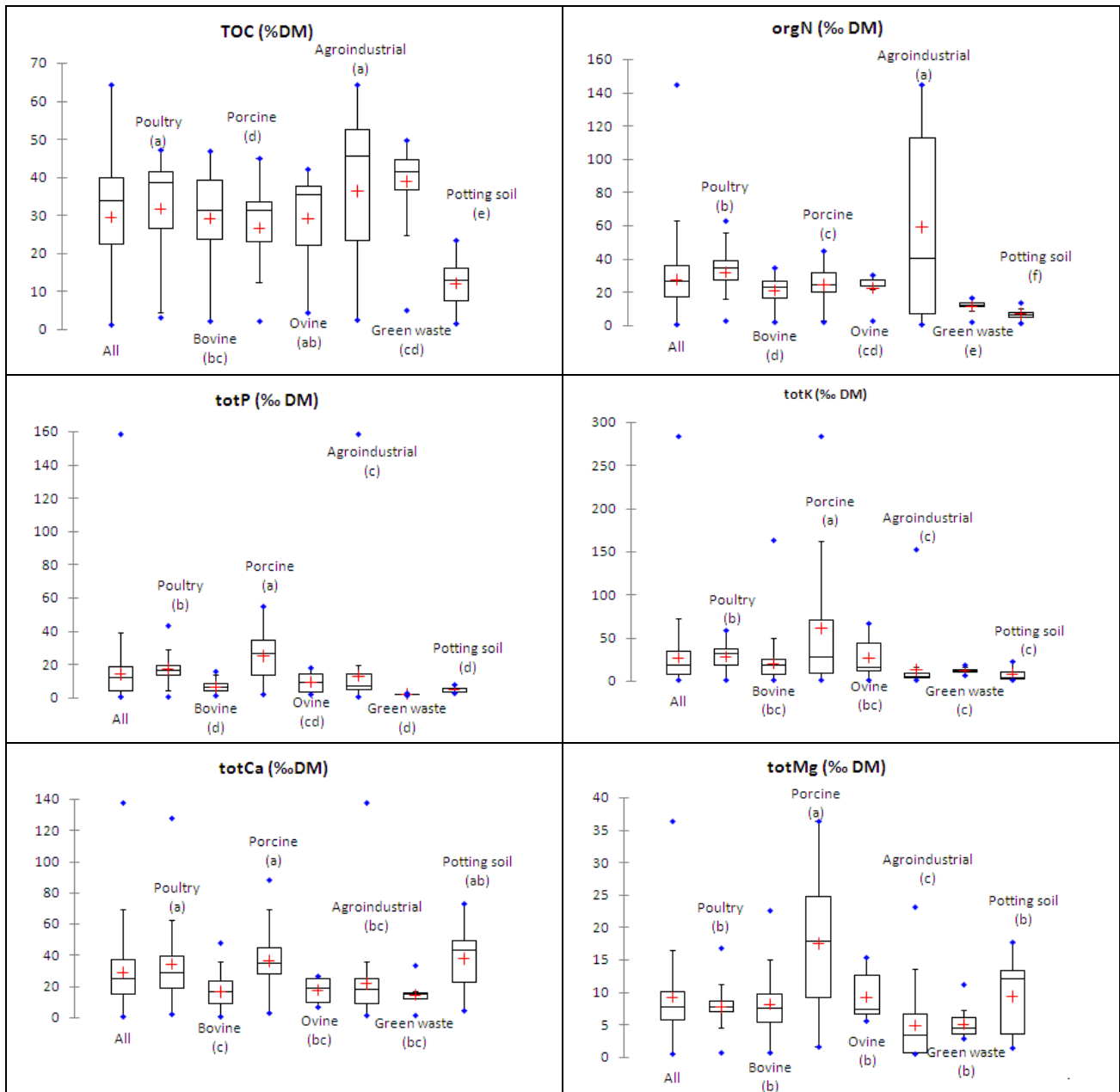


Figure 2.1 : Boxplot showing the distribution of each constituent (TOC, orgN, totP, totK, totCa, totMg) depending on EOM origin.
Different letters between brackets for a given category stand for significant difference between Means

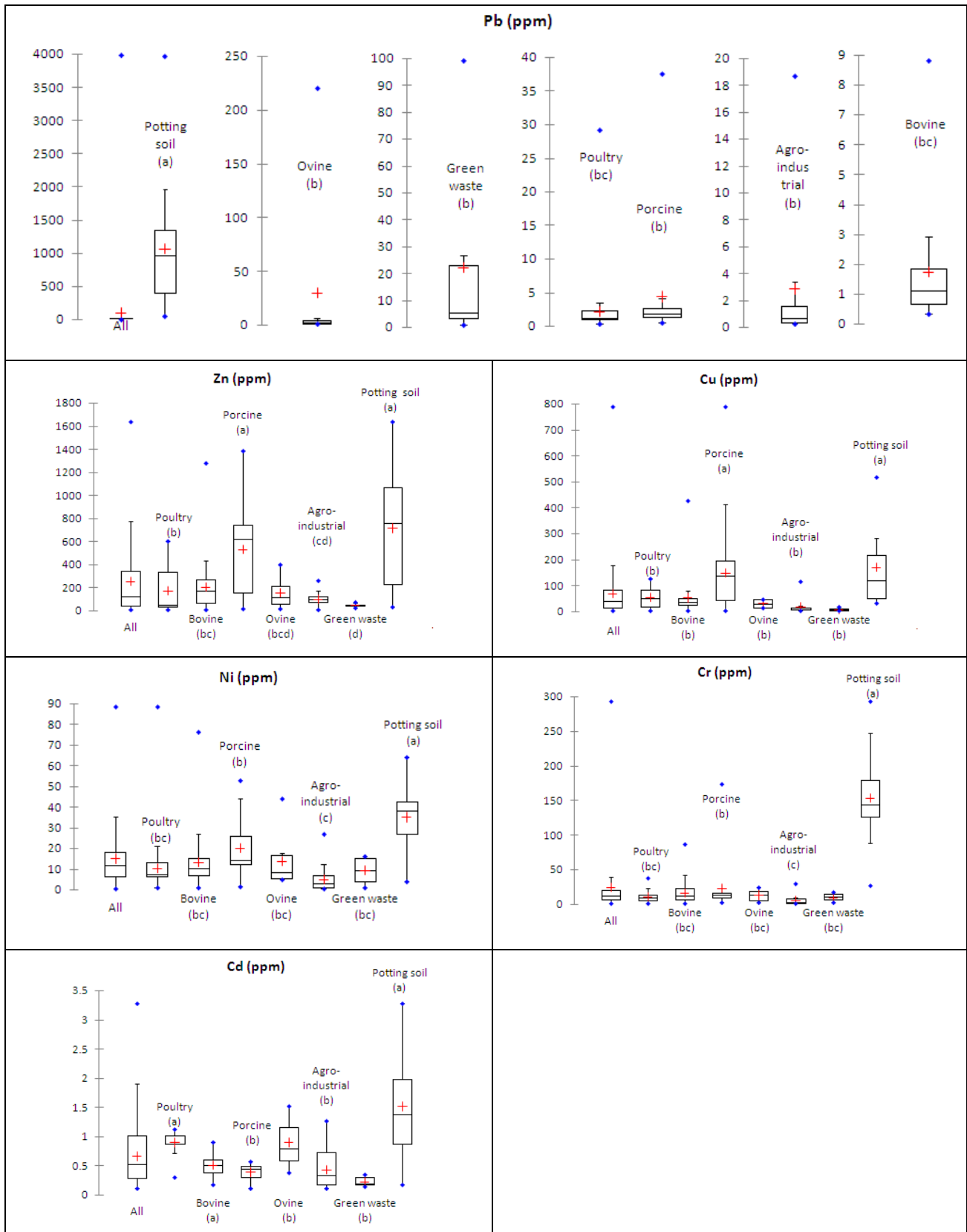


Figure 2.2 : Boxplot showing the distribution of trace elements (Zn, Cu, Ni, Cr, Pb, Cd) depending on EOM origin Different letters between brackets for a given category stand for significant difference between Means



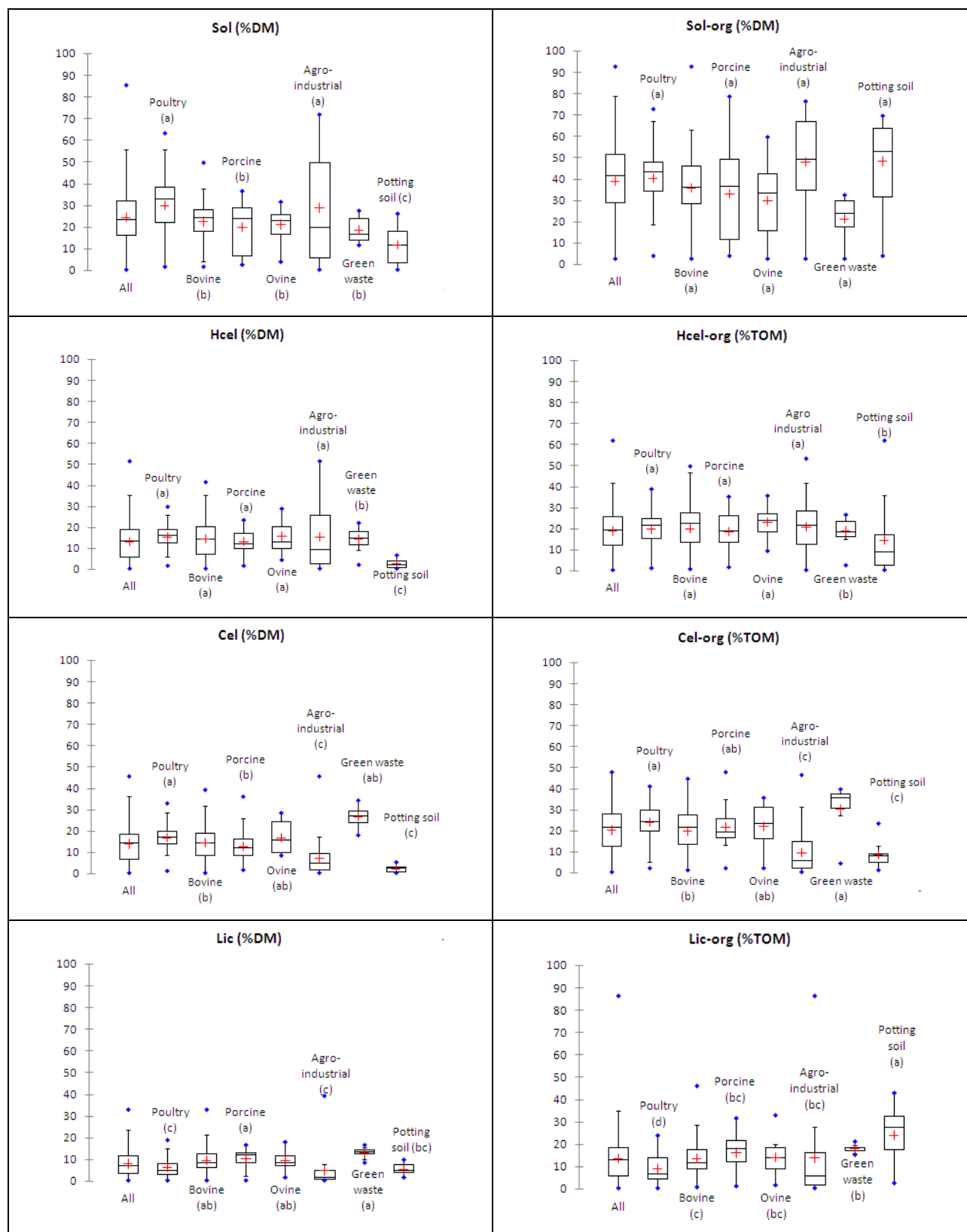


Figure 2.3 : Boxplot showing the distribution of biochemical fractions (Sol, Sol-org, Hcel, Hcel-org, Cel, Cel-org, Lic, Lic-org) depending on EOM origin.
Different letters between brackets for a given category stand for significant difference between Means

2.3.2 NIRS prediction of EOM characteristics

2.3.2.1 Principal Components Analysis

The PCA built with the 2199 EOM samples did not allow a distinction nor the EOM origin (animal, agroindustrial or urban) and nor the EOM category (raw or composted materials, manures with or without litter). Figure 2.4 presents this PCA.

As can be seen with the boxplot and the PCA, it will be not necessary to deal with each EOM category for building the NIRS equations.

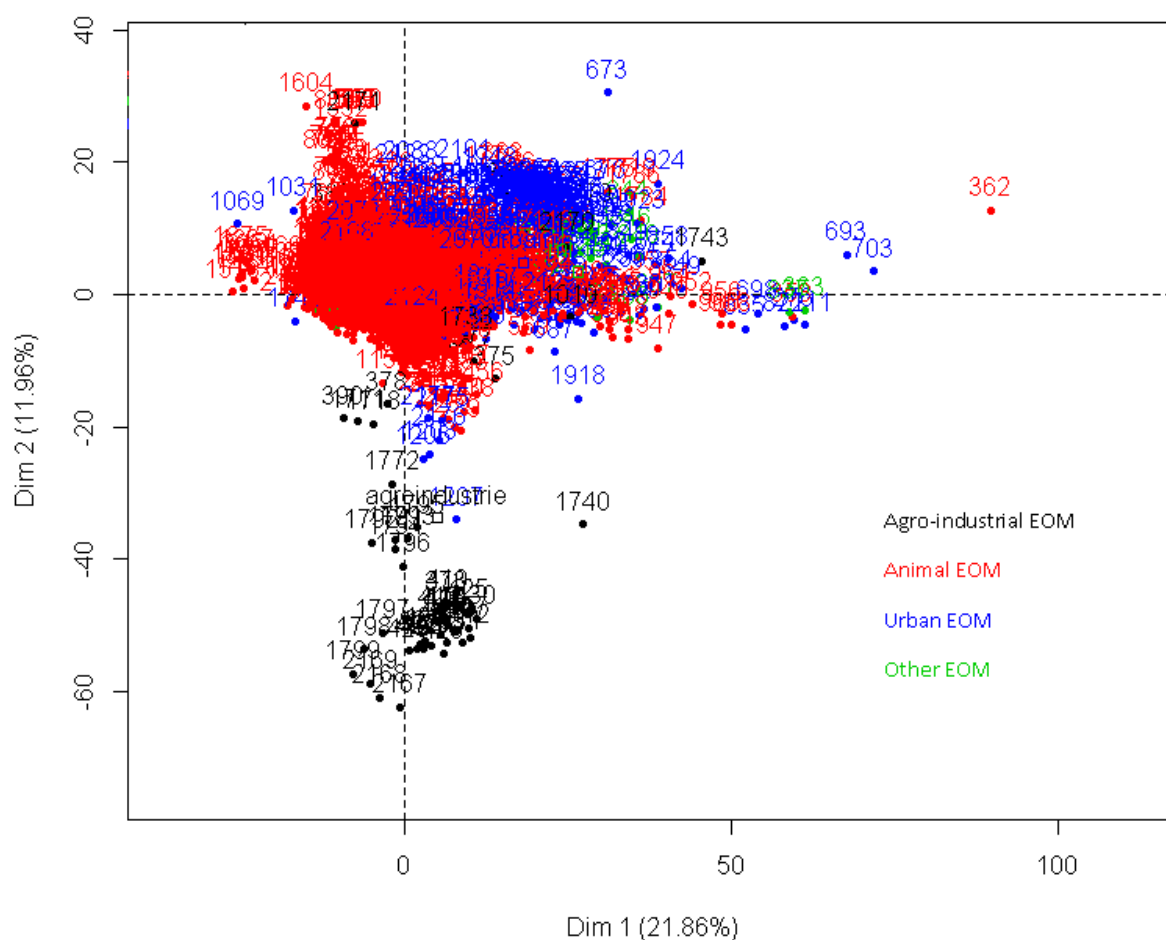


Figure 2.4 : Principal components analysis based on the 2199 samples spectra

Axis 1 and axis 2 represent respectively 21.86% and 11.96% of the total spectra variability

Table 2.2 : Pearson correlation coefficients (r) between analytical characteristics.

(a) Total organic C: TOC, organic Nitrogen: orgN, total organic matter: TOM. With 915 samples, the correlations are significant ($p < 0.001$), r values > 0.5 are in bold

Variables	TOC	orgN	TOM
TOC	1		
orgN	0.54	1	
TOM	0.98	0.53	1

(b) Total organic C: TOC, total phosphorus: totP, total potassium: totK, total calcium: totCa; total magnesium: totMg. With 448 samples, the correlations are significant ($p < 0.001$) from $r = 0.14$, for more relevant interpretations, only r values > 0.5 are in bold

Variables	TOC	totP	totK	totCa	totMg
TOC	1				
totP	-0.03	1			
totK	-0.08	0.22	1		
totCa	-0.26	0.64	0.01	1	
totMg	-0.20	0.58	0.14	0.27	1

(c) Total organic C: TOC, and trace elements: zinc: Zn, copper: Cu, nickel: Ni, chromium: Cr, lead: Pb, cadmium: Cd. With 163 samples, the correlations are significant ($p < 0.001$) from $r = 0.19$, for more relevant interpretations, only r values > 0.5 are in bold

Variables	TOC	Zn	Cu	Ni	Cr	Pb	Cd
TOC	1						
Zn	-0.33	1					
Cu	-0.29	0.68	1				
Ni	-0.43	0.19	0.22	1			
Cr	-0.62	0.60	0.57	0.40	1		
Pb	-0.50	0.50	0.61	0.27	0.58	1	
Cd	-0.20	0.72	0.60	0.09	0.45	0.42	1

(d) Total organic C: TOC and Van Soest biochemical fractions: soluble: SOL, hemicellulose-like: HCEL, cellulose-like: CEL, and lignin & cutin-like: LIC. With 163 samples, the correlations are significant ($p < 0.001$) from $|r| = 0.13$, for more relevant interpretations, only r values > 0.5 are in bold

Variables	TOC	Sol	Hcel	Cel	Lic	Ash	Sol-org	Hcel-org	Cel-org	Lic-org
TOC	1									
Sol	0.63	1								
Hcel	0.70	0.40	1							
Cel	0.58	-0.03	0.40	1						
Lic	0.18	-0.36	-0.11	0.40	1					
Ash	-0.94	-0.66	-0.76	-0.64	-0.16	1				
Sol-org	-0.13	0.59	-0.24	-0.60	-0.62	0.14	1			
Hcel-org	0.31	0.07	0.81	0.60	-0.22	-0.36	-0.33	1		
Cel-org	0.28	-0.30	0.15	0.89	0.41	-0.34	-0.69	0.04	1	
Lic-org	-0.33	-0.61	-0.47	-0.09	0.68	0.41	-0.50	-0.40	0.04	1

2.3.2.2 NIRS calibration and validation statistics

Table 2.3 presents the statistics of the calibration and cross-validation statistics of our calibration set. Validation with samples not included in the calibration set is an essential step in NIR calibration building process. However in relatively small datasets such as some datasets used in this study, the number of validation samples is necessarily limited. Cross-validation, as used in former sections, is therefore complementary as it uses successively all samples in calibration and validation processes.

The calibration (CAL) subset included 80% selected spectra considering as representative spectra in our database. The validation (VAL) subset included 20% of analyzed samples for each parameter. Table 4 presents the statistics of the validation set (20% reference values). The means and SD of the VAL-subset are quite similar to those the whole EOM samples. The VAL subset thus encompasses the variability of the entire dataset.

Table 2.3 : Calibration and validation statistics for the determination of EOM properties

Variables	Units	Calibration									Validation					
		n_c	Mean _C	SD _C	out _C	SE _C	R ² _C	SE _{CV}	R ² _{CV}	RPD _{CV}	n_v	Mean _V	SD _V	SE _P	R ² _P	RPD _P
orgN	g.kg ⁻¹ dw	692	29.16	15.17	48	3.56	0.88	5.10	0.89	2.0	170	34.53	6.96	3.29	0.79	1.6
TOC	g.100g ⁻¹ dw	806	34.51	8.21	55	2.47	0.89	3.72	0.79	2.0	200	38.30	4.50	1.81	0.84	2.3
TOM	g.100g ⁻¹ dw	806	67.76	15.97	55	4.60	0.90	7.28	0.79	2.0	200	76.72	9.05	3.55	0.85	2.3
Ash	g.100g ⁻¹ dw	261	35.68	18.49	12	5.61	0.90	8.72	0.78	2.1	59	24.41	10.19	6.68	0.57	1.2
Sol	g.100g ⁻¹ dw	261	25.98	12.48	15	5.15	0.77	7.05	0.68	1.5	59	32.55	10.26	6.64	0.60	1.0
Hcel	g.100g ⁻¹ dw	261	14.13	7.91	12	3.96	0.70	5.32	0.55	1.4	59	16.51	4.87	3.50	0.49	1.1
Cel	g.100g ⁻¹ dw	261	15.37	8.18	13	2.93	0.85	3.78	0.79	2.0	59	18.51	5.50	3.65	0.57	1.3
Lic	g.100g ⁻¹ dw	261	8.85	5.35	18	2.40	0.72	3.57	0.55	1.3	59	8.01	4.99	2.43	0.78	1.5
orgSol	g.100g ⁻¹ TOM	261	40.74	14.49	17	7.84	0.67	10.17	0.51	1.3	59	42.71	10.40	7.10	0.54	1.0
orgHcel	g.100g ⁻¹ TOM	261	21.06	8.86	17	4.94	0.62	7.26	0.33	1.1	59	21.62	4.92	4.33	0.33	1.0
OrgCel	g.100g ⁻¹ TOM	261	23.45	9.57	14	4.21	0.78	5.44	0.68	1.7	59	24.36	6.28	4.07	0.59	1.3
orgLic	g.100g ⁻¹ TOM	261	14.85	10.20	14	4.26	0.71	7.30	0.49	1.1	59	11.30	7.73	3.81	0.76	1.6
totP	g.kg ⁻¹ dw	402	15.15	12.11	1	5.89	0.76	6.02	0.75	2.0	90	17.90	5.03	3.78	0.53	1.4
totK	g.kg ⁻¹ dw	402	31.55	41.24	7	14.03	0.88	17.93	0.81	2.3	90	37.98	28.11	9.34	0.89	3.0
totCa	g.kg ⁻¹ dw	336	32.82	24.62	9	14.39	0.61	18.96	0.40	1.2	80	31.66	9.38	7.36	0.39	0.8
totMg	g.kg ⁻¹ dw	336	10.21	6.70	4	3.23	0.76	3.58	0.71	1.8	80	9.05	4.23	2.89	0.60	1.5
totZn	ppm	195	321.30	306.60	2	142.73	0.75	179.48	0.66	1.6	45	451.81	191.94	113.88	0.68	1.7
totCu	ppm	195	78.02	102.90	7	46.27	0.56	85.26	0.31	0.8	45	101.33	47.65	38.21	0.37	0.9
totNi	ppm	177	20.05	28.39	7	8.96	0.46	24.90	0.23	0.5	40	12.42	7.40	11.60	0.05	0.9
totCr	ppm	177	20.18	30.21	8	9.83	0.63	19.76	0.57	0.8	40	11.33	7.49	6.31	0.30	0.7
totPb	ppm	177	61.72	218.11	6	52.87	0.45	125.04	0.67	0.6	40	8.90	34.78	12.00	0.91	2.3
totCd	ppm	124	0.54	0.46	5	0.17	0.74	0.32	0.51	1.1	25	0.80	0.34	0.11	0.90	2.6

Organic N: orgN, total organic C: TOC, total organic matters: TOM, total phosphorus: totP, total potassium: totK, total calcium: totCa; total magnesium: totMg, trace elements (zinc: Zn, copper: Cu, nickel: Ni, chromium: Cr, lead: Pb, cadmium: Cd), Van Soest biochemical fractions (soluble: Sol, hemicellulose-like: Hcel, cellulose-like: Cel, and lignin & cutin-like: Lic), DW: dry weight, ppm: mg.kg⁻¹
n: number of available data for the variable considered, Mean: SD: standard deviation, out_C: calibration outliers, SE: standard error, R²: determination coefficient, RPD: ratio performance to deviation; index C, CV and V are related respectively to calibration, cross-validation, and validation.

2.4 Discussion

2.4.1 Heterogenous EOM dataset

As shown in our results, the composition of the studied sample varied greatly according to their origin.

Animal waste had higher TOC, TOM, and orgN contents than the EOM from urban and agroindustrial activities. In many reports, animal wastes are well known as organic matter source, due to their capacity to restore soil fertility, and nutrients providers for plant. Their quality and characteristics mainly depend on:

- The animal, the animal age, the origin and type of feed, ... (Nennich *et al.*, 2005; Bonneau *et al.*, 2008)
- The type of livestock farming: the bedding type (rice straw, sugarcane straw, crytomeria, ...), the maximum stock densities, the water dilution (according to different zone in the animal house), ... (Meyer *et al.*, 2011; Mc Geough *et al.*, 2012)
- The animal dejections storage (Paillat *et al.*, 2005; Rigolot *et al.*, 2010)

Some animal waste as poultry effluents and pig effluents had interested total phosphorus and total potassium contents. Due to their diet, poultry and pig may ingest these elements. It was reported that 70% of phosphorus and till 90% of potassium ingested in their feed can be rejected in their dejections (Chabalier *et al.*, 2006). The presence of metals in animal waste was due to trace elements that were contained in animal diet or other health supplements (European Commission, 2003; Petersen *et al.*, 2007). However, the concentration of metals in manure was generally moderate, especially for toxic Cd and Pb. Micronutrients like Cu and Zn could reach substantial levels because the animal is usually overdosed with these oligoelements to increase productivity and disease resistance (Nicholson *et al.*, 1999; Brock *et al.*, 2006).

Agro-industrial waste studied may have high TOC and orgN according to their nature (e.g. the sewage sludge from chicken slaughterhouse). As can be read in the literature, slaughterhouse effluents resulted of fresh meat preparation and carcasse recovery, which are fat-rich and protein-rich by-products (Salminen *et al.*, 2002; Hejnfelt *et al.*, 2009).

As can be noticed in this study, urban waste and especially landfill potting soil from Madagascar had the highest trace elements contents. This fact can be explained by the absence of sorting at the source and separate treatment for certain hazardous waste (Falinirina, 2010). Composted green waste collected in Réunion had also high metals contents, as

reported by Doelsch *et al.* (2008). However, the source of these contaminations were not yet clear but the natural high trace elements amount in Réunion soil was supposed.

2.4.2 Accuracy of NIRS prediction of EOM characteristics

2.4.2.1 Elemental composition prediction of EOM by using NIRS

The combination of large diversity in sample origin and chemical diversity in our collection of EOM was an important asset of the present NIR calibrations. RPD_{CV} and RPD_P allow an appreciation of the calibration or prediction accuracy according to the criteria reported by Saeys *et al.* (2005). TOC, orgN and TOM were predicted accurately for all EOM dataset. These results for TOC and TOM calibration were in accordance with those reported by Peltre *et al.* (2011). However, orgN was well better predicted in our study than those obtained by Peltre *et al.* (2011). The excellence of prediction by NIRS of these constituents were explained by the strong absorbance of C-N, N-H and C=O groups in NIRS. Due to the heterogeneity of our dataset which included composted manure with and without litter, our models were not as performing as those for composted biowaste (Albrecht *et al.* (2009) with RPD_{CV} of 3.8 and 3.2 for TOC and orgN, respectively.

2.4.2.2 Macroelements prediction of EOM by using NIRS

The reports of some researchers indicated that totP content in poultry origin EOM (Reeves III, 2001), or dairy origin EOM (Millmier *et al.*, 2000; Reeves III *et al.*, 2000), and hog (Millmier *et al.*, 2000) manure was not predicted successfully by the NIRS method. However, other researchers have demonstrated that the NIRS method could be used to predict totP concentration in hog (Malley *et al.*, 2002) and broiler (Smith *et al.*, 2001) manures. The reason may be attributed to the presence of spectrally active P bonds. Some studies have suggested that P may exist in forms detectable by NIRS, at least in some grasses and legumes (Clark *et al.*, 1987). For totK, approximate quantitative prediction was possible when considering all EOM samples with calibration/validation subset. These results were consistent with previous studies (Reeves III, 2001; Yang *et al.*, 2006). For totCa, calibration allowed just an approximate quantitative determination if excellent prediction of totCa in poultry EOM has already reported by Smith *et al.*(2001). For totMg, calibration allowed approximation for all samples EOM. The poor prediction results for totK, totCa and totMg could be explained by the fact that there is a lack of spectral absorption for minerals in the NIR region and that calibrations were generally not good because they depended on the relationships between organic components and the minerals, which are indirect calibrations (Shenk *et al.*, 1992). The problem with such indirect calibrations is that they are only as accurate as the correlation

between the organic component and the mineral of interest and can easily produce erroneous results (Yang *et al.*, 2006).

2.4.2.3 Trace elements prediction of EOM by using NIRS

Calibration built for predicting trace elements had poor accuracy. In fact, no absorption bands for minerals exist in the near-infrared region; however, organic complexes and chelates may be detected (Shenk *et al.*, 1992). However, acceptable predictions for trace elements were reported in literature (Huang *et al.*, 2008). The estimation of mineral elements by NIRS was generally dependent on the occurrence of those elements in organic or hydrated molecules (Clark *et al.*, 1987; Vasquez de Aldana *et al.*, 1995), or mineral levels may simply be correlated to some organic material that the NIRS can easily measure.

2.4.2.4 Biochemical fraction prediction of EOM by using NIRS

In general, RPD_{cv} was below 1.5 excepted for Cel and Cel-org. This suggested that for biochemical fraction only a distinction between low and high value can be done with such calibration. As can be seen here, increasing the diversity of samples in dataset generally causes a reduction in calibration accuracy (Stenberg *et al.*, 2004; Thuriès *et al.*, 2005; Galvez-Sola *et al.*, 2010). As a consequence and in view of the broad heterogeneity of our EOM dataset, the accuracy of our predictions was sometimes poorer than that reported in studies dealing with more homogeneous types of EOM (Vergnoux *et al.*, 2009).

2.5 Conclusion

Characterize a broad heterogeneous range of tropical EOM was the aim of our study. By using laboratory analyses, new references of elemental, trace elements and biochemical components data were produced. By using NIRS technique to determine the content of tropical EOM, predictions were acceptable for TOC, TOM, Ash, orgN, totP, totK and Cel, gave approximate values for Sol, Lic, totMg, Zn and not usable for Hcel, totCa, Cu, Ni, Cr, Pb, Cd. In order to have first appreciation of EOM, NIRS can represent a valuable alternative to expensive and time-consuming reference methods in the laboratory. The NIRS estimations seem sufficiently precise and very profitable for our purpose of a typology of tropical EOM establishment. In our final chapter, the predicted data will be used as entry to a multicriteria analysis procedure.

Chapitre 3. Matières Organiques Exogènes en milieu tropical : Quel potentiel agronomique ? Apport de la spectroscopie proche infrarouge dans la modélisation de leur transformation dans les sols

Avant-propos

Le chapitre développé ci-après a pour objectif principal de renseigner sur le potentiel agronomique des MOEx en milieu tropical. Ce potentiel agronomique est associé à 2 fonctions de la MOEx :

- Sa capacité amendante, ou encore l'aptitude des MOEx à approvisionner le stock de carbone organique dans le sol pour maintenir sa fertilité ; et
- Sa capacité fertilisante, liée à la fourniture d'éléments nutritifs nécessaires à la croissance de la plante.

On se propose alors d'apporter des éléments de réponse en termes de dynamique du carbone organique et de transformation l'azote organique des MOEx une fois apportée au sol.

36 MOEx issues des activités agricoles, urbaines et agroindustrielles de la Réunion et de Madagascar ont été étudiées suivant les normes françaises : caractérisations chimique et biochimique (AFNOR XPU 144-62 (2009)) et suivi de la minéralisation du carbone (C) et de l'azote (N) lors d'une incubation (AFNOR XPU 144-63 (2009)) dans un sol typique de chaque île. Les expérimentations au laboratoire ont duré 6 mois pour les suivis de minéralisation du carbone et de l'azote.

Des modèles prédictifs liant les données biochimiques de MOEx avec des transformations de MOEx dans le sol ont été développés pour pallier cette lourde et longue manipulation. Le modèle TAO (Transformation des Apports Organiques) est proposé dans cette étude pour prévoir les transformations des MOEx: la minéralisation de C et la minéralisation de N, l'immobilisation de N et la reminéralisation de N immobilisé. TAO est entièrement dépendant de la biochimie des MOEx. La structure de TAO pour le C divise les MOEx en trois compartiments comme la plupart des modèles de matière organique de sol plus complexes (Pansu *et al.*, 2004) . Il a été simplifié en utilisant uniquement deux paramètres qui ont défini la fraction très labile et la fraction stable des MOEx et avaient été liés avec des propriétés biochimiques des MOEx (Thuriès *et al.*, 2002). TAO pour le N a été défini en utilisant en complément de TAO pour le C deux nouveaux paramètres (Pansu *et al.*, 2003), et qui avait été de nouveau lié avec les propriétés des MOEx (Pansu *et al.*, 2003). TAO a été calibré à partir d'incubations de MOEx (d'origine tempérée comme tropicale : cornes de bovin, tourteaux de café, de cacao...) utilisées en tant que matières premières ou produits finis du principal fabricant d'engrais organiques en France. Les incubations menées pour la calibration de TAO avaient concerné un Fluvisol du sud de la France. TAO a été récemment testé avec succès

avec un aride Ferric Lixisol du Burkina Faso (Kaboré *et al.*, 2011). Il est à noter que l'établissement du profil biochimique d'une MOEx se fait en une semaine.

Développé dans le chapitre précédent, la spectroscopie proche infrarouge est un outil permettant d'accéder rapidement à certaines caractéristiques des MOEx. Dans cette optique, nous avons donc voulu tester les potentialités de la SPIR pour prédire directement la taille des différents compartiments d'une MOEx nécessaires en paramètres d'entrée du modèle TAO. Cette approche a été validée récemment dans les travaux de Kaboré *et al.* (2012).

Afin de connaître le potentiel agronomique d'une MOEx en milieu tropical humide, nous allons donc :

- déterminer leur composition biochimique et suivre la dynamique de minéralisation de leur carbone et azote organique, et
- tester différentes approches (optimisation, paramètres biochimiques, SPIR) pour connaître la taille des compartiments des MOEx mise en jeu dans le modèle TAO
- comparer le potentiel agronomique des MOEx étudiées avec celui des MOEx métropolitaines françaises. La classification des MOEx suivant leur propriété amendante se fera suivant les valeurs de l'Indice de Stabilité de la Matière Organique (ISMO) développé par Lashermes *et al.* (2009) et des classes vis-à-vis de l'azote établi par Lashermes *et al.* (2010) pour leur propriété fertilisante.

3.1 Introduction

Soil application of EOM could both contribute to environmental issue of improving C sinks to mitigate CO₂ emissions and to the restoration of soil properties related to soil organic matter content (Loveland *et al.*, 2003). Tools for predicting the effect of EOM application on soil organic C would contribute to improvement of their management in farming systems and at the territory scale (Lashermes *et al.*, 2009). On the other hand, tropical farming systems mainly rely on organic fertilizers such as manure, compost, slurry, and other recycled organic matter to maintain crops nitrogen (N) nutrition. Unlike in most mineral fertilizers, the N contained in organic fertilizers only becomes gradually available after application, through a microbial-based decomposition process. It is one of the key challenges of tropical farming to match N release from organic fertilizers and crop demand for N (Cadish *et al.*, 1997). However, predicting N release from organic fertilizers is difficult as it results from many interactions between biotic and abiotic factors (Nett *et al.*, 2010).

EOM decomposition could be assessed by standardized laboratory incubation (AFNOR, 2009). The efficiency of EOM in increasing soil organic matter depends on EOM degradation kinetics following EOM application on soils. This efficiency can be determined by the organic matter composition, such as the different constitutive pools of EOM. A biochemical characterization of EOM using the Van Soest fractionation procedure (Van Soest *et al.*, 1991) has been applied to the characterization of EOM such as animal manure and their compost (Charest *et al.*, 2002; Thuriès *et al.*, 2002; Morvan *et al.*, 2006; Francou *et al.*, 2008), wastewater sewage sludge (Parnaudeau *et al.*, 2004) and is now standardized in France (AFNOR, 2009). An indicator of the fraction of added EOM that might remain in soils has been defined, based both on the quantification of Van Soest biochemical fractions and on the mineralization of added carbon during short-term incubations (Lashermes *et al.*, 2009): the Index of Remaining Organic Carbon (I_{ROC}), now standardized in AFNOR NF XPU-163 (2009).

However, this method is costly and time-consuming. Numerous studies have tried to establish relationship between chemical and biochemical fractions and C or N mineralization of EOM during incubation under controlled conditions (Parnaudeau *et al.*, 2004; Morvan *et al.*, 2006). Henriksen *et al.* (1999) and Thuriès *et al.* (2002) used fiber contents from sequential analysis of EOM for modeling C or N dynamics in soil.

Near infrared reflectance (NIR) spectroscopy has proven its usefulness (compared with classical time-consuming biochemical methods) for the estimation of a variety of parameters

in diverse natural/agricultural products. Total organic matter, carbon and fibers have also been estimated by NIR for evaluation of various EOM quality (e.g.(Peltre *et al.*, 2011)) and decomposition rate.

Predictive models were needed to link EOM biochemical data to EOM transformations in soil. The TAO model (Transformation of Added Organic materials) was proposed to predict the EOM transformations. The TAO-C structure divided into two compartments, a labile one and a stabilized one (Thuriès *et al.*, 2002). The TAO-N model to predict the N mineralization was also parameterized (Pansu *et al.*, 2003). Thuriès *et al.* (2002) proposed a statistical relation between these two C pools and the biochemical composition of the EOM assessed by the Van Soest method, and proposed the TAO-Bioch model (Thuriès *et al.*, 2002). This relation was built up on EOM from organic fertilizer industry of the temperate industrial zone in a South France Fluvisol (FAO-IUSS-ISRIC, 2006) and was successfully tested in the context of the Burkina Faso in West Africa (Kaboré *et al.*, 2011). Kaboré *et al.* (2012) proposed also a prediction of the two C compartments by using Near Infrared Spectroscopy and showed that the model TAO-NIRS could be a relative good tool to predict the C and N mineralization in controlled conditions.

The objectives of this study were: (1) to measure the biochemical composition and the potential C and N mineralization of selected EOM from Réunion and Madagascar, (2) to test different approaches of TAO-model for the C and N mineralization prediction.

3.2 Material and methods

3.2.1 Characterization of Exogenous Organic Matter

3.2.1.1 EOM dataset

The EOM used in this experiment included a range of fresh and transformed organic materials from agricultural, urban and agro-industrial waste applied in agriculture. The dataset included 6 slurries, 10 manures, 5 composted animal dejections, 6 agro-industrial wastes, 6 composted urban wastes and 3 potting soils.

3.2.1.2 Chemical and biochemical characterization of EOM

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 and total nitrogen N (totN) content were determined using the Dumas method. The biochemical composition of EOM was determined using the Van Soest method (Van Soest *et al.*, 1991) as described under the French standard XP U 44-162 (AFNOR, 2009).

3.2.1.3 NIR spectra acquisition and detection of spectral outlier

Two replicates of each sample were packed in circular cups and then scanned in reflectance mode on a monochromator spectrometer (XDS, Foss, Silver Spring, MD, USA), for Réunion samples, and on an ASD spectrometer (Analytical Spectral Devices LabSpec, ASD Inc., Boulder, CO, USA), for Madagascar samples. Spectral data were collected every 2nm from 400 to 2498nm. The spectra (average of 32 scans) were recorded as log (1/reflectance). Each sample was scanned twice (two different cup fillings) and the spectra were averaged after control of the RMS value (Root Mean Square). Because Madagascar spectra and Réunion spectra have been acquired with different instruments, spectrum standardization was necessary. The standardization was performed using the WINISI IV Software (Foss).

3.2.2 Soil and Exogenous Organic Matter (EOM) incubations

3.2.2.1 Soil

The soil (0–10 cm depth) used for these incubations were an Andosol collected at Les Colimaçons [55°18'E; 21°07'S] from Reunion Island and a Ferralsol sampled at Lazaina [47°32'; 18°46'] from Madagascar. The main characteristics (dry matter basis) of these soils are presented in Table 3.1. The collected soil sample was air-dried and sieved to 2 mm.

3.2.2.2 Selected Exogenous Organic Matter (EOM)

Six groups of EOM were selected for the incubation experiment. These EOM corresponded to representative EOM mainly collected in Réunion and Madagascar.

Selected EOM and their characteristics are presented in Table 3.2.

3.2.2.3 Incubation experiments

Incubation experiments were carried out according to the French standard (AFNOR, 2009). Briefly, three replicates of 30 g of air-dried soil mixed with 0.5 g of EOM were incubated in hermetically sealed jars (1L) during 182 days at $28 \pm 1^\circ\text{C}$ in a dark room at 66% soil water-holding capacity. A control sample of 30 g soil without EOM was also incubated.

Incubation results were expressed in $\text{g CO}_2\text{-C g}^{-1}$ added C for C mineralization and in $\text{gInorganic N.g}^{-1}$ added C for N mineralization, in accordance with Thuriès *et al.* (2001) and Pansu *et al.* (2003)

Table 3.1 : Main characteristics of soils used for incubations

	Clay (%)	Fine silt (%)	Coarse silt (%)	Fine sand (%)	Coarse sand (%)	orgC (g.kg ⁻¹)	totN (g.kg ⁻¹)	C-to-N	pH (H ₂ O)
Lazaina	30.7	15.6	2.3	12.9	38.3	18.7	1.4	13.7	5.5
Colimaçons	17.6	26.0	12.1	24.2	20.0	27.0	5.5	4.9	6.1

Table 3.2 : Main characteristics measured on the Exogenous Organic Matter (EOM)

Category	Class	Origin	Nature	Code	Measured data (g.100g ⁻¹ DM)						
					C	N	Sol	Hcel	Cel	Lic	Ash
Agricultural waste	Slurry	Réunion	Dairy slurry	DS-Run	45.3	2.7	26.9	25.7	21.1	8.5	17.7
			Centrifuged pig slurry	PSc-SJ	33.9	2.0	12.7	22.4	17.9	12.7	34.3
		Madagascar	Poultry droppings	PID-P	32.9	5.1	34.9	29.9	8.9	3.4	22.9
			Poultry droppings	PID-V	22.3	2.4	10.5	14.3	20.5	13.0	41.6
			Pig slurry	PS-LiP	15.0	0.8	4.4	11.9	14.6	14.2	54.9
			Dairy slurry	DS-LiB	26.1	2.0	26.5	15.9	20.7	13.0	23.8
	Manure	Réunion	Dairy manure	DM-Run	43.4	2.5	23.6	25.6	23.2	7.9	19.7
			Goat manure	GM-Run	34.8	3.0	31.5	9.6	9.7	11.4	37.8
			Chicken manure	PIM-Av	41.1	4.2	45.4	17.8	18.2	2.2	16.4
			Chicken manure	PIM-Pon	35.8	4.1	34.3	15.9	15.3	4.9	29.5
		Madagascar	Dairy manure	DM-Bb	33.7	2.4	16.1	6.9	17.9	27.7	31.5
			Dairy manure	DM-Bp	29.6	1.9	19.2	20.0	17.4	13.6	29.8
			Rabbit manure	RM	13.3	1.2	26.5	3.9	6.1	10.8	52.7
			Goat manure	GM-Mdg	40.4	2.2	8.5	12.7	15.7	18.1	45.0
			Pig manure	PM-Mdg	20.1	1.2	2.9	9.9	22.6	12.7	51.9
	Composted manure/ slurry/ droppings	Réunion	Compost of chicken manure	CCM-Co	39.0	3.4	40.7	10.1	18.0	6.4	24.9
			Compost of chicken manure	CCM-Rep	26.3	2.2	19.1	5.8	15.8	7.9	51.4
			Compost of pig slurry	CPS Co	31.6	2.1	30.7	7.9	11.3	11.6	38.5
			Compost of centrifuged pig slurry	CPSc-SJ	31.3	3.5	23.5	12.8	11.4	11.9	40.4
		Madagascar	Composted dairy manure with bagasse	CoA	14.9	1.1	12.6	7.7	6.6	8.9	64.1
			Compost of sheep manure and coffee cake	VGT	42.3	2.5	31.3	7.5	15.4	16.2	29.6

Table 3.2 (continued)

Category	Class	Origin	Nature	Code	Measured data (g.100g ⁻¹ DM)						
					C	N	Sol	Hcel	Cel	Lic	Ash
Agro-industrial waste	Agro-industrial waste	Réunion	Slaughter sludge	PSS	64.2	5.4	66.2	20.7	2.4	1.6	9.2
			Sugar scum (lime)	SCUM	29.4	1.5	26.6	18.7	13.5	4.1	37.1
		Madagascar	Slaughterhouse waste	SHW	40.3	9.9	49.5	31.2	1.6	1.5	16.1
			Oil mill	OMW	46.1	7.1	71.2	17.3	3.5	1.4	6.5
			Fishery	FSW	22.9	4.0	29.3	5.4	8.6	0.4	56.3
			Zebu ground horn	ZGH	23.6	7.4	1.1	2.5	6.0	39.4	51.0
Urban waste	Composted urban waste (fermentable waste, green waste, ±manure.)	Réunion	Composted green waste with sewage sludge	CGWSS	27.2	2.8	31.7	5.7	7.3	9.1	46.2
			Composted green waste	CGW-LP	14.3	1.4	20.1	0.0	3.3	3.6	73.3
			Composted green waste	CGW-SP	23.0	1.4	18.9	3.0	10.2	8.9	58.9
		Madagascar	Composted fermentable waste	CFW-M	18.5	1.0	16.6	2.7	2.6	9.0	69.1
			Composted fermentable waste	CFW-U	13.2	0.6	15.1	0.7	2.9	9.8	71.5
	Potting soil from landfill	Madagascar	Potting soil from landfill	LPS-A	19.6	0.8	12.0	1.4	1.8	13.1	71.7
			Potting soil from landfill	LPS-I	11.0	0.6	7.4	0.9	0.8	5.7	85.1
			Potting soil from landfill	LPS-T	9.9	0.5	2.2	1.9	0.7	3.7	91.5

3.2.3 Exogenous Organic Matter modelling : The TAO model

3.2.3.1 Description of TAO model

TAO-C is a parallel three-compartment model using only two parameters (very labile: P'_L and stable: P_S fraction of EOM) to predict C mineralization. TAO-N used two additional parameters to predict N transformations (fraction P_{im} of transformed EOM which is re-immobilized, rate k_{remin} of re-mineralization of this immobilized fraction). For few N-rich EOM a further parameter was used, the rate k_V for gaseous losses of produced inorganic-N. Thuriès *et al.* (2001) showed that the mineralization rates of very labile (k'_L) and resistant (k_R) compartments of EOM could be considered as constants for a wide range of raw materials from plant or animal origins, manures, organic fertilizers used in the French organic fertilizer industry with:

$$k'_L = 0.4 \pm 0.15 \text{ day}^{-1} \text{ (half life } T_{1/2} = 1.7 \text{ d)} \quad \text{Equation 3.1}$$

$$\text{and } k_R = 0.012 \pm 0.003 \text{ day}^{-1} \text{ (} T_{1/2} = 58 \text{ d)} \quad \text{Equation 3.2}$$

The mineralization rate of the Stable compartment $[S]$ was set to 0 for a 6-month experiment. So the remaining added organic carbon fraction (RAOCF) after C mineralization was obtained at a given time of incubation (t) from time of EOM application (t_0) by:

$$RAOCF = P'_L e^{-0.4(t-t_0)} + (1 - P'_L - P_S) e^{-0.012(t-t_0)} + P_S \quad \text{Equation 3.3}$$

Where $P_R = (1 - P'_L - P_S)$ corresponded to the fraction of intermediary resistant compounds.

Writing P'_L , P_R , P_S , the C-to-N ratios of very labile, resistant and stable EOM-compartments, respectively, the remaining added organic nitrogen fraction (RAONF) was:

$$RAONF = \frac{P'_L}{\eta_L} e^{-0.4(t-t_0)} + \frac{1 - P'_L - P_S}{\eta_R} e^{-0.012(t-t_0)} + \frac{P_S}{\eta_S} \quad \text{Equation 3.4}$$

3.2.3.2 TAO parameters optimisation : TAO-Par

TAO-Par was programmed on VENSIM 4.2 (Ventana systems Inc., Harvard, MA, USA). Simulation was run without any modification of the initial model equations and parameter estimations (Thuriès *et al.*, 2002; Pansu *et al.*, 2003). The input data were added organic C (AOC) and added organic N (AON) and all biochemical fractions of each EOM. The output data were the predicted transformation of C and N forms of each EOM during 182 days of incubation. The outputs curves of C mineralization were total AOC, labile, resistant and stable AOC. For N transformations the selected predictive curves were non-transformed AON, immobilized AON and inorganic N from EOM.

3.2.3.3 TAO parameters defined with EOM characteristics: TAO-Bioch

TAO-Bioch adjusted the different compartments to the mineralization data collected on each EOM. For TAO-C, the linkage between TAO parameters and biochemical characteristics of EOM were established in Thuriès *et al.* (2002). For TAO-N, Pansu *et al.* (2003) defined the formula used to link EOM properties and N mineralization.

3.2.3.4 TAO parameters predicted by NIRS calibration: TAO-Nir

Pre-processed spectral data were calibrated to P'_L and P_R values. These two parameters were previously adjusted from the TAO-Par equation applied to the mineralization data collected on each EOM. The stepwise multiple linear regressions (MLR) was chosen to select the most informative wavelengths and for its good predictive power compared to modified partial least square regression (mPLS) in this case due to the few samples in our dataset (Geladi *et al.*, 1986). The spectra were transformed using the multiplicative scatter correction (MSC) second derivative and smoothing calculated over five data points on both sides which enhances spectral features. MLR calibration was performed using cross-validation. The outliers for calibration (i.e. samples with Student t test > 2.5) were removed and other cross-validations were performed, the procedure being carried out twice. The model performance was assessed using the determination coefficient R^2 and the ratio of performance to deviation ($RPD = SD / SE$), SD and SE stand respectively for standard deviation and standard error.

Depending on the matrix, predictions can be characterized as successful for $RPD > 2$ (Chang *et al.*, 2001), or moderately successful for RPD from 2.5 to 3 (Malley *et al.*, 2004). However, as mentioned by Bellon-Maurel *et al.* (2010), awareness have to be taken when using RPD as calibration accuracy assessment. RPD had some limits and critical points because SE depends on the range of the reference values (calibration set and validation set) and SD does not describe correctly the spread of population in skewed populations. In order to assess the accuracy of our prediction, SE will be better compared with the SEL, the standard error of laboratory.

3.2.3.5 Testing the accuracy of the different TAO versions to predict carbon and nitrogen mineralization

As detailed in Kaboré *et al.* (2012), F-tests were used for significances of TAO-Par, TAO-Bioch or TAO-NIR

The significance of TAO predictions compared to the mean of measured values was tested by:

$$F = \frac{\sum_{i=1}^n (\bar{y}_i - \bar{y})^2 / (n-1)}{\sum_{i=1}^n (\bar{y}_i - \hat{y}_i)^2 / (n-p)} \quad \text{Equation 3.5}$$

Where $i = 1, \dots, n$ is the number of sampling occasions, p the number of model parameters ($p=2$ for TAO-Par, $p=0$ for TAO-Bioch and TAO-NIR), $\bar{y}_i$ the mean measured RAOCF value at i , $\hat{y}_i$ the corresponding predicted value by TAO-Par, TAO-Bioch or TAO-NIR and $\bar{y}$ the mean of the data series.

3.2.4 Classification of Exogenous Organic Matter

3.2.4.1 Classification: Stable organic C in EOM

The indicator of remaining organic carbon in soil (I_{ROC}) estimates the stable pool of EOM-TOC potentially remaining in soil over the long term after application. The I_{ROC} is expressed as a percentage of TOM (Lashermes *et al.*, 2009). It was calculated by using the SOL, CEL and LIC fractions of Van Soest fractionation expressed in $\text{g.100g}^{-1}\text{TOM}$ and the quantity of EOM-TOC mineralized after 3 days of incubation (C_{3d}) expressed in $\text{g.100g}^{-1}\text{addedC}$, according to the formula:

$$I_{ROC} = 44.5 + 0.5 \text{ SOL} - 0.2 \text{ CEL} + 0.7 \text{ LIC} - 2.3C_{3d}$$

In theory, I_{ROC} value was supposed to be close to the non mineralized C part after 182 days. I_{ROC} -theory can be calculated as following:

$$I_{ROC_theory} = 100 - C_{182d}$$

where I_{ROC} was expressed in $\text{g.100g}^{-1}\text{TOM}$;

and mineralized-C after 182 days (C_{182d}) expressed in $\text{g.100g}^{-1}C_{added}$

3.2.4.2 N classification

Figure 3.1 summarizes the classification of EOM according to the N typology based on chemical and biochemical characteristics of EOM as described by Lashermes *et al.* (2010).

The classes of potential N availability of EOM established by Lashermes *et al.* (2010) according to the estimation of the N released in field condition based on the extrapolation of the N mineralized during laboratory incubations suggested to categorize EOM in 6 classes: (i) very high N mineralization, (ii) high N mineralization, (iii) medium N mineralization, (iv)

medium to low N mineralization, (v) low N mineralization/risk of induced N immobilization and (vi) risk of induced N immobilization

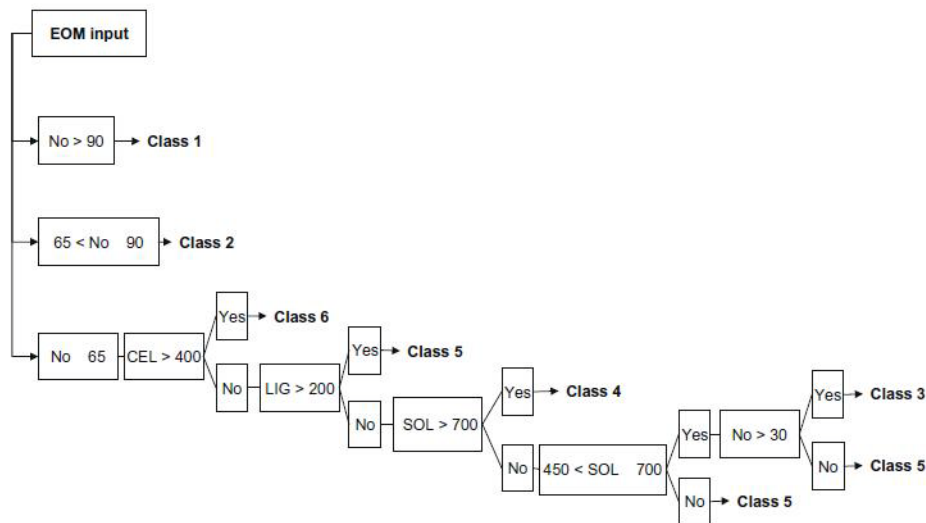


Figure 3.1 : EOM classification according to the N typology described by Lashermes *et al.* (2010)

EOM: Exogenous Organic Matter, No: organic Nitrogen, CEL: Cellulose fractions, LIG: Lignine and cutins fractions, SOL: Soluble fractions

3.3 Results

3.3.1 Measured mineralization

3.3.1.1 Measured C mineralization

Kinetics of C mineralization were different for each EOM. Most of EOM from animal origin were rapidly mineralized. For different slurries and droppings, 52% (PS-LiP) and up to 100% (PID-V and PID-P) of EOM-C were respired. A over mineralization was observed for PID-V and PID-P. This could refer to the "priming effect" process where soil organic matter could be mineralized when fresh organic matter was added into soil (Kuzyakov *et al.*, 2000; Fontaine *et al.*, 2003). For manures, mineralized C was between 22% and 69% according to their origin. For example, only 32% of DM-Bb added C was mineralized during the 182 days. This suggests that the non-mineralized C was stabilized or was processed for stabilization. Mineralization of composted manures varied with a range of mineralized C from 28 (CPSc-SJ) to 84% (VGT). For the composted urban waste, the minimum and maximum mineralized C were respectively 30% (CGW-LP) and 80% (CFW-U). Three of the six studied agro-industrial wastes presented a C mineralization up to 100% of the initial added C (SHW, OMW and FSW) that supposed a "priming effect" process. For the other, C mineralization ranged between 67% and 89%. The potting soil showed an important intra significant difference

between LPS-A and LPS-I on one hand, and LPS-T on the other hand because mineralized C were respectively 10%, 25% and 115% for LPS-A, LPS-I and LPS-T.

3.3.1.2 Measured N mineralization

The soil inorganic N dynamics and the amounts of net N mineralization after addition of the EOM were variable. Three types of kinetics were identified:

- (i) An initial substantial net mineralization which decreased after 14 days (e.g. PID-P, PIM-Av1, CPSc-SJ, SHW)
- (ii) Very low N mineralization or immobilization (e.g. DS-LiB, DM-Bb, SCUM, CGW-SP)
- (iii) Net N immobilization during the first 10 days followed by net N mineralization until the end of the incubation (e.g. PSc-SJ, CCM-Co, VGT)

Figure 3.2: Measured and predicted C mineralization

The x-axis represents the time of incubation in days, the y-axis represents the mineralized added carbon of EOM, symbols represent experimental data (n=3), lines represent the prediction according to TAO-Bioch, TAO-Par or TAO-Nir, vertical bars represent the maximum cumulative of cumulative confidence intervals at 95%.

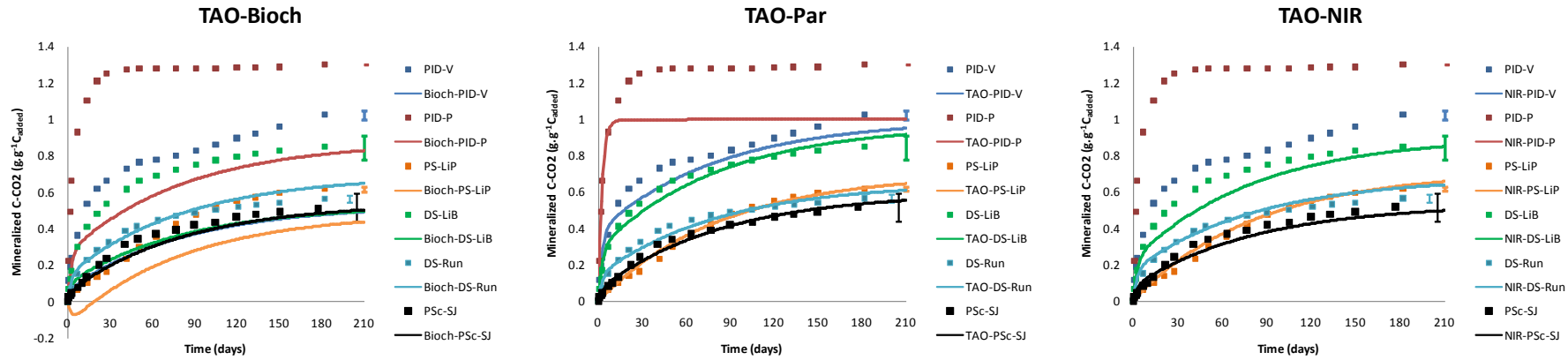
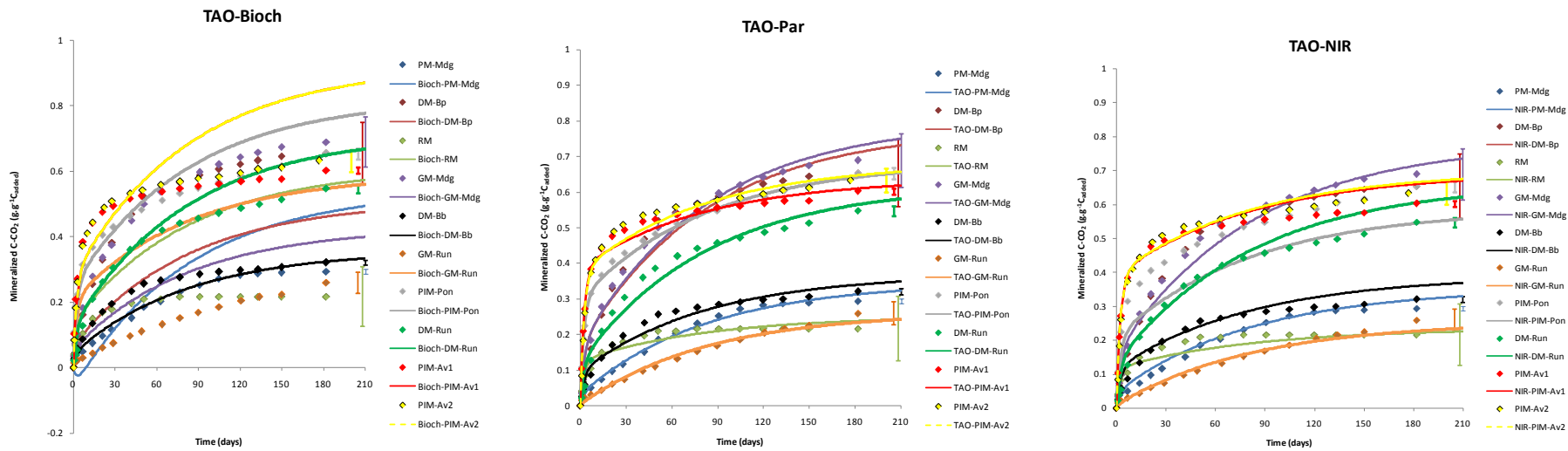
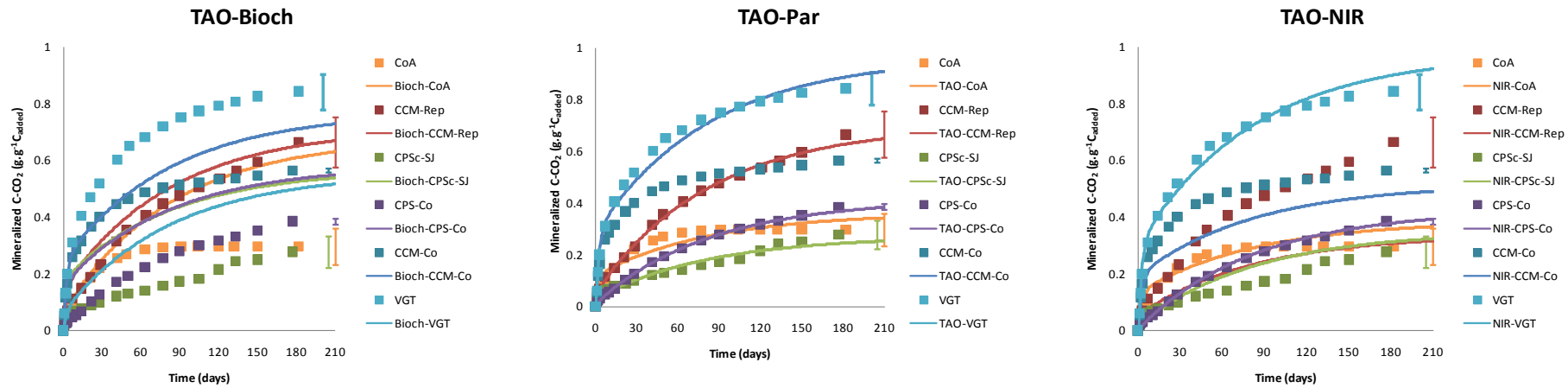
C measured and modelled mineralization for Slurries**C measured and modelled mineralization for Manures**

Figure 3.2 (continued)

C measured and modelled mineralization for Composted Animal Waste



C measured and modelled mineralization for Composted Urban Waste

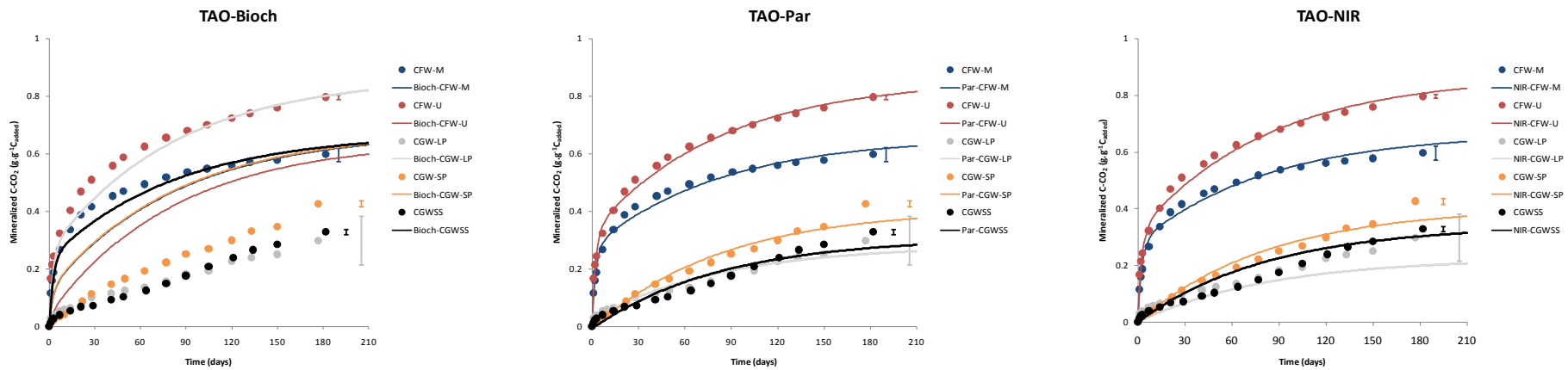
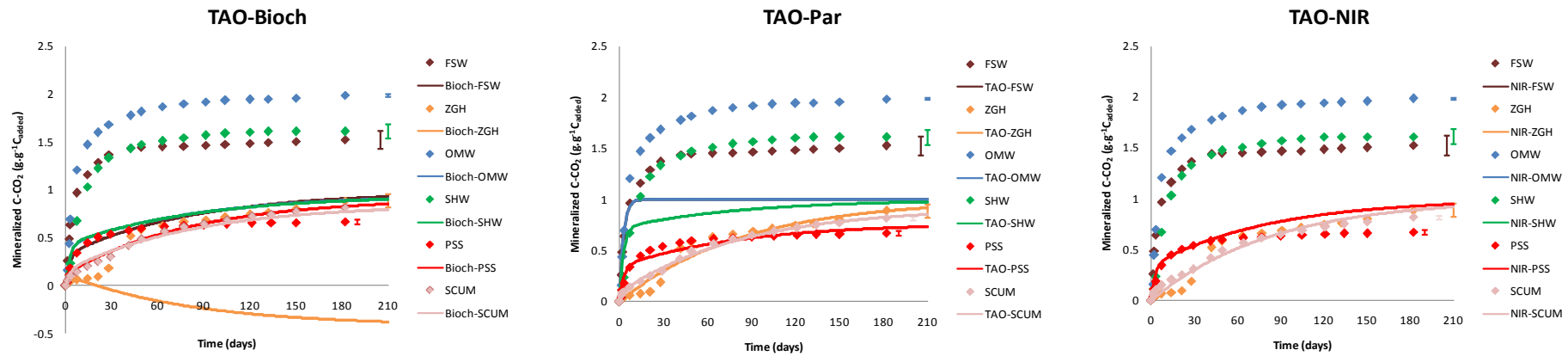
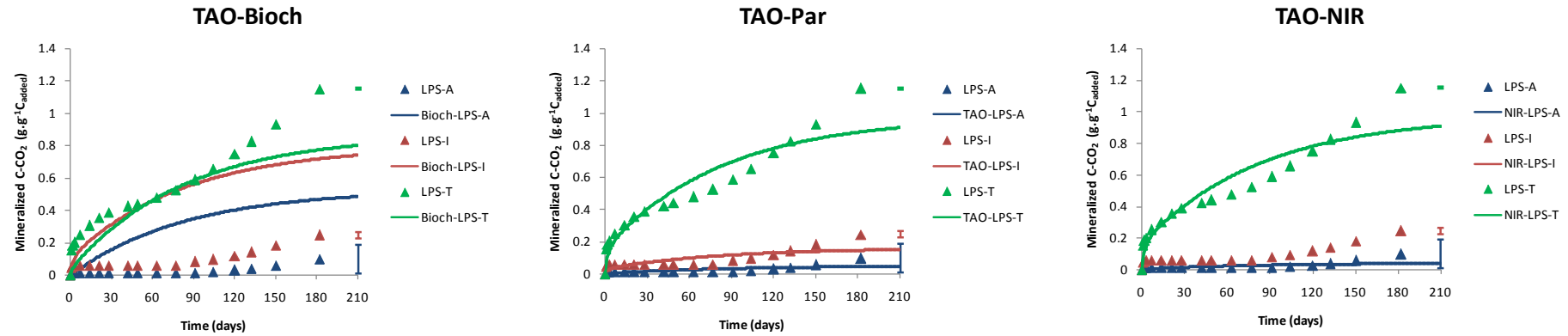


Figure 3.2 (continued)

C measured and modelled mineralization for Agroindustrial waste



C measured and modelled mineralization for Potting soil



3.3.2 Modelling Exogenous Organic Matter transformation by using TAO

3.3.2.1 Modelling C mineralization by different TAO definitions

Data and different TAO predictions of C mineralization are presented in Figure 3.2.

3.3.2.1.1 Accuracy of TAO-parameters model

The TAO-parameters (TAO-Par) model is based on the P'_L and P_S compartments adjustments of measured C mineralization data. TAO-Par assessed accurately the C mineralization of EOM which mineralization did not exceed 100%. Such result was not surprising because TAO-Par was not defined to take into account the interaction between the EOM and the native soil organic matter that would explain the “priming effect” phenomena. The F-tests did not show any significant difference between the laboratory measurements and the predicted values for the 10 manures, 5 composted animal waste, 6 composted urban waste, 5 slurries, 3 agro-industrial wastes and 1 potting soil. For EOM that presented a priming effect, the TAO-Par for C reached a ceiling at 100 % and was not represented in the corresponding figures.

3.3.2.1.2 Accuracy of TAO-C biochemical model

The TAO-C biochemical (TAO-Bioch) model was based on the assessment of the P'_L and P_S compartment by the biochemical composition of EOM. P'_L , and P_S compartments were variable between EOM groups. As reported in Table 3, the F-tests showed significant difference at a level of 10% for 50% of slurries, 60% of manures, 60% of composted animal manures, 67% of agro-industrial waste, 83% of composted urban waste and 67% of potting soil. TAO-Bioch gave good prediction for a few proportion of EOM.

3.3.2.1.3 Near infrared spectroscopy prediction of TAO parameters

Table 3.3 shows the results of NIR spectroscopy calibration of the P'_L and P_R compartments using multiple linear regressions (MLR) between spectral data and reference data. Reference data were the P'_L and P_R values assessed by TAO-Par, namely the Vensim-optimized P'_L and P_R measured values. The RPD values of 3.0 for P'_L and 3.4 for P_R indicated an accurate an accurate model of the prediction of the two compartments. Figure 3.3 plots P'_L -NIR and P_R -NIR spectroscopy predictions versus optimized values from measured incubation data.

Table 3.3: Accuracy of the NIR spectroscopy calibration by multi-linear regression (MLR) of the TAO parameters

Constituent	N	Pre-processing method	Mean	SD	SE	R ²	RPD	Terms number
P' _L	28	MSC 255	0.133	0.126	0.042	0.88	3.0	7
1-P' _L -P _S	29	MSC 255	0.422	0.207	0.060	0.91	3.4	9
P _S	26	MSC 255	0.425	0.249	0.153	0.61	1.6	3

MSC: Multiplicative Scatter Correction

Terms number: Number of selected wavelengths in the models

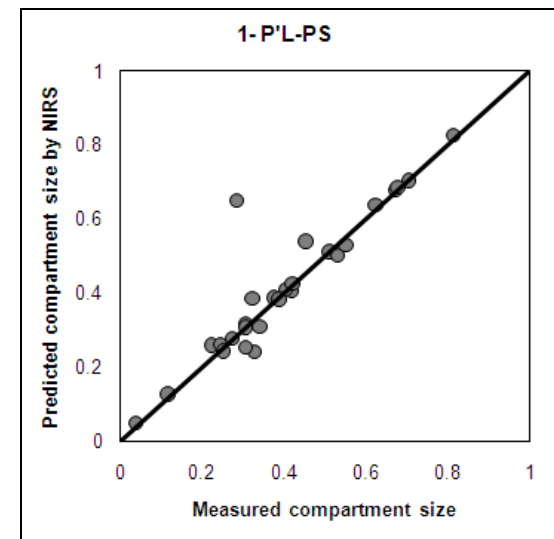
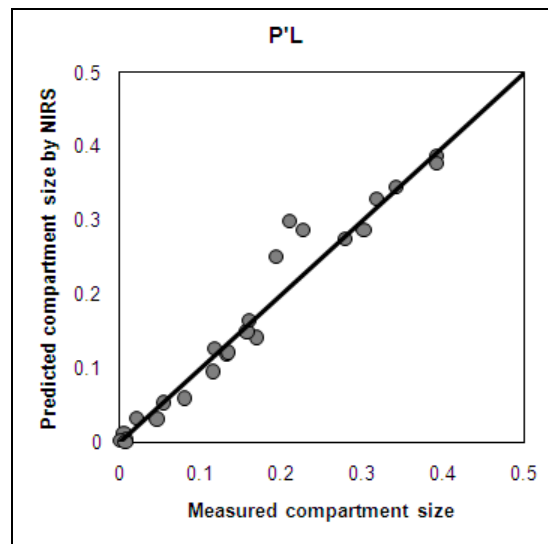


Figure 3.3 : Measured vs predicted compartments size expressed in proportion of added C by using NIRS

3.3.2.1.4 Comparative predictions of carbon mineralization

Table 3.4 summarizes the results of three model predictions of EOM-C mineralization in soil by TAO using:

- (i) Optimized values of P'_L , P_R and P_S in the TAO-Par model
- (ii) P'_L , and P_S calculated from biochemical data (TAO-Bioch)
- (iii) P'_L , P_R and P_S calculated from spectral data (TAO-NIR)

The TAO-NIR model predicted significantly EOM-C mineralization of 42/57 EOM used for calibration, 36 at risk <1% and 6 at risk <5%. Most of the non-significant EOM-C mineralization predictions concerned stable EOM with high P_S values and low variation of RAOCF around the mean value of the data series. In many cases, despite the non-significant F test, most NIR spectroscopy predictions were included in the confidence intervals of measured data.

TAO-Bioch predicted significantly RAOCF of 14 out of the 21 tested EOM, similar to that of TAO-NIR for 12 EOM. TAO-Bioch predicted RAOCF significantly better than TAO-NIR for two EOM and significantly lower for 7 EOM.

In all cases, it was not surprisingly that the TAO-Par model gave the best predictions of the three TAO versions, but F-value was not significant for 24 EOM (i.e. the two model versions gave similar predictions). TAO-NIR was less accurate than TAO-Par at 5% risk for 4 EOM and at 1% risk for 29 EOM, but 26 of the 29 considered EOM for TAO-NIR predictions were included in the 95% confidence intervals of the measured data.

3.3.2.2 Modelling N mineralization by TAO

The TAO-Par model is based on the optimization of P_{im} , k_{remin} and C-to-N ratio. The F-tests did not show any significant difference between the laboratory measurements and the predicted values for the 7 manures, 5 composted animal wastes, 4 composted urban wastes, 3 slurries, 3 agro-industrial wastes and 2 potting soils. TAO-Par were significant at a level of 10% for 1 slurry, 1 manure, 2 composted wastes, 1 potting soil and 3 agro-industrial waste; at a level of 5% for 1 slurry, 1 manure, 1 agro-industrial waste and 2 composted animal wastes, at a level of 1% for 1 slurry and 1 manure.

For EOM which presented N immobilization during the first month, the mineral N was overestimated by TAO-N, but for the next five months when the mineral N were relatively constant, TAO-N allowed a better assessment of N kinetics.

Table 3.4 : Comparison of prediction of labile and resistant compartment by TAO-Bioch (P'_L , P_R and P_S calculated from biochemical data), TAO-Par (optimized values of P'_L , P_R and P_S), and TAO-NIR (P'_L , P_R and P_S predicted from NIR spectra)

Groups		Bioch			Par			NIR			RISK	mes	mes	mes	bioch	bioch	par
		P'_L	P_R	P_S	P'_L	P_R	P_S	P'_L	P_R	P_S		vs.	vs.	vs.	vs.	vs.	vs.
												bioch	par	nir	par	nir	nir
Slurry	n	6	6	6	6	6	6	4	4	4	ns	33%	83%	83%	17%	33%	67%
	mean	0.082	0.529	0.389	0.311	0.525	0.164	0.122	0.588	0.291	*						
	min	0	0.433	0.122	0.000	0.003	0.000	0.008	0.454	0.094	**	17%	17%				
	max	0.264	0.614	0.513	0.997	0.707	0.402	0.227	0.707	0.465	***	50%			83%	33%	
Manure	n	10	10	10	10	10	10	9	9	9	ns	40%	100%	90%		20%	90%
	mean	0.137	0.505	0.358	0.176	0.368	0.456	0.175	0.343	0.482	*						
	min	0	0.316	0.079	0.003	0.126	0.199	0.009	0.117	0.215	**					10%	
	max	0.277	0.645	0.641	0.387	0.637	0.748	0.392	0.625	0.765	***	60%			100%	60%	
Composted manure/ slurry/ droppings	n	5	5	5	5	5	5	5	5	5	ns	40%	100%	80%		40%	100%
	mean	0.161	0.503	0.336	0.094	0.384	0.522	0.082	0.322	0.596	*						
	min	0.066	0.391	0.229	0.012	0.241	0.299	0.006	0.253	0.483	**						
	max	0.246	0.614	0.430	0.250	0.648	0.727	0.194	0.421	0.660	***	60%		20%	100%	60%	
Agro-industrial waste	n	6	6	6	6	6	6	1	1	1	ns	33%	50%	17%	50%		17%
	mean	0.260	0.445	0.296	0.525	0.423	0.052	0.342	0.422	0.236	*						
	min	0.116	-0.536	0.016	0.000	0.000	0.000	0.342	0.422	0.236	**						
	max	0.423	0.794	1	1.000	1.000	0.231	0.342	0.422	0.236	***	67%	50%		50%	17%	
Composted urban waste (fermentable waste, green waste, ±manure.)	n	6	6	6	6	6	6	6	6	6	ns	17%	100%	100%			100%
	mean	0.142	0.541	0.317	0.152	0.428	0.420	0.150	0.432	0.419	*						
	min	0.040	0.438	0.131	0.000	0.259	0.036	0.000	0.225	0.023	**						
	max	0.262	0.607	0.444	0.328	0.677	0.718	0.317	0.675	0.775	***	83%				100%	
Potting soil from landfill	n	3	3	3	3	3	3	2	2	2	ns	33%	33%	33%	33%	33%	67%
	mean	0.042	0.689	0.269	0.061	0.335	0.604	0.081	0.428	0.492	*						
	min	0	0.533	0.132	0.002	0.049	0.026	0.003	0.040	0.026	**		33%				
	max	0.101	0.839	0.473	0.149	0.825	0.950	0.158	0.816	0.957	***	67%	33%	33%	67%	33%	

n : number of samples in the category, **mean** : mean value of the compartment size in the category, **min**: minimum value of the compartment size in the category, **max**: maximum value of the compartment size in the category, **ns**: percentage of EOM presenting non significant difference between measured and predicted values or between 2 predicted values, *: percentage of EOM presenting significant difference at level of 0.1 between measured and predicted values or between 2 predicted values, **: percentage of EOM presenting significant difference at level of 0.05 between measured and predicted values or between 2 predicted values, ***: percentage of EOM presenting significant difference at level of 0.001 between measured and predicted values or between 2 predicted values

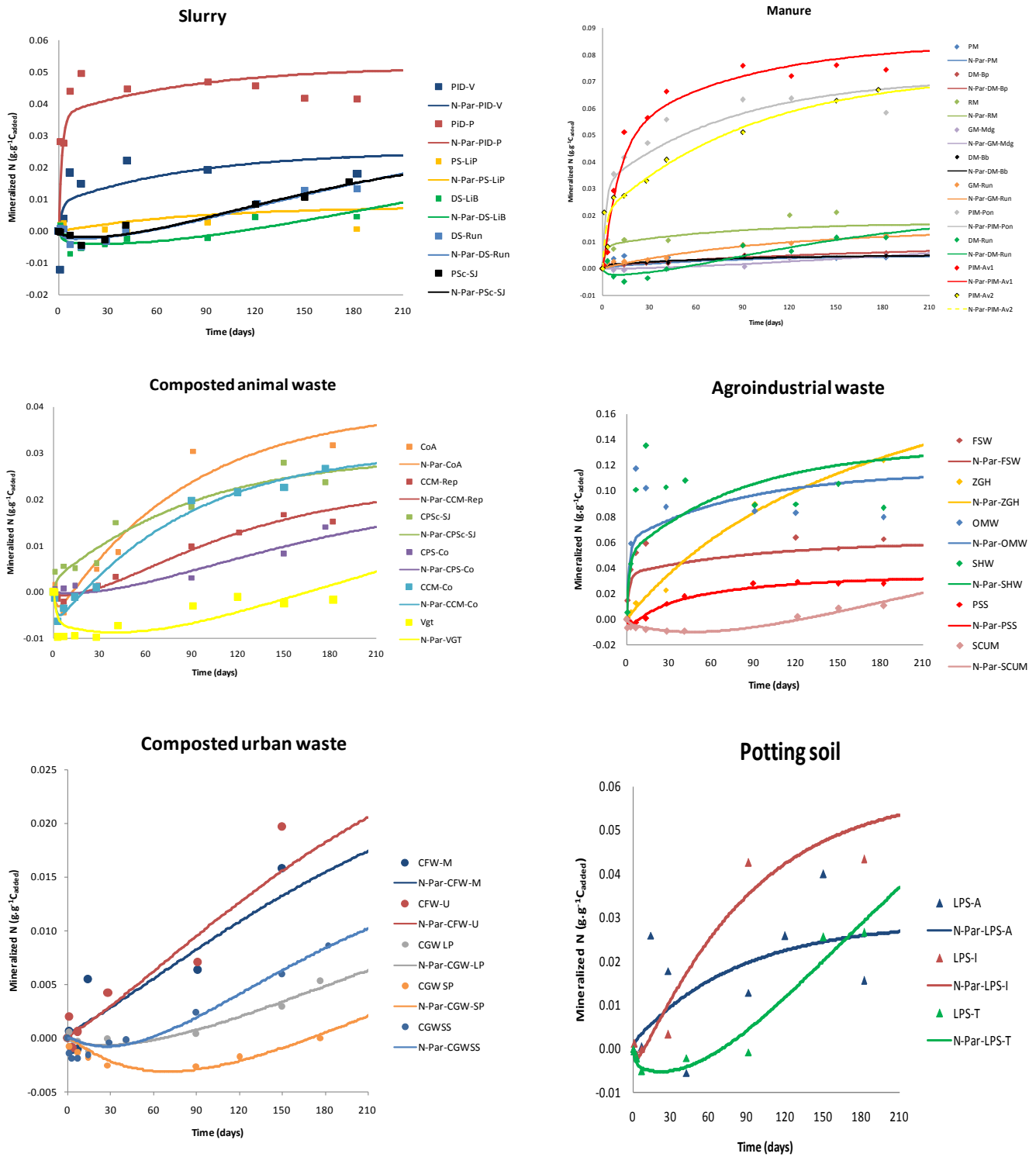


Figure 3.4 : Measured end predicted nitrogen mineralization

The x-axis represents the time of incubation in days, the y-axis represents the mineralized added nitrogen of EOM, symbols represent experimental data (n=3), lines represent the prediction according to TAO-Par.

Table 3.5 : Comparison of prediction of P_{im} , k_{remin} and C-to-N ratio by TAO-Bioch (k_{remin} and C-to-N ratio calculated from biochemical data), TAO-Par (optimized values of P_{im} , k_{remin} and C-to-N ratio)

Groups		Bioch			Par			RISK	Mes vs. bioch	Mes vs. par
		P_{im}	k_{remin}	C-to-N	P_{im}	k_{remin}	C-to-N			
Slurry	n	6	6	6	6	6	6	ns		50%
	mean	0	0.002	13.6	1.062	0.003	13.5	*		16%
	min	0	0.001	6.4	0.818	0.000	5.0	**		17%
	max	0	0.003	18.5	1.418	0.011	21.2	***	100%	17%
Manure	n	10	10	10	10	10	10	ns		70%
	mean	0	0.0015	13.4	0.725	0.013	14.1	*		10%
	min	0	0	8.8	0.075	0.000	7.5	**		10%
	max	0	0.004	18.8	1.550	0.100	30.0	***	100%	10%
Composted manure/ slurry/ droppings	n	5	5	5	5	5	5	ns		100%
	mean	0	0.002	12.3	1.108	0.024	17.6	*		
	min	0	0.001	9.0	0.221	0.010	9.1	**		
	max	0	0.002	15.3	1.524	0.032	30.0	***	100%	
Agro-industrial waste	n	6	6	6	6	6	6	ns		50%
	mean	0	0.003	8.4	0.933	0.010	8.2	*		
	min	0	0.000	3.2	0.640	0.000	3.3	**		17%
	max	0	0.009	19.1	1.424	0.054	22.971	***	100%	33%
Composted urban waste (fermentable waste. green waste. ±manure.)	n	6	6	6	6	6	6	ns		67%
	mean	0	0.002	15.6	1.212	0.005	19.1	*		
	min	0	0.001	9.9	0.951	0.002	11.5	**		33%
	max	0	0.004	21.4	1.629	0.009	27.8	***	100%	
Potting soil from landfill	n	3	3	3	3	3	3	ns		67%
	mean	0	0.002	20.9	0.822	0.019	4.1	*		
	min	0	0.002	17.2	0.000	0.004	1.7	**		
	max	0	0.003	25.5	1.277	0.043	8.0	***	100%	33%

n : number of samples in the category, **mean** : mean value of the compartment size in the category, **min**: minimum value of the compartment size in the category, **max**: maximum value of the compartment size in the category, **ns**: percentage of EOM presenting non significant difference between measured and predicted values, *: percentage of EOM presenting significant difference at level of 0.1 between measured and predicted values, **: percentage of EOM presenting significant difference at level of 0.05 between measured and predicted values, ***: percentage of EOM presenting significant difference at level of 0.001 between measured and predicted values

Table 3.6 : N mineralization repartition of each category of EOM according to the N mineralization typology defined by Lashermes *et al.*, (2010)

Groups	Considered parameters	N mineralization typology					
		Class 1	Class 2	Class 3	Class 4	Class 5	Class 6
Slurry	N content and biochemical composition			17%		83%	
	Measured N mineralization			17%	17%	66%	
	Predicted N mineralization by TAO-Par			17%	17%	66%	
Manure	N content and biochemical composition			10%		80%	10%
	Measured N mineralization		10%	20%	10%	60%	
	Predicted N mineralization by TAO-Par		10%	20%	10%	60%	
Composted manure/ slurry/ droppings	N content and biochemical composition					100%	
	Measured N mineralization				40%	60%	
	Predicted N mineralization by TAO-Par				20%	80%	
Agro-industrial waste	N content and biochemical composition	17%	33%		17%	33%	
	Measured N mineralization	33%		33%	17%	17%	
	Predicted N mineralization by TAO-Par	33%		50%		17%	
Composted urban waste (fermentable waste. green waste. ±manure.)	N content and biochemical composition				17%	83%	
	Measured N mineralization					83%	17%
	Predicted N mineralization by TAO-Par					83%	17%
Potting soil from landfill	N content and biochemical composition					100%	
	Measured N mineralization				67%	33%	
	Predicted N mineralization by TAO-Par				33%	67%	

Class 1 : very high N mineralization

Class 2 : high N mineralization

Class 3 : medium N mineralization

Class 4 : medium to low N mineralization

Class 5 : low N mineralization/risk of induced N immobilization

Class 6 : risk of induced N immobilization

In each category of EOM, percentages indicate the EOM classified in the N-class

3.3.2.3 Classification of tropical Exogenous Organic Matter

3.3.2.3.1 Index of Remaining Organic Carbon (I_{ROC}) values for C classes

The I_{ROC} values varied according to their formulations:

- (i) for the theoretical I_{ROC} which is based on the C mineralization asymptote, values ranged between 15 and 78 g.100g⁻¹TOM; and
- (ii) for formulated I_{ROC} as defined by Lashermes *et al.* (2009) using measured Ct_3 , I_{ROC} ranged between 7 and 80 g.100g⁻¹TOM.

Figure 3.5 shows the comparison between theoretical I_{ROC} and the calculated I_{ROC}

In order to compare the I_{ROC} obtained with the tropical MOEx and those I_{ROC} repartition according to their category published by Lashermes *et al.* (2009), boxplot and circles were superimposed in Figure 3.6.

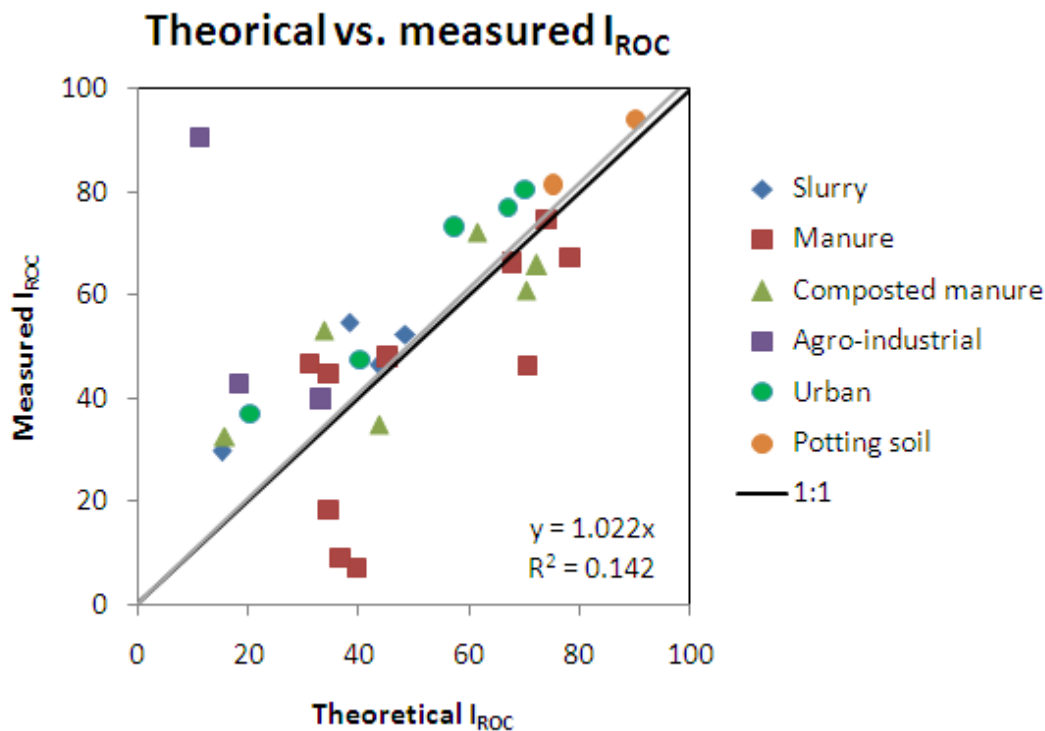


Figure 3.5 : Comparison between theoretical and measured I_{ROC}

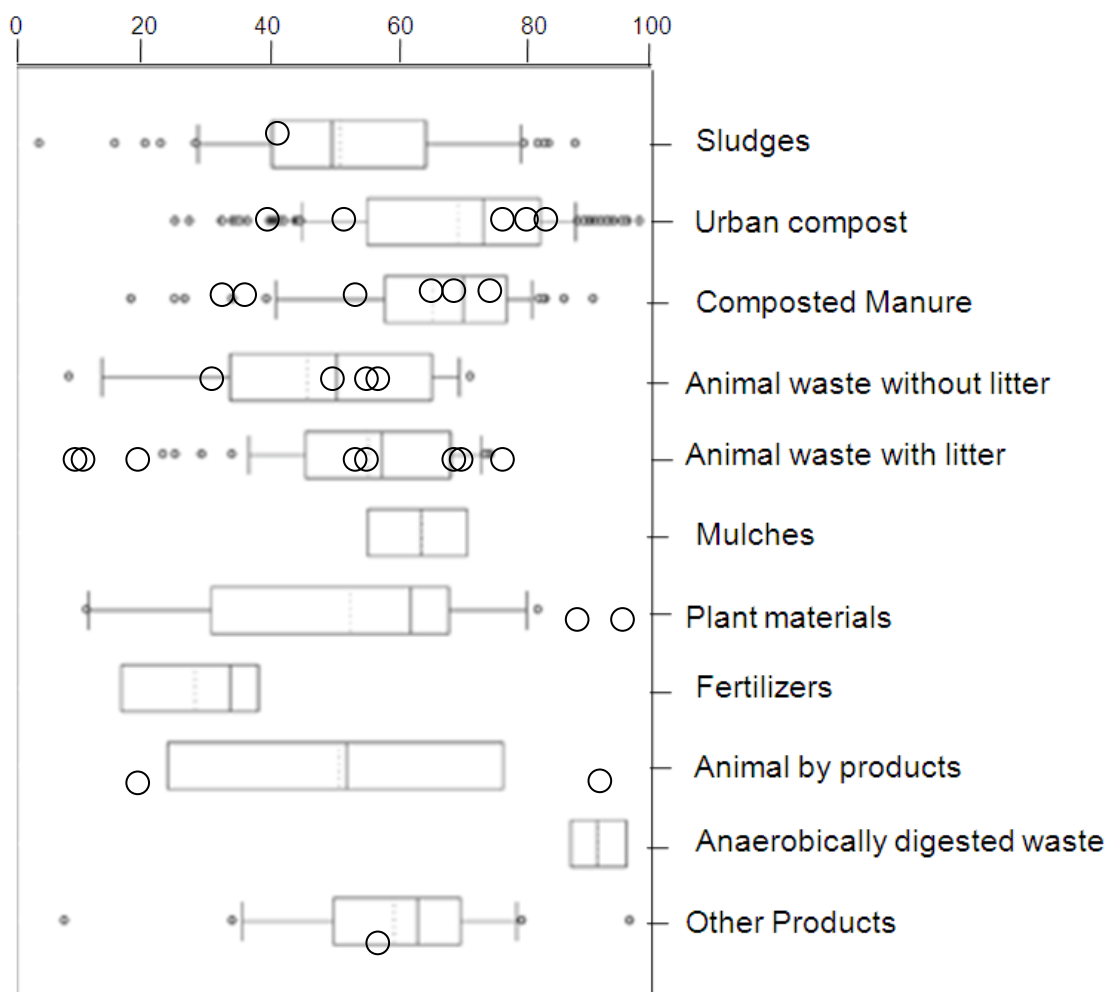


Figure 3.6 : Overlapping of initial I_{ROC} boxplot as established by Lashermes *et al.* (2009) and those I_{ROC} calculated (in circle) for the studied EOM

3.3.2.3.2 N classes

Chemical and biochemical characteristics of EOM, measured N mineralization and predicted by N-TAO-Par allowed a classification of N potential mineralization.

Table 3.5 summarizes the repartition of EOM in these different classes. 28 out of 36 tropical EOM (78%) were classified as materials with low N mineralization presenting a risk of induced N immobilization in soil (class 5) regarding their low N content ($< 6.5\%$) and high lignin+cutin fraction ($LIC > 20\%$) according to Lashermes *et al.*(2010). Taking into account the actual measured N-mineralization, 20 of 36 tropical EOM (56%) were now classified in this category. Some EOM classified in class 5 in the first approach can have a medium or low N mineralization and did not induce immobilization as expected. When dealing with predicted N mineralization, 22 of 36 tropical EOM can potentially have low N mineralization and risk of induced N immobilization in soil.

3.4 Discussion

3.4.1 Usefulness of the TAO-C model

3.4.1.1 The TAO-C three compartment model kinetics

The present study enables the three-compartment scheme of TAO, proposed from materials of the French fertilization industry (Thuriès *et al.*, 2001), recently validated for materials in the Soudano-Sahelian area (Kaboré *et al.*, 2011), to be generalized to 36 EOM that are available for fertilization in two humid tropical environments. A new attempt to optimize the kinetic constants of decomposition of L' and R compartments simultaneously with P'_L and P_R for each of the 36 EOM in this study gave:

$$k'_L = 0.399 \pm 0.403 \text{ day}^{-1}$$

$$k_R = 0.013 \pm 0.001 \text{ day}^{-1}$$

(mean values $\pm$ standard deviation).

These values are very similar to the first ones [Equations 1 & 2] originally calculated from very different organic materials and laboratory experimental conditions. The kinetics constants calculated for our EOM being close to those assessed in other studies, these results confirmed that the prediction of C mineralization only requires assessing the P'_L and P_S compartments size. On this basis, the TAO-C-Par model allows EOM-C mineralization kinetics to be optimized, excepted EOM inducing “priming effect”, using only the two parameters: very labile P'_L and stable P_S fractions of the OM.

3.4.1.2 The TAO-C parameters (TAO-Par) model

The mineralized C prediction by optimized P'_L and P_S compartments of 36 EOM were presented in Figure 2. We noticed that the TAO-Par assessed accurately the C mineralization of EOM which mineralization did not exceed 100%. Such results confirmed that a parallel first order equation with 3 compartments (labile, resistant and stable fractions) with fixed kinetic constants (k'_L and k_R) could be used to predict the C transformation into soil from EOM originating from humid tropics. This study validated and even extrapolated the results of Thuriès *et al.* (2001) and Kaboré *et al.* (2011). Our results showed that the TAO model was suitable for the prediction of the C transformation into soil from very different EOM and climatic conditions.

3.4.1.3 The TAO-C biochemical data (TAO-Bioch) model

The linkage between the biochemical data and the compartment size was tested by using the TAO-Bioch approach. TAO-Bioch gave good prediction for the C transformation of a few proportion of EOM (30%). TAO-Bioch overestimated C-mineralization for composted materials and manures, and underestimated C transformation for slurries and agro-industrial wastes. Such results were in accordance with those reported by Kaboré *et al.* (2011). The overestimation of C-mineralization in compost may occur due to their weak transformation in soil (Thuriès *et al.*, 2002) and also the biochemical changes during composting (Francou *et al.*, 2008).

3.4.1.4 The TAO-C Near InfraRed Spectroscopy (TAO-Nir) model

The relationship between the spectra data and the compartment size was tested by using the TAO-Nir approach. The prediction of P'_L and P_R by NIR spectra at the wavelengths selected by the MLR procedure was accurate. Because P'_L was known as being linked to labile components and P_R linked to the stable ligneous fraction. Due to the organic molecules composition of labile and ligneous fractions, it was not surprising that NIR can predict these 2 compartments accurately as ever done by Kaboré *et al.* (2012).

3.4.2 Usefulness of the TAO-N model

For TAO-N, predicted kinetics strongly depended on the ratio C-to-N as demonstrated by Pansu *et al.* (2003). After the ratio C-to-N optimization, the added organic N transformation was well predicted by TAO-N for EOM which produced immediate and net mineral N. However EOM which presented a rapid N mineralization followed by N immobilization cannot be accurately modeled by TAO-N. This suggested that the N losses occurred and the

parameter for N-volatilization (k_v) should be taken into account in the modelization (Pansu *et al.*, 2003)

3.4.3 Classification of EOM according to the IROC

When compared the Theoretical I_{ROC} and those calculated according to Lashermes *et al.* (2009) with the 30 considered EOM did not show a strong correlation (Figure 3.5). This suggested that the original calibration of I_{ROC} should be reviewed by taking into account other EOM. As can be noticed in Figure 3.6, only 19 of the 30 (63%) I_{ROC} values were in the range defined by Lashermes *et al.* (2009). I_{ROC} were different especially for animal by-products and plant materials. Such result was not surprising because this kind of EOM was not comprised in the range of selected materials which were used for the original calibration of I_{ROC} .

For N mineralization, 81% of studied EOM were in accordance with their supposed behavior after being added into soil, measured N-mineralization, compared either with the typology based with N contents and biochemical characteristics (Lashermes *et al.*, 2010) or with the N-mineralization predicted by TAO-N. As for I_{ROC} value, we have to pay much attention for agro-industrial and urban materials transformation into soil.

In order to assess the EOM transformation into soil, knowing I_{ROC} and the agronomic class towards N and biochemical content according to Lashermes *et al.* (2009) constitutes a preliminary approach of tropical EOM classification. Indeed, N-class and I_{ROC} values were the same as established by Lashermes *et al.* (2010) for animal effluents and composts. However, there is a class mismatching for agro-industrial and urban effluents. We suggest the establishment of a new and adapted typology for the Malagasy and Réunion EOM.

3.5 Conclusion

The description of the in-soil transformation of EOM can be achieved by a 6-months laboratory experiment or by calculating model predictions (with optimized parameters, with biochemical fractions, with NIR spectroscopy). Apart from urban and agro-industrial EOM, the behavior of a wide majority of the agricultural waste from humid tropics was similar to the main types of French EOM applied to soil. The majority of the studied EOM presented a low N mineralization and may induced N immobilization in soil. The classification and index based on the French EOM can be taken as a first approach to categorize Malagasy and Réunion EOM. The establishment of a new/adapted typology is suggested to allow more reliable results in order to improve the prediction of their behaviors in soil. Building a database with a wide range of tropical EOM encountered in Madagascar and Réunion would be beneficial for the improvement of the agricultural management of EOM. A robust

classification would be achieved taking into account the diverse C content, N content, and biochemical fractions originating from a large EOM panel. Finally, it seems that our understanding of the EOM transformation into soil would be accelerated by the help of NIRS which is a powerful, non-destructive and time-saving method.

3.6 Acknowledgments

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Chapitre 4. New heating value prediction models for organic waste based on chemical composition or near infrared spectroscopy

Avant-propos

Le principal objet du chapitre présenté ici est d'évaluer le pouvoir calorifique des MOEx en milieu tropical.

En effet due à la demande croissante de la consommation énergétique mondiale, la valorisation de la biomasse ou MOEx en tant que nouvelles ressources énergétiques est promue. Avant toute installation de systèmes bioénergétiques de combustion, il est impératif de connaître le pouvoir calorifique de cette biomasse (Yin, 2011). Le pouvoir calorifique est un paramètre standard qui exprime l'énergie contenue dans un fuel. La détermination de ce pouvoir calorifique est conduite expérimentalement dans une bombe calorimétrique adiabatique. Bien que la manipulation d'un tel appareil soit facile, peu de chercheurs ont encore accès à cet instrument. Aussi de nombreuses approches permettant de connaître rapidement le pouvoir calorifique ont été développées (Cordero *et al.*, 2001; Sheng *et al.*, 2005; Erol *et al.*, 2010). On peut citer les équations empiriques et la spectrométrie proche infrarouge pour prédire le pouvoir calorifique des MOEx. Les équations empiriques sont généralement établies à partir des caractéristiques élémentaires (carbone, hydrogène, oxygène, azote), des caractéristiques proximaux (cendres, matières organiques, ...) ou des caractéristiques biochimiques (soluble, hémicellulose, cellulose, lignine) des MOEx (Vargas-Moreno *et al.*, 2012). La spectrométrie proche infrarouge suivie de méthodes chimiométriques permettent de faire le lien entre un spectre et le pouvoir calorifique des MOEx (Gillon *et al.*, 1997; Huang *et al.*, 2009; Everard *et al.*, 2012).

Dans notre étude, nous nous proposons alors d'évaluer le pouvoir calorifique de 200 MOEx tropicales de la Réunion (i) en testant 12 équations utilisées dans la bibliographie, (ii) en développant de nouvelles corrélations via les caractéristiques élémentaires et/ou proximaux et/ou biochimiques des MOEx (iii) en développant des calibrations SPIR.

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New heating value prediction models for organic waste based on chemical composition or near infrared spectroscopy

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Abstract:

The effective use of valuable organic waste (VOW) is being promoted in Réunion to ensure a sustainable fuel and electricity supply on the island. It is essential to know the heating value before analyzing and designing any bioenergy systems. In this study, new higher heating value (HHV) prediction methods were developed for a broad range of fresh and transformed organic waste, and they were analyzed with respect to forecasting errors. The chemical composition of 200 organic waste samples was analyzed. The data were used to test published correlations and develop new ones (multiple linear regressions). Their corresponding spectra were also used to calibrate a near infrared spectroscopy (NIR) model for HHV prediction. Among all of the HHV estimations obtained (using published correlations, new proposed correlations or the proposed NIR model), those of the NIR-based model were found to be the most accurate, with a standard error of prediction (SEp) of 0.33 MJ.kg⁻¹ for the entire dataset, and 0.21 and 0.22 MJ.kg⁻¹ for the poultry manure and green waste datasets, respectively. We showed that the NIR spectrum contained as much information required for predicting HHV as could be obtained via complete biochemical analysis. For the island of Réunion, NIR will be useful for characterizing HHV directly on site on poultry farms or in green waste deposits.

Highlights:

► ~ 200 higher heating values (HHV) for valuable organic waste were determined in Réunion
► Rapid determination of HHV based on chemical composition or spectra were tested ► In Réunion, poultry manure and green waste are an interesting source of renewable energy ► Near-infrared spectroscopy (NIRS) is a promising tool for fast determination of HHV ► NIRS prediction is equally or more precise than prediction from chemical composition

Keywords:

Biomass, Recycling, Renewable energy, Calorific value, Réunion, Near infrared spectroscopy

4.1 Introduction

The earth's fossil resources are being rapidly depleted and this situation is responsible for the current global energy crisis (Magdoff, 2013). This is one of the most pressing global issues in recent times. The use of alternative fuel sources such as organic wastes has been heavily promoted in many countries to overcome this predicament. These biomass fuels can generate heat and electricity. Using such auxiliary fuels for small-scale combustion or thermochemical conversion is clearly beneficial since these resources are inexpensive and renewable, while also providing an opportunity to dispose of these wastes (Yin, 2011).

Réunion has been undergoing strong economic and demographic growth over the last two decades. Electricity consumption on the island is increasing at a rate of 5% a year, with fuel consumption rising by 2% a year, so its consumption has doubled in 15 years. Being an island, Réunion has to be able to ensure a steady supply fuel and electricity to meet its increasing needs. Réunion has to import fossil fuels to meet 87.5% of its transport energy and electricity production needs (Counil, 2011). Renewable energy generation circumvents the need to tap fossil resources for electricity, heat and fuel production. Moreover, valuable organic wastes (VOW) may be used as an energy source, while also addressing several sustainable development issues such as waste management.

VOW broadly concerns organic matter, derived from spontaneous or induced biological processes, that can be used as a source of energy. It usually includes certain types of wood, energy crops, marine algae, agricultural and silvicultural residues, and some animal, industrial and human wastes (Saidur *et al.*, 2011). In Réunion, VOW are of diverse origins, natures and compositions. The most abundant VOW (over 100 kT on dry matter basis) come from the sugarcane industry (bagasse, cane fiber, distillery waste), firewood and agricultural wastes (animal dejections). Less abundant VOW (5 to 100 kT on dry matter basis) include sewage sludge, food waste, meat-based waste, waste edible oils, household waste (fermentable fraction), greasy waste, green waste, etc. (Petit, 2012). After bagasse, other excellent candidates for renewable energy production are poultry manure (PM) (Lynch *et al.*, 2013) and green waste (GW).

It is essential to know the heating value (HV) of biomass before using it as a fuel in thermal and electrical applications (Cordero *et al.*, 2001; Sheng *et al.*, 2005; Erol *et al.*, 2010; Callejón-Ferre *et al.*, 2011; Yin, 2011). HV is a standard way to express the energy content of a fuel (Demirbas *et al.*, 2004; Sheng *et al.*, 2005; Erol *et al.*, 2010). It is often expressed as a higher heating value (HHV) or lower heating value (LHV) (Yin, 2011). HHV refers to the heat

released from fuel combustion with the original and generated water in a condensed state, while LHV is based on a gaseous water product. The experimental or direct determination of the HHV of biomass using an adiabatic bomb calorimeter is burdensome (Cordero *et al.*, 2001; Sheng *et al.*, 2005; Erol *et al.*, 2010; Callejón-Ferre *et al.*, 2011; Yin, 2011). Bomb calorimeters are relatively easy to use and accurate, but researchers may not always have access to such instruments. To circumvent this problem, researchers with access to an elemental analyzer usually conduct elemental (carbon, hydrogen, oxygen, nitrogen, etc.), proximate (ash, organic matter, fixed carbon) or biochemical (hemicellulose, cellulose, lignin, extractives) analysis and then use the resulting data to determine the heating value via established empirical correlations (Vargas-Moreno *et al.*, 2012).

Over the past two decades, emphasis on renewable fuels has prompted many researchers to find empirical correlations based on data from elemental and proximate analyses of biomass fuels, while focusing especially on agricultural wastes. Tillman (1978) suggested that HHV of biomass material is closely dependent on its carbon content and a popular correlation used to estimate the HHV of wood and wood bark ($\text{HHV} = 0.4373 \cdot [\text{C}] - 1.6701$) was subsequently developed.

The potential of near infrared reflectance (NIR) spectroscopy for characterizing organic wastes, such as animal manure, compost, sewage sludge and green waste, is well established (Huang *et al.*, 2007; Vergnoux *et al.*, 2009; Soriano-Disla *et al.*, 2010). Many studies have highlighted the accuracy of using NIR spectra to assess carbon, nitrogen and organic matter (Gillon *et al.*, 1999; Aiken *et al.*, 2005). Attempts to predict the biochemical fraction have also been reported, with variable results (Peltre *et al.*, 2011), but there are few published references on HV (Gillon *et al.*, 1997; Huang *et al.*, 2009; Bastianelli *et al.*, 2010; Everard *et al.*, 2012). This parameter is not essential for the analysis of VOW for agricultural uses, whereas it is crucial for determining potential energy uses of this biomass.

Since predictive models already exist for other biomass resources, the present study focused on developing a model for VOW in Réunion, especially with respect to poultry manure (PM) and green waste (GW). This study aimed: (i) to test existing correlations for determining the HHV of VOW samples, (ii) to develop new correlations for calculating the HHV of VOW samples from their measured and predicted elemental, proximal and biochemical analyses, and (iii) to develop NIR calibrations for predicting HHV.

4.2 Material and methods

4.2.1 Valuable organic waste (VOW) dataset

This dataset included 208 VOW samples covering a broad range of fresh and transformed organic materials. It included 135 poultry manures (PM) with or without litter, 35 green wastes (GW) from sugarcane and municipal green waste, 15 composted municipal green wastes, 8 manures with or without litter, 6 agro-industrial wastes, 6 composted animal effluents and 3 sewage sludges.

4.2.2 Valuable organic waste (VOW) characterization

All VOW samples were oven-dried at 40°C and finely ground (<1 mm) before analysis. The VOW samples were characterized in terms of elemental (carbon, C, and nitrogen, N), proximal (total organic matter, TOM), biochemical (soluble (SOL), hemicellulose-like (HCEL), cellulose-like (CEL) and lignin+cutin-like (LIC) fractions) and heating value (HV) parameters. Total organic C and N contents were quantified by dry combustion using an elemental analyzer according to the Dumas method. TOM content was determined by loss on ignition at 480°C. The biochemical composition of VOW (SOL, HCEL, CEL, LIC) was determined using the Van Soest method (Van Soest *et al.*, 1991), according to the French standard XPU 44-162 (AFNOR, 2009). All biochemical fractions were expressed as a percentage dry weight (%DW) after deducting the corresponding ash contents. HV was measured by combustion using an isoperibol bomb calorimeter (C7000, IKA, Heitersheim, Germany).

In some situations in which TOM was not measured, it was estimated from the total C content with an equation formulated on the basis of a large VOW database ($TOM = 2.0 * [C]$; $R^2=0.94$; $N=584$; data not shown).

For the above-ground sugarcane biomass, intermediary ash was not measured during the Van Soest analysis, which could introduce analytical bias. The values used for SOL, HCEL, CEL and LIC were therefore corrected using equations linking fiber parameters with and without ash: $SOL=1.06*SOL^{\#}$; $R^2=0.94$; $N=194$, $HCEL=0.91*HCEL^{\#}$; $R^2=0.93$, $N=192$; $CEL=0.96*CEL^{\#}$, $R^2=0.96$, $N=252$. $SOL^{\#}$, $HCEL^{\#}$, $CEL^{\#}$ were the fractions measured without ash. The formulation of these equations was founded on a large VOW database, while taking the majority of the VOW studied here into account.

4.2.3 Heating value modelling

4.2.3.1 Published models

Twelve mathematical models were tested to estimate the HHV of our VOW. These equations included relations built with elementary (C and N), proximal (TOM) and biochemical analysis (SOL, HCEL, CEL and LIC) data. Table 4.1 presents the published correlations (PC). Different types of biomass were considered when drawing up these equations: wood and wood bark (Tillman, 1978), field crops (Ebeling *et al.*, 1985), lignocellulosic fuels (Demirbas *et al.*, 2004), biomass materials (Ebeling *et al.*, 1985; Sheng *et al.*, 2005), greenhouse crop residues (Callejón-Ferre *et al.*, 2011), municipal solid waste (Kathiravale *et al.*, 2003) and straw (Huang *et al.*, 2008).

Each equation was used to predict the HHV of our (i) 208 samples, (ii) 135 PM and (iii) 35 GW with measured HHV. The accuracy of the published correlation was evaluated on the basis of the bias, which is the average difference between the estimated and measured HHV, and the precision was estimated on the basis of the standard error of prediction corrected for bias (SE_p).

4.2.3.2 New proposed multiple linear regression models based on the chemical composition

Multiple linear regression (MLR) was adopted to formulate the equation to predict HHV of VOW samples from C, N, TOM contents and biochemical fractions. All correlations were developed using a stepwise method. The accuracy of the model fit was evaluated through examination of various statistical parameters, including the regression coefficient (R^2), Akaike criteria (AIC) (Akaike, 1973), bias and standard error (SE). The best model was considered to be the equation with the lowest AIC. All procedures, including equation construction and statistics, were performed using XL STAT software (Addinsoft, Paris, France).

Three series of MLR were developed using: i) the entire 208 VOW set with measured HHV, ii) the 135 PM alone, and iii) the 35 GW alone.

4.2.3.3 Heating value modeling by NIR spectroscopy

4.2.3.3.1 NIR spectra acquisition

All samples were scanned on a monochromatic NIR spectrophotometer (NIR 6500, Foss NIRsystems, Laurel, MD, USA). Spectra were recorded in reflectance mode in small circular cups (diameter 50 mm) with a quartz glass cover. Spectral data were collected every 2 nm from 400 nm to 2500 nm. Samples were scanned a second time after repacking and duplicate spectra were averaged.

Table 4.1: Published correlations (PC) for HHV determination from elemental (C, N), proximate (TOM, ASH) and biochemical (SOL, CEL, LIC) analysis.

Published correlation based on analysis		Type of biomass	Sources
PC-1	$\text{HHV} = 0.437 [\text{C}] - 1.670$	Wood and wood bark	[13]
PC-2	$\text{HHV} = 0.322 [\text{C}] + 3.754$	Field crops	[26]
PC-3	$\text{HHV} = 0.370 [\text{C}] - 1.318$	Lignocellulosic fuels	[11]
PC-4	$\text{HHV} = 0.326 [\text{C}] + 3.460$	Wide range of biomass materials	[10]
PC-5	$\text{HHV} = 0.006 [\text{C}]^2 + 5.736$	Greenhouse crop residue	[7]
PC-6	$\text{HHV} = 20.067 - 0.220 [\text{ASH}]$	All biomass	[26]
PC-7	$\text{HHV} = 18.960 - 0.225 [\text{ASH}]$	Rice and wheat straw	[28]
PC-8	$\text{HHV} = 0.356 [\text{TOM}] - 6.998$	Municipal solid waste	[27]
PC-9	$\text{HHV} = 26.601 - 0.304 [\text{ASH}] - 0.082 [\text{TOM}]$	All biomass	[26]
PC-10	$\text{HHV} = -2.057 - 0.092 [\text{ASH}] + 0.279 [\text{TOM}]$	Greenhouse crop residue	[7]
PC-11	$\text{HHV} = 86.191 - 2.051 [\text{ASH}] - 1.781 [\text{C}] - 237.722 [\text{ASH}]^{-1} + 0.030 [\text{ASH}]^2 + 0.025 [\text{C}]^2 + 0.026 [\text{N}]^2$	Greenhouse crop residue	[7]
PC-12	$\text{HHV} = (1 - ([\text{ASH}]/([\text{CEL}] + [\text{LIC}] + [\text{SOL}]))) * ((0.174 * [\text{CEL}]) + (0.266 * [\text{LIC}]) + (0.322 * [\text{SOL}])))$	Wide range of biomass materials	[37]

4.2.3.3.2 NIR calibration and validation process for HHV

Calibration was performed by partial least square (PLS) regression on spectra after their transformation in absorbance ($\log 1/R$) (Geladi *et al.*, 1986). It is recommended that calibrations be developed with MLR for sample sets of under 80 references and spectra (Geladi *et al.*, 1986). The stepwise MLR procedure was thus chosen to select the most informative wavelengths (Shenk *et al.*, 1991) for GW, whereas PLS regressions were developed for all VOW and PM. Both regressions were performed using WinISI IV software (Infrasoft International, Port Matilda, PA, USA). The calibration procedure involved elimination of major prediction outliers in order to avoid bias due to spectral and laboratory errors. Outlier detection was based on the studentized residual ($\text{error}/\text{SE}_{\text{CV}}$) with a cut-off of 2.5. The SE_{CV} was the standard error of cross-validation. Two outlier elimination passes were carried out. Calibration performance was described through a coefficient of determination (R^2) and standard error of calibration (SE_C).

Cross-validation was performed on four groups, with three being used to develop the model and one for prediction. The procedure was performed four times to use all groups for both model development and prediction in order to obtain the SE_{CV} calculation. The “performance to deviation” ($\text{RPD}_{\text{CV}} = \text{SD}/\text{SE}_{\text{CV}}$) ratio was used as an indicator of model quality. An RPD value between 1.5 and 2.0 provides a possibility to distinguish between high and low values, while a value between 2.0 and 2.5 makes approximate quantitative predictions possible. For values between 2.5 and 3.0 and above 3.0, the prediction is classified as good and excellent, respectively (Saeys *et al.*, 2005). Unlike SE_C and SE_{CV} , RPD_{CV} has the advantage of being independent of the parameter units (Sinnaeve *et al.*, 1994) and allows a between-parameter comparison. Validation was performed on the same database and led to the calculation of the standard error of prediction (SE_P). Bias and slope of the regression predicted vs. measured values were recorded and bias-corrected SE_P (SE_{PC}) was calculated as an indication of the prediction accuracy.

4.3 Results

4.3.1 Chemical characterization of VOW

The statistics of the measured chemical data are presented in Table 4.2. As expected, the constituent ranges and variability were high. Hence, the HHV ranged from 7.7 to 22.8 MJ.kg⁻¹, 9.8 to 21.0 MJ.kg⁻¹ and 13.4 to 18.5 MJ.kg⁻¹ over the whole VOW dataset, PM and GW, respectively. Pearson's correlation coefficient (r) was calculated to determine the levels of correlation between the chemical data. C and TOM contents were highly correlated with the HHV ($0.76 < r < 0.92$, $p < 0.0001$ for C and $0.90 < r < 0.92$, $p < 0.001$ for TOM) and were also correlated with each other ($0.83 < r < 0.96$, $p < 0.0001$). Correlations between HHV and TOM were higher than those between HHV and C. Depending on the matrix (all VOW, PM or GW), N, HCEL, CEL and LIC had relatively significant correlations with HHV.

4.3.2 Evaluation of the published equations for VOW samples

The published correlations (PC) were validated on the basis of our experimental data in order to test the reliability of the estimated HHV. For each PC, Figure 4.1 compares the predicted HHV with our HHV measures by taking the elemental, proximal and biochemical characteristics of the studied VOW dataset into account.

For all 208 VOW samples tested, the bias ranged between -3.55 and 6.88, and the SEp between 0.83 and 5.13. Four published correlations (PC-5, PC-6, PC-7, PC-9) were retained according to the available parameters because they gave minimum bias or/and minimum SEp. For PC-5, SEp was the lowest, with a value of 0.83, and the lowest bias was given by PC-7 with the value of -0.28.

For the HHV predicted for PM alone, the bias and SEp ranged between -1.74 and 4.22, and 0.81 and 1.21, respectively. Five published equations (PC-3, PC-5, PC-7, PC-9, PC-11) were more accurate, with low bias and/or low SEp. However, PC-7 predicted the HHV with the lowest bias (0.05).

For the HHV calculated for GW alone, the bias and SEp ranged from -11.95 to 7.48, and from 0.57 to 14.56, respectively. Only two equations (PC-6 and PC-7) had acceptable accuracy when bias and SEp were considered. With PC-6, the SEp was 0.57 and the bias was 0.70, whereas the SEp was 0.59 and the bias was -0.48 with PC-7.

Among the PC, PC-7 was acceptable for all VOW, PM and GW datasets because the biases obtained with this PC were the lowest. Regarding the minimum SEp values, PC-5 was good for VOW and PM, whereas PC-6 was accurate for GW.

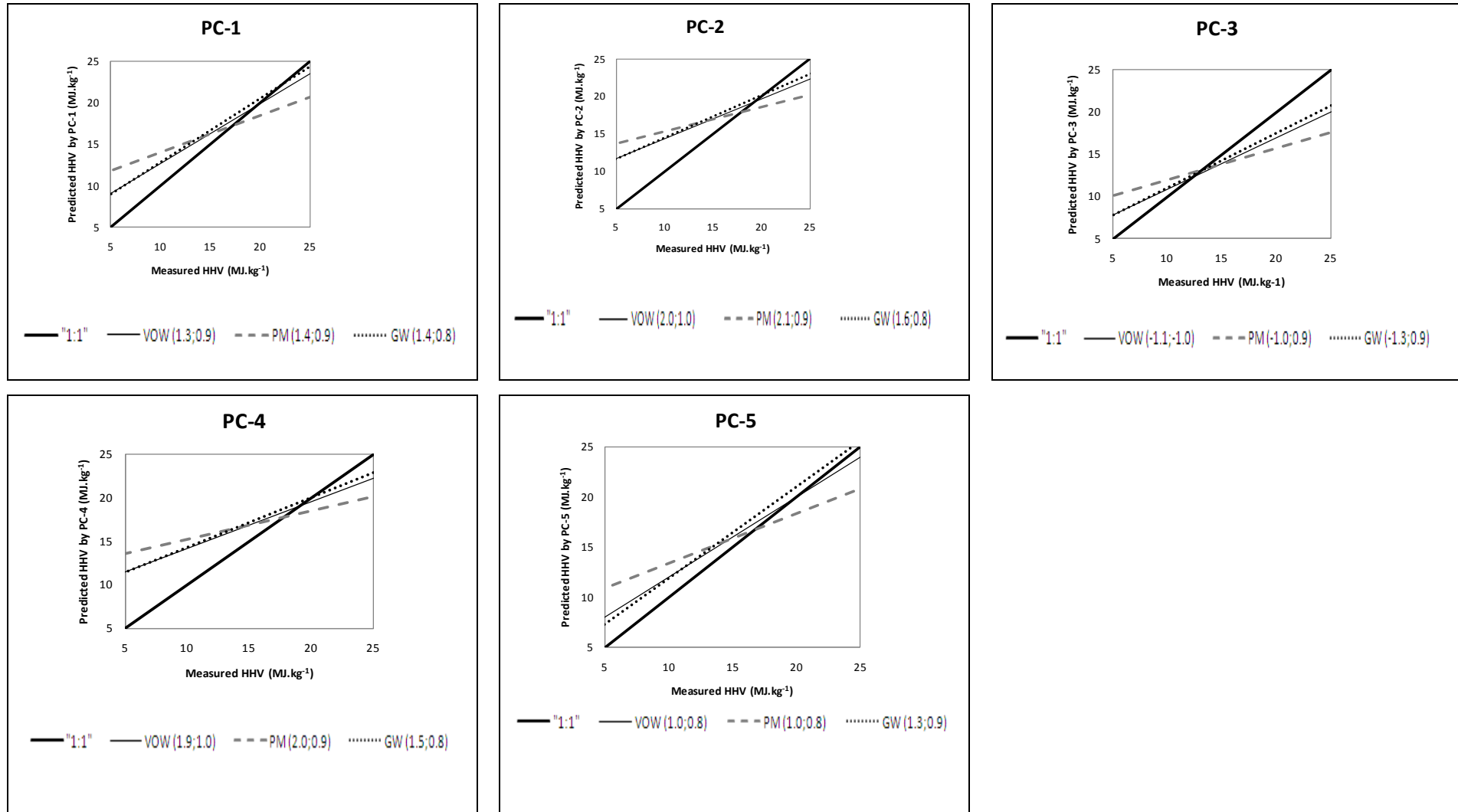
Table 4.2: Chemical characterisation of the VOW samples.

Constituent	N	Mean	SD	Minimum	Maximum
C (%)	208	41.1	4.5	23.0	53.5
N (%)	158	3.3	2.3	0.1	14.5
TOM (%)	208	81.0	9.0	39.8	98.1
ASH (%)	119	18.2	10.2	1.9	58.9
SOL (%)	94	32.6	13.4	8.4	57.3
HCEL (%)	94	18.6	6.9	3.0	34.9
CEL (%)	94	22.1	8.5	3.9	41.7
LIC (%)	94	7.1	4.4	0.4	24.6
HHV (MJ.kg ⁻¹)	208	15.0	2.4	7.7	22.8

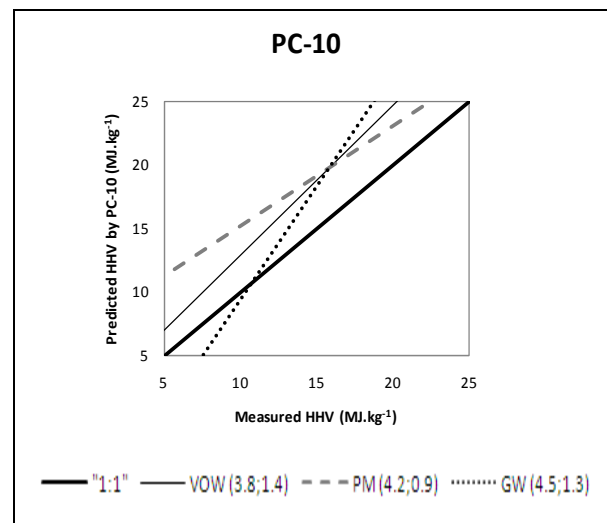
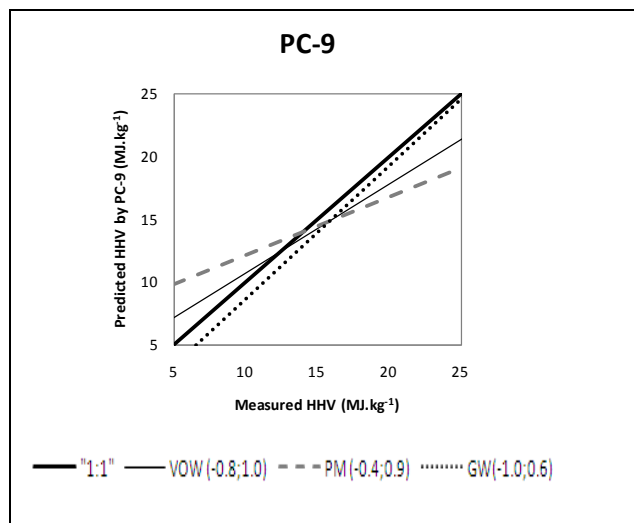
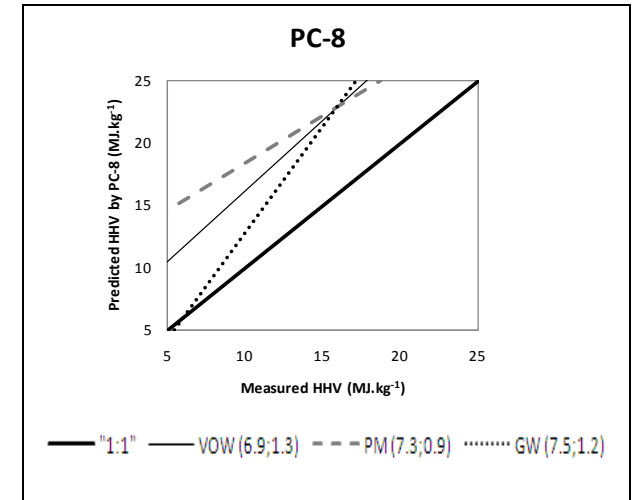
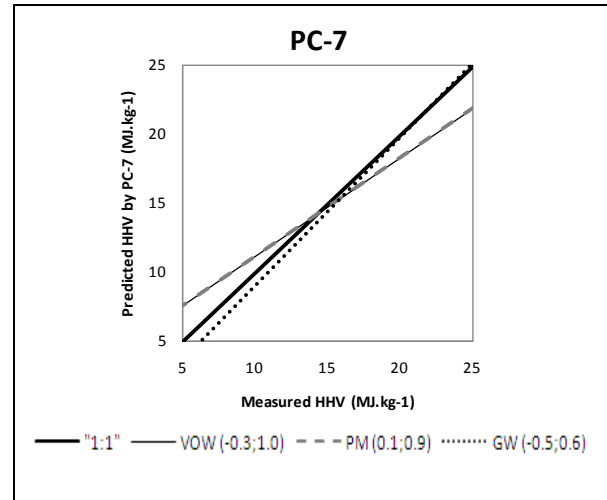
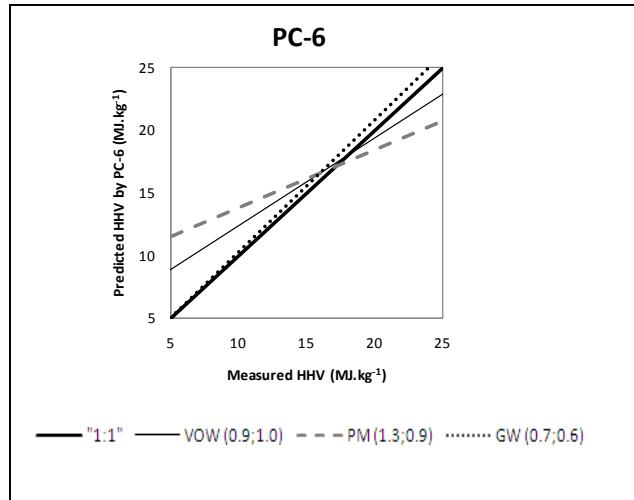
Biochemical fractions (SOL, HCEL, CEL, and LIC) are expressed as percentage of dry matter.

Figure 4.1: Comparison of measured HHV values with those predicted using published correlations (PC, see Table 4.1; numbers in brackets are bias and SEP, respectively).

(a) PC developed with C contents



(b) PC developed with TOM contents



c) PC developed with chemical (C,N), proximal (TOM, ASH) and biochemical parameters (SOL, HCEL, CEL, LIC)

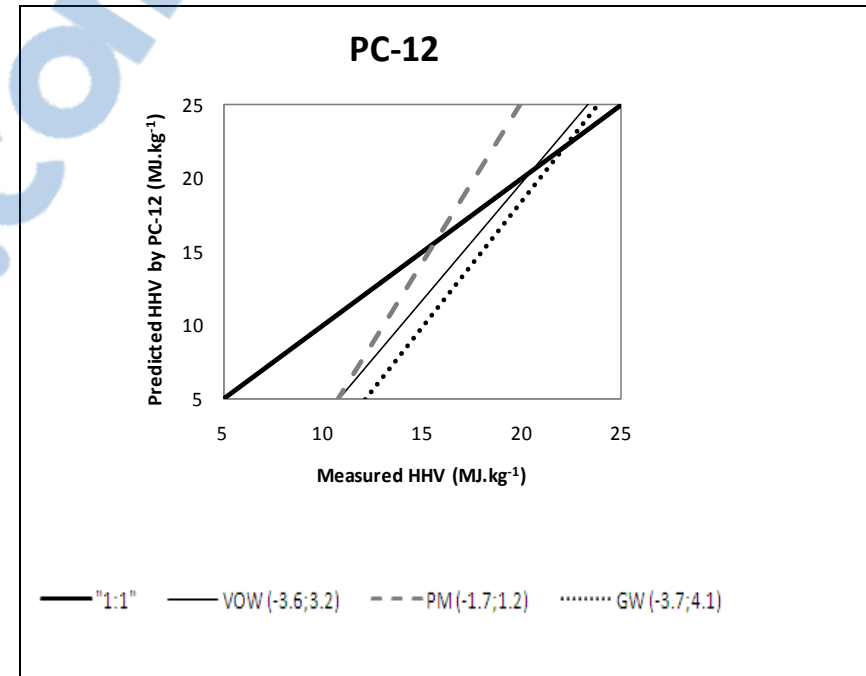
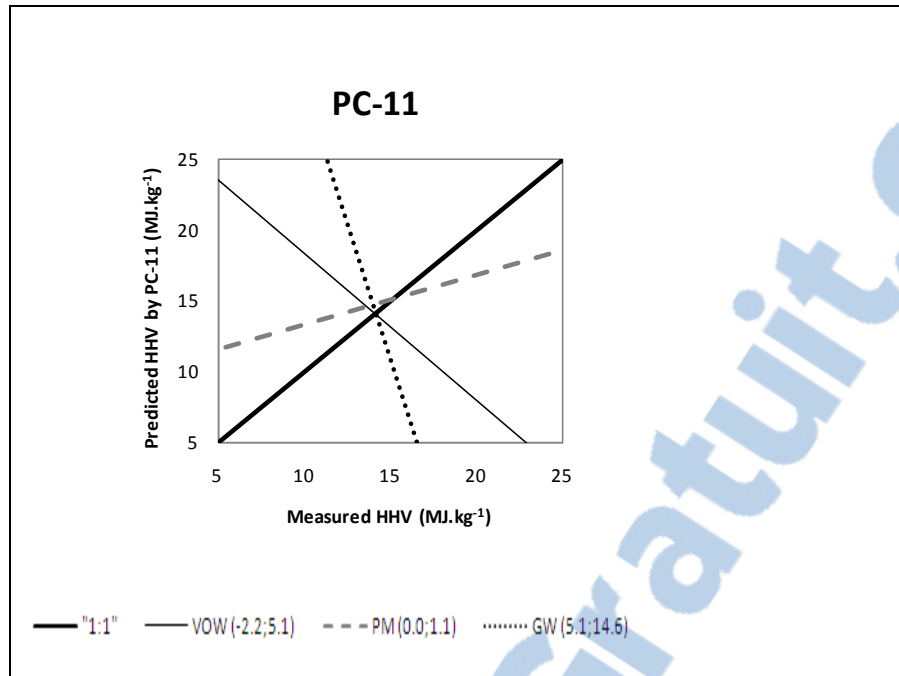


Table 4.3: New MLR models based on chemical composition of the whole VOW dataset, or of PM or GW datasets alone.

		All VOW	PM	GW
Univariate models				
MLR-1	C	HHV= 0.366 x [C]	HHV= 0.362 x [C]	HHV= 0.369 x [C]
MLR-2	N	HHV= 3.202 x [N]	HHV= 3.609 x [N]	HHV= 15.198 x [N]
MLR-3	TOM	HHV= 0.185 x [TOM]	HHV= 0.182 x [TOM]	HHV= 0.190 x [TOM]
Multivariate models				
MLR-4	C and N	HHV= 0.352 x [C] + 0.2 x [N]	HHV= 0.297 x [C] + 0.715 x [N]	HHV= 0.385 x [C] – 0.904 x [N]
MLR-5	TOM and N	HHV= 0.177 x [TOM] + 0.248 x [N]	HHV= 0.149 x [TOM] + 0.704 x [N]	HHV= 0.190 x [TOM]
MLR-6	SOL, HCEL, CEL, and LIC	HHV= 0.156 x [SOL] + 0.248 x [HCEL] + 0.140 x [CEL] + 0.258 x [LIC]	HHV= 0.179 x [SOL] + 0.180 x [HCEL] + 0.127 x [CEL] + 0.290 x [LIC]	HHV= 0.172 x [SOL] + 0.239 x [HCEL] + 0.169 x [CEL] + 0.187 x [LIC]
MLR-7	N, SOL, HCEL, CEL, and LIC	HHV= – 0.179 x [N] + 0.169 x [SOL] + 0.276 x [HCEL] + 0.111 x [CEL] + 0.284 x [LIC]	HHV= 0.178 x [SOL] + 0.186 x [HCEL] + 0.123 x [CEL] + 0.288 x [LIC]	HHV= 0.172 x [SOL] + 0.239 x [HCEL] + 0.169 x [CEL] + 0.187 x [LIC]
MLR-8	C, N, SOL, HCEL, CEL, and LIC	HHV= – 0.126 x [N] + 0.331 x [C] + 0.077 x [HCEL]	HHV= 0.178 x [SOL] + 0.186 x [HCEL] + 0.123 x [CEL] + 0.288 x [LIC]	HHV= 0.172 x [SOL] + 0.239 x [HCEL] + 0.169 x [CEL] + 0.187 x [LIC]
MLR-9	TOM, N, SOL, HCEL, CEL, and LIC	HHV*= -0.218 x [N] + 0.098 x [TOM] + 0.074 x [SOL] + 0.191 x [HCEL] + 0.194 x [LIC]	HHV= 0.172 x [TOM] + 0.034 x [LIC]	HHV= 0.173 x [TOM] + 0.067 x [HCEL]
MLR-10	C, N, TOM, SOL, HCEL, CEL, and LIC	HHV= 0.331 x [C] – 0.126 x [N] + 0.077 x [HCEL]	HHV*= 0.172 x [TOM] + 0.034 x [LIC]	HHV*= 0.173 x [TOM] + 0.067 x [HCEL]
*Best correlations in bold				

4.3.3 New MLR models based on the chemical composition of the VOW dataset

Table 4.3 lists 10 selected MLR models from the possible models that were developed during this study. The MLR models were built by taking the elemental (C, N), proximal (TOM), and biochemical (SOL, HCEL, CEL and LIC) parameters into account. They concerned all VOW samples or only the PM or GW samples.

For models using only one variable developed with C, N, and TOM contents, the SE ranged between 1.24 and 8.40 MJ.kg⁻¹ when considering all VOW, 1.28 and 3.13 MJ.kg⁻¹ when considering PM, and 0.62 and 9.31 MJ.kg⁻¹ when considering GW. The model obtained with the C content had the lowest SE for VOW, and models obtained with TOM contents had the minimum SE for PM and GW.

For multivariate models, the SE ranged between 0.72 and 1.27 MJ.kg⁻¹, between 0.28 and 1.28 MJ.kg⁻¹, and between 0.32 and 0.81 MJ.kg⁻¹ for the entire VOW set, for PM and GW, respectively. Figure 4.2 summarizes the performance (R², AIC criteria and SE) of the 10 MLR when all VOW, PM or GW were considered. As noted in Figure 2, MLR-9 and MLR-10 associated both the lowest AIC criteria and SE and the highest R². For VOW, MLR-9 gave the best performance. This equation was obtained by stepwise regression of 6 variables (TOM, N, SOL, HCEL, CEL and LIC) and finally 5 variables were significant for HHV prediction. Although MLR-10 for VOW considered only 3 variables after stepwise regression of all variables, the AIC values differed, thus dismissing MLR-10 for our choice. For PM and GW, the best HHV prediction could be calculated using MLR-9 or MLR-10. However, initially variables used for the stepwise regression differed, same equation was obtained. TOM and LIC were significant for PM and TOM, and HCEL were important for GW in the HHV prediction. Surprisingly, the C parameter was never taken into account in any of the stepwise procedures adopted here.

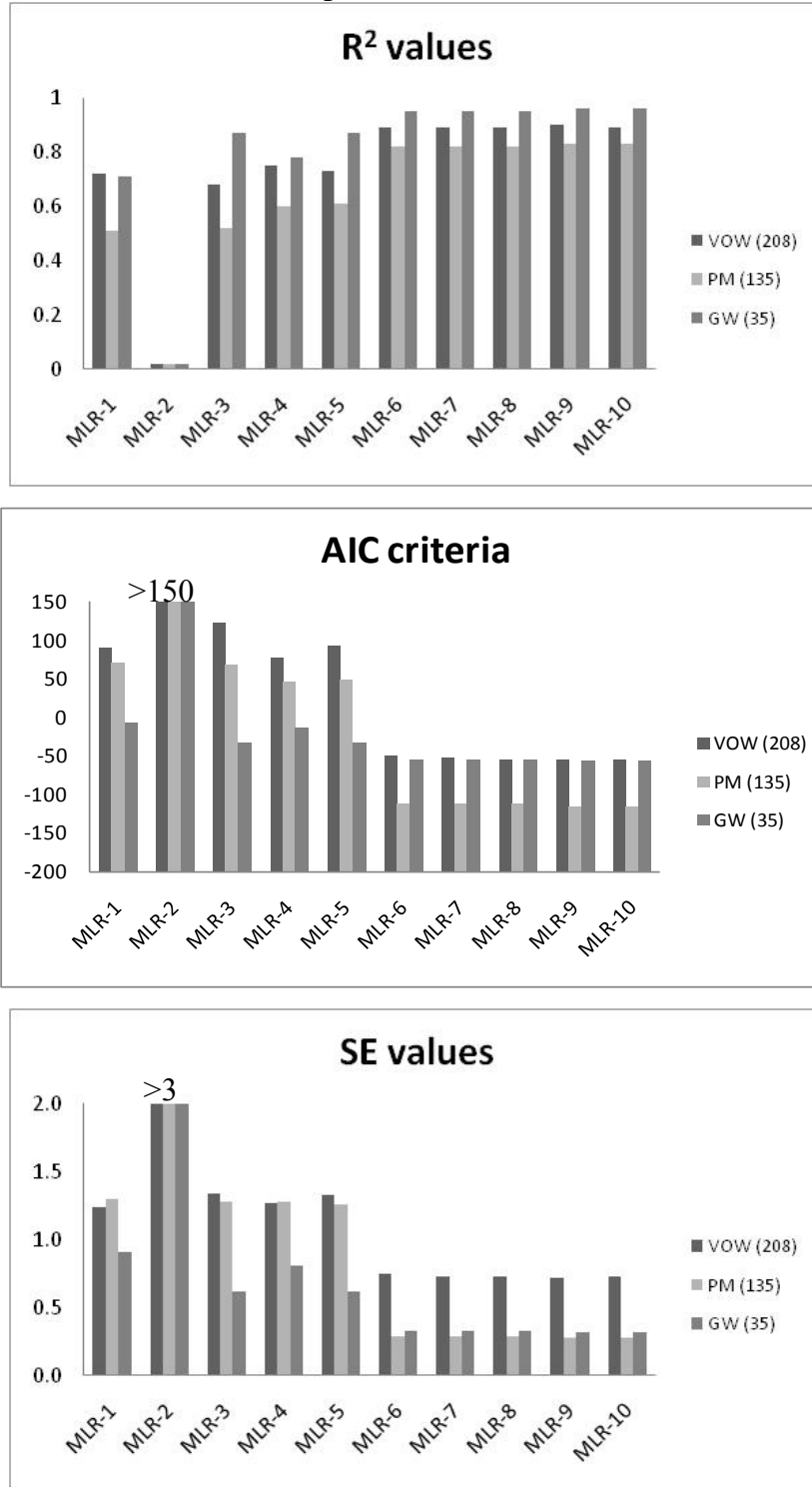
Figure 4.3 shows a graphical comparison between the measured and predicted HHV by the best established MLR. The following equations were considered in this figure:

- For VOW, HHV = -0.218 x [N] + 0.098 x [TOM] + 0.074 x [SOL] + 0.191 x [HCEL] + 0.194 x [LIC] (MLR-9)
- For PM, HHV = 0.172 x [TOM] + 0.034 x [LIC] (MLR-9 or 10)
- For GW, HHV = 0.173 x [TOM] + 0.067 x [HCEL] (MLR-9 or 10)

In comparison with published correlations, standard errors from predicted HHV with our MLR were lower than those predicted with PC. For VOW, PC-5 SE_P (0.83) was higher than

MLR-9 SE (0.72). For PM, PC-5 SE_p (0.81) was higher than MLR-9 or 10 SE (0.28). For GW, PC-6 SE_p (0.57) was greater than MLR-9 or 10 SE (0.32).

Figure 4.2: Performance of implemented MLR.



R^2 , AIC and SE designed respectively the coefficient of determination, the Akaike criteria and the standard error of the multiple linear regression

4.3.4 NIR prediction of HHV

The spectral treatments used here were: i) a full multiple scatter correction (MSC) second derivative with a smoothing of spectra on four consecutive points and a derivation gap of four points for all VOW and PM, ii) a detrend (DET) first derivative with smoothing of spectra on five consecutive points and a derivation gap of five points for GW. A total of 16 samples from all VOW datasets and nine PM (none GW) were spectral outliers and thus eliminated for further analysis.

Table 4.4 presents: (i) the parameters of the calibration model obtained with all VOW, PM alone and GW alone, and (ii) the cross-validation parameters. The coefficients of determination of cross-validation R^2_{CV} were above 0.85 with $R^2_{CV} (GW) > R^2_{CV} (PM) > R^2_{CV} (VOW)$. As noted in this table, RPD_{CV} values indicating the calibration performance were over 2.5. We found that as the dataset homogeneity increased, the RPD_{CV} ($RPD_{CV} (GW) > RPD_{CV} (PM) > RPD_{CV} (VOW)$) increased. This indicated that the intragroup calibration (PM or GW, thus homogeneous) was more efficient as compared with the heterogeneous one (all VOW).

Table 4.5 reports the calculated RPD_P , bias and SE_{PC} . The performance (RPD_P) was above 3 for the materials used in this study. RPD_P for GW is the highest (5.5), followed by the RPD_P for PM (4.4) and the lowest RPD_P was obtained for VOW (3.3). Biases were -0.01, -0.02 and 0.03 for VOW, PM and GW, respectively. As compared to biases obtained with PC, which ranged between -0.8 and 7.5, the NIR model biases were low. The HHV predicted by the NIR models were thus closer to the measured HHV than the HHV calculated by PC. The SE_{PC} values obtained with the NIR model were 0.33, 0.21 and 0.22 MJ.kg⁻¹ for VOW, PM and GW, respectively. Compared to the respective SE obtained for the best models built on the basis of the chemical composition, these values were lower for VOW and GW and equal for PM. This indicated that the NIR model was more accurate than the chemical composition based model. Although the chemical composition model took elemental, proximate or biochemical contents into account, and the NIR model was based on the spectrum, the HHV prediction accuracy was comparable. It seemed that the NIR spectrum contained as much information as the complete chemical characterization of VOW, PM and GW to predict the HHV.

Table 4.4: NIRS model calibration for the prediction of HHV from all VOW, PM or GW.

Dataset	N	Spectrum Outlier	N _C	Calibration Outlier	λ	Mean	SD _C	SE _C	R ² _C	SE _{CV}	R ² _{CV}	RPD _{CV}
VOW	208	16	182	12	689	14.95	1.84	0.46	0.94	0.68	0.89	2.7
PM	135	9	121	5	689	14.45	1.35	0.34	0.94	0.39	0.93	3.4
GW	35	0	34	1	5	16.48	1.75	0.28	0.97	0.42*	0.94	4.2

N is the number of samples, N_C is the number of samples used for calibration, λ is the number of wavelengths used to built the model, Mean is the mean value for the calibration set, SD_C is the standard deviation for the calibration set, SE_C is the standard error of calibration, R²_C is the coefficient of determination of calibration, SE_{CV} is the standard error of cross-validation, R²_{CV} is the coefficient of determination of cross-validation, RPD_{CV} is the performance ratio of cross-validation.

*due to Multiple Linear Procedure used for building this calibration, this number indicated the Predictive Residual Error Sum of Squares (PRESS)

Table 4.5: NIRS model validation for the prediction of HHV from all VOW, PM or GW.

Dataset	N _P	SD _P	SE _P	RPD _P	Bias	SE _{PC}
VOW	194	1.89	0.57	3.3	-0.01	0.33
PM	126	1.57	0.36	4.4	-0.02	0.21
GW	35	1.71	0.31	5.5	0.03	0.22

N_P is the number of samples used for validation, SD_P is the standard deviation for the validation set, SE_P is the standard error of validation, RPD_P is the performance to deviation ratio, bias and SE_{PC} are the standard error of prediction

4.3.5 Comparison between measured HHV values and those predicted by NIR

Figure 4.4 shows a graphical comparison of measured versus NIR-predicted HHV.

In comparison to the SE values from previous equations used for the HHV prediction, we noted that:

- For VOW, $SE_{PC} (NIR) = 0.33 < SE (MLR-9) = 0.72 < SE_p (PC-7) = 0.83$
- For PM, $SE_{PC} (NIR) = 0.21 < SE (MLR-9) = 0.28 < SE_p (PC-7) = 0.81$
- For GW, $SE_{PC} (NIR) = 0.22 < SE (MLR-9) = 0.32 < SE_p (PC-6) = 0.57$

These results suggested that NIR models provided the best tool for estimating HHV because SE was the lowest by modeling HHV with spectra acquisition.

4.4 Discussion

4.4.1 Accuracy of published equations

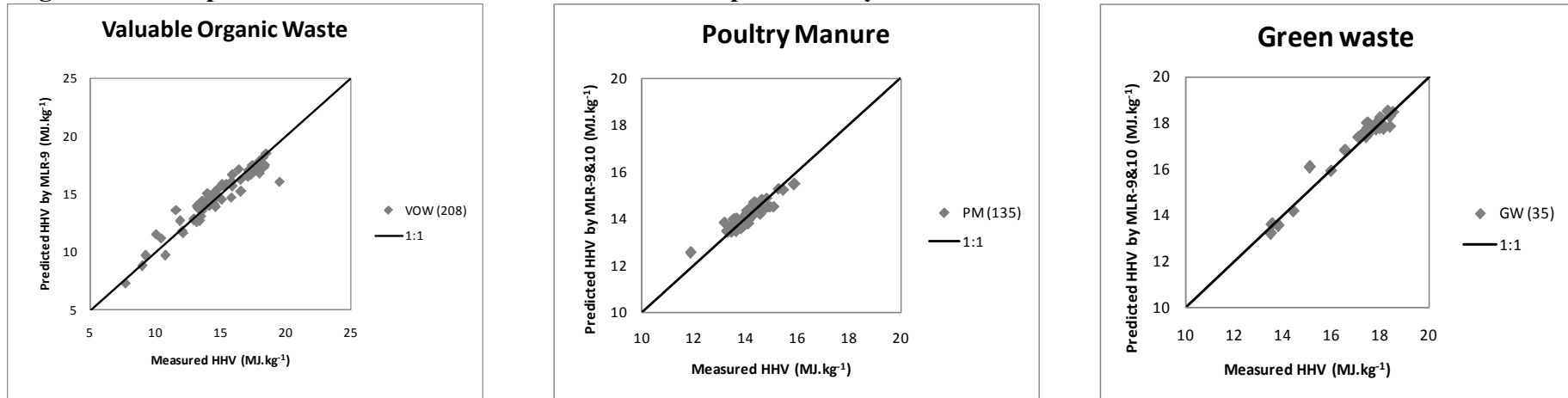
Among the published equations presented in this study, prediction of HHV with PC-5 and PC-7 were retained for the entire dataset and PM, while PC-6 and PC-7 could be used for GW. These equations were formulated with C and ASH contents, indeed $ASH (\%) = 100 - TOM (\%)$.

Most published equations predict the HHV on the basis of C contents. Having an acceptable accuracy of HHV with C content has been demonstrated in numerous studies because C is a basic organic chemistry element and used by all known living organisms. The carbon concentration is positively related with the HHV (Telmo *et al.*, 2010; Callejón-Ferre *et al.*, 2011). These equations, however, did not seem accurate for our dataset due to the difference in the type of biomass used to formulate these equations. Although Tillman (1978) and Sheng *et al.* (2005) developed an equation with a wide range of biomass materials, the bias and SEP were not satisfactory when applied to the VOW of the present study.

Some published equations include highly correlated parameters such as TOM and ASH. This is surprising because such collinearity limits extrapolation of the equation, i.e. the coefficients may overlap each other and thus become irrelevant.

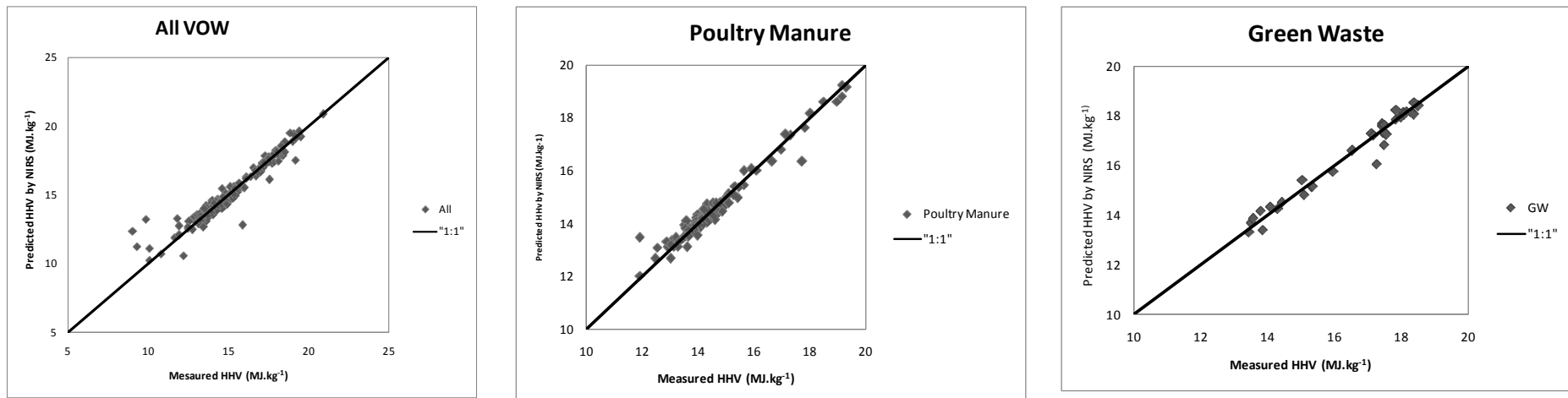
According to Sheng *et al.* (2005), the accuracies are generally not high, mainly due to the fact that the correlations are based on a small number of samples, as also reported by Nhuchhen (2012) who also tested published correlations.

Figure 4.3: Comparison of measured HHV values with those predicted by the best MLR.



MLR-9 was the best correlation found for VOW, MLR 9 & 10 gave the same best equation for PM and GW.

Figure 4.4: Comparison of measured HHV values with those predicted by NIRS.



4.4.2 Accuracy of new proposed equations based on chemical composition

Our study revealed that, for green waste (GW), our TOM-based univariate model was accurate in evaluating the HHV of the samples. The other univariate models did not give a very high accuracy when the SE value was taken into account. The HHV increases with TOM (Saidur *et al.*, 2011). Fuels with high TOM content are preferable, such as wood, certain types of straw and fruit residues (Obernberger *et al.*, 2006). Biochemical analysis of biomass is particularly important when producing derived fuels and chemical products, and studying its combustion and may be useful in HHV determination (Saidur *et al.*, 2011). A combination of different parameters using a stepwise regression is needed. A good prediction cannot be obtained when using only elemental parameters, proximate parameters or biochemical parameters because each VOW constituent plays an important role in its combustion capacity. Although C and N contents are significant for multilinear models, they did not explain more than 75% of the HHV variance for all VOW, 60% for PM, 78% for GW, respectively.

In terms of biochemical fractions, SOL, HCEL, CEL and LIC were all important in determining the HHV. As noted in Figure 4.2, the R^2 values seemed to explain up to 89%, 90% and 95% of the HHV variability for all VOW, PM and GW, respectively. A more complete model was developed by Jiménez and Gonzalez (1991), and was tested here, but it produced highly biased predicted HHV values when applied to the VOW under study. To enhance the accuracy, and despite the fact that SOL, HCEL, CEL and LIC are TOM components, it seems important to determine the contributions of each fraction when assessing the HHV value. Based on the aforementioned research, high lignin and extractive contents and low wood ash and hemicellulose levels would likely offer a higher gross calorific value (White, 1987).

When all the variables (C, N, TOM, SOL, HCEL, CEL, LIC) were taken into account, we showed that:

- N, TOM, SOL, HCEL and LIC were important for a heterogeneous set of VOW
- TOM and LIC were sufficient for PM
- TOM and HCEL were sufficient for GW

Surprisingly, the C content was absent in all the best established MLR, while TOM played a role in HHV building. This preference for TOM for modeling HHV could be justified by the fact that: (i) TOM was more correlated with HHV than C in our study, and (ii) C and TOM were highly correlated so they could not be jointly considered in the regression.

For heterogeneous VOW, we developed a new accurate model, i.e. MLR-9, based on 5 parameters (N, TOM, SOL, HCEL and LIC). This equation was close to those developed by Jiménez and Gonzalez (Jiménez *et al.*, 1991) with a wide range of biomass materials.

For PM, only 2 parameters, i.e. TOM and LIC, were sufficient to predict the HHV. They were taken into account in MLR-9 or MLR-10. LIC was found to be an important parameter in HHV modelling due to the manure composition. Indeed, in Réunion, *Cryptomeria japonica* (a tropical wood, thus containing LIC) is commonly used as litter in poultry farming.

For GW, modelling HHV considering MLR-9 or MLR-10 required TOM and HCEL assessment. HCEL was chosen for HHV prediction due to the importance of this biochemical fraction in GW and the above-ground sugarcane biomass composition.

We noted that when the VOW dataset was broad and heterogeneous more variables were necessary to model the HHV.

4.4.3 Accuracy of NIR calibration

For NIR prediction, accuracy can be ordered as all VOW < PM < GW, in accordance with the RPD_{cv} value. Indeed, according to NIR predictions, increasing the diversity of samples in a dataset generally reduces the calibration accuracy (Stenberg *et al.*, 2004; Thuriès *et al.*, 2005; Brunet *et al.*, 2007; Galvez-Sola *et al.*, 2010). Consequently, and in view of the broad heterogeneity of our 208 VOW samples, the accuracy of our predictions was poorer than that of more homogenous types of VOW (Malley *et al.*, 2002; Sorensen *et al.*, 2007).

When the SEp value of PM is considered, our results were consistent with those reported on poultry excreta (2010) and were better than those recorded on broiler excreta (2001).

For forest fuels, Gillon *et al.* (1997) reported SEp values of 0.36 and 0.21 MJ.kg⁻¹ for *Arbustus unedo* L. and *Erica arborea* L.. The SEp for GW obtained in the present study was therefore comparable to the values reported by these authors.

4.4.4 Best way to predict HHV of VOW

In the present study, new models were built on the basis of the chemical composition. These equations were more accurate than published models and were acceptable for estimating the biomass HHV when multivariate correlations were taken into account. Hence, the SE_p was lower than SE for the VOW, PM and GW datasets. We confirmed the observations recently reported by Erol *et al.* (2010), Quiroga *et al.* (2010) and Nhuchhen *et al.* (2012). However, models developed using chemical composition were hard to implement due to the use of chemicals according to the protocols required for determination of the different parameters.

These models are of interest for estimating HHV of VOW, whose chemical compositions are already available.

The SEp and SE values allowed a comparison between our proposed MLR based on chemical composition and the NIR equation. We noted that the prediction accuracy increased as the SE decreased. In this study, SE_{MLR} was higher than SE_{NIR} for the whole VOW, PM and GW datasets. These results could be explained by the fact that standard chemical methods cannot easily measure the size and diversity of chemical molecular bonds (Paustian *et al.*, 1997). In contrast, spectra from 1100 to 2500 nm (NIR region) contain all the information on chemical composition, provided by overtones and combination bands of the stretching and bending vibrations from major chemical molecular bonds (OH, CH, NH) (Shenk *et al.*, 1996). According to Gillon *et al.*(1999), NIR can clearly predict litter decomposability more accurately than the chemical composition of the initial litter measured by standard chemical methods. Recently, Everard *et al.*(2012) reported that visible and NIR spectroscopy has the potential to rapidly characterize biomass according to its gross calorific value.

The accuracy of the NIR equation was slightly better than that of the best MLR equation based on chemical composition. Although the procedures and costs of developing the equations differed, both NIR and MLR equations accurately predicted HHV. This study demonstrated that NIR spectra were able to give information as well as a chemical description of VOW.

However, NIR predictions are more convenient than predictions obtained using the MLR equation for potential *in situ* analysis. NIR accelerated the determination of HHV in VOW by circumventing the burdensome techniques required for biochemical characterization. On a Réunion scale, NIR will be useful for characterizing HHV directly on site in poultry farms or green waste deposits.

VOW for sustainable energy supply in Réunion as an alternative to their soil amendment use. To date, on the island of Réunion, PM are mainly collected by truck farmers and used as amendments or organic fertilizers for market gardening or sugarcane crops. This situation has some constraints. First, due to the irregularity of visits, breeders are dependent on truck farmers for selling PM (Médoc, 2006). Secondly, even if French regulations are respected (maximum nitrogenous inputs in soils balanced by the real export capacities of the crops), the main constraint is that PM has to be sanitized before use (other regulations relative to organic amendments) (AFNOR, 2006). Considering the GW case, Réunion has 3 main composting platforms located at Saint Pierre, Le Port and Sainte Rose (Direction de l'Environnement de

l'Aménagement et du Logement, 2012). Composted GW may be used as organic amendment if this material complies with the NF U 44-051 standard. However, due to the high heavy metal contents derived from the naturally high heavy metal contents in volcanic soils on the island (Doelsch *et al.*, 2006; Doelsch *et al.*, 2008), composted GW cannot be used without violating the regulations (Doelsch *et al.*, 2008). Spreading of composted GW on soils is hampered by these constraints, leading to saturation of the composting platforms.

Since it is difficult or even impossible to use PM and GW as soil fertilizer or amendments, alternative uses must be considered. PM (Lynch *et al.*, 2013) and GW (Saidur *et al.*, 2011) were reported to have boiler feedstock potential. In Réunion, the thermal power plants of Bois Rouge (60 MW) and Le Gol (64 MW) produce approximately 900 GWh per year based on coal or bagasse combustion. About 45% of the electricity produced in the island comes from bagasse combustion. The thermal power plants are equipped with two boilers capable of burning 130 and 140 t/h of bagasse, respectively, supplying vapor (80 bar, 525°C) to the two turbo alternators (Rouanne, 2003). The challenge for less coal-dependancy in Réunion could be addressed by using PM and/or GW instead of coal. This could be an environment-friendly and cost-effective energy alternative.

In our study, PM and GW produced in Réunion showed interesting HHV values, suggesting that these materials could be effectively used as coal substitute in the existing boilers. Moreover, rapid HHV determination could be possible by enhancing NIR calibration. On an industrial scale, NIR calibration is a promising approach for defining and controlling well balanced cogeneration mixtures.

4.5 Conclusion

Many empirical formulae based on elemental, proximate and biochemical data are available in the literature to estimate HHV. The accuracy of these formulae was statistically assessed in the present study. The accuracies were generally not high, mainly due to the limiting features of the samples (heterogeneous VOW). New correlations based on chemical composition and NIR prediction were thus proposed. The correlation quality was improved via these two approaches. HHV predicted by NIR was found to be better. We demonstrated that NIR could generate much of the required information and the complete analytical vector was also effective for predicting HHV. Rapid determination of HHV for PM and GW could accelerate the use of VOW as energy supply for Réunion.

4.6 Acknowledgements

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Chapitre 5. Prédiction par la Spectroscopie Proche Infrarouge du potentiel méthanogène des Matières Organiques Exogènes en milieu tropical

5.1 Introduction

Un des grands enjeux environnementaux de La Réunion est d'atteindre l'autonomie énergétique visée à l'horizon 2025-2030. La gestion appropriée et la valorisation de déchets organiques ou matières organiques exogènes (MOEx) par des processus anaérobies tels que la méthanisation représentent une solution intéressante permettant de combiner la production d'énergie renouvelable et le traitement des déchets (Esposito *et al.*, 2012). La méthanisation consiste à produire du biogaz à partir de la décomposition biologique des déchets, puis à le valoriser en énergie électrique et/ou thermique. En fonction de la teneur en matière sèche du déchet, plusieurs types de méthanisation existent. Le plus courant est l'infiniment mélangé destiné aux substrats liquides comme les lisiers. La méthanisation par voie sèche s'applique aux substrats solides, comme les fumiers, dont la teneur en matière sèche est supérieure à 15-20% (ARER, 2013). Prochainement, la station d'épuration (STEP) du Grand Prado et la distillerie Rivière du Mât sont les premiers sites à mettre en œuvre cette technologie à la Réunion (ARER, 2013).

Un premier travail d'évaluation des ressources a permis de montrer que le gisement le plus important est représenté par les effluents d'élevage, les industries agroalimentaires – abattoirs, brasseries, laiteries et distilleries- ainsi que les stations d'épuration (Douard, 2010). Sur l'ensemble des déchets produits sur l'île, les effluents d'élevage représentent un gisement important de déchets organiques, 752.000 t par an, soit 72% du potentiel méthanogène (ARER, 2013). Majoritairement issus de la production bovine, porcine et avicole, leur répartition sur le territoire est hétérogène. On trouve une forte concentration d'élevages plutôt dans les Hauts (Le Tampon, Saint-Paul...) et des zones à faible densité dans les Bas (Sainte-Suzanne, Saint-Denis...) en raison de l'urbanisation et de la prédominance de la canne à sucre. Aujourd'hui, les effluents d'élevages sont épandus sur les terres agricoles sans valorisation énergétique. A La Réunion, le potentiel de production électrique qui peut être généré par la méthanisation des déjections animales est estimé à 85 GWh/an, ce qui correspond à l'alimentation d'environ 29.000 foyers réunionnais (à raison de 2.976 kWh/an/foyer). Plus de la moitié de ce potentiel proviendrait des litières accumulées des volailles de chair. En effet, le pouvoir méthanogène de ces fientes (sans litière) est supérieur aux autres types de fumiers. Il serait intéressant de valoriser ce gisement associé à d'autres effluents d'élevage par la méthanisation. Le substrat peut aussi être mélangé avec des déchets non agricoles comme les déchets verts incluant seulement les feuilles et les résidus de tonte, invendus de fruits et légumes, déchets de cantine... (ARER, 2013).

Face à ces différents enjeux liés à la gestion des déchets et le développement de la méthanisation, il est alors important de déterminer le potentiel méthanogène de ces déchets (en anglais, BMP : Biochemical Methane Potential) qui consiste à mesurer en laboratoire la quantité ultime de méthane pouvant être produite en conditions anaérobies. Le BMP fournit les informations permettant de choisir le meilleur substrat, ou mélange de substrats, pour l'optimisation du fonctionnement du digesteur (Raposo *et al.*, 2011).

Mais la mise en œuvre du test BMP en laboratoire prend beaucoup de temps (30-50 jours) et coûte relativement cher. Cela rend le protocole de BMP peu adapté pour les industriels souhaitant optimiser la méthanisation. De nouvelles technologies permettant une détermination rapide du BMP sont alors nécessaires. A partir des caractéristiques biochimiques des déchets, il a été possible de développer de nombreux modèles pour la prédiction des valeurs de BMP; ils sont rapportés dans la revue de littérature de Lesteur *et al.* (2011). Bien que les valeurs de BMP soient connues plus rapidement en adoptant ces modèles, de lourdes manipulations de laboratoire restent toujours nécessaires (dosages de la teneur en matière organique, teneur en fibres, dosages du carbone organique dissous, ...)

D'autres alternatives ont été étudiées. Il a été démontré que la spectrométrie proche infrarouge (SPIR) est une méthode adaptée pour la prédiction rapide des caractéristiques organiques pour les résidus de cultures, les déchets ou les sols. De plus, un avantage non négligeable de la SPIR consiste au fait que une grande variété de paramètres peuvent être prédits simultanément avec succès par une simple acquisition de spectre. La pertinence de la SPIR a été démontrée pour le contrôle de processus de digestion anaérobie (Lomborg *et al.*, 2009; Jacobi *et al.*, 2011; Reed *et al.*, 2011; Ward *et al.*, 2011), le contrôle des matières premières entrantes (Jacobi *et al.*, 2011), le contrôle des biodigesteurs (Luck *et al.*, 2010; Stockl *et al.*, 2012), pour la prédiction de BMP des déchets solides municipaux (Lesteur *et al.*, 2011), des herbes de pré (Raju *et al.*, 2011), et d'une large gamme de substrats organiques (Doublet *et al.*, 2013).

L'utilisation de la SPIR pour la prédiction du BMP est une alternative prometteuse pour La Réunion. L'objectif de ce travail est de mesurer des BMP de MOEx susceptibles d'être valorisées en méthanisation à La Réunion et ensuite de construire un modèle SPIR en vue de la prédiction de BMP d'autres MOEx.

5.2 Matériel et méthodes

5.2.1 Matières Organiques Exogènes (MOEx) étudiées

Le choix des MOEx a été dicté par le fait d'alimenter notre base de données de BMP sur les MOEx tropicales et également d'obtenir une large gamme de valeurs BMP en vue d'avoir des valeurs basses utiles dans tout procédé d'établissement d'équation d'étalonnage.

Les MOEx étudiées ont été les suivantes :

- Des déjections sans litières : Lisier de bovin, Lisiers de porc, Fientes de volaille
- Des déjections avec litières : Fumier de volaille, Fumier de bovin
- Des boues : Boues STEP et boues carnées
- Des composts : Compost de lisier de porc, compost de fumier de volaille, compost de déchets verts, compost de déchets verts et boues STEP

5.2.2 Caractérisation des Matières Organiques Exogènes (MOEx)

Pour toutes les MOEx étudiées, le BMP a été déterminé à partir d'échantillons séchés à 40°C et broyés à 1mm. Un dispositif de mesure du potentiel méthanogène (Automatic Methane Potentiel Test System II - AMPTS II) est utilisé pour nos déterminations. Pour réaliser un test, il est nécessaire de disposer d'un inoculum (idéalement des souches bactériennes issues d'une installation de méthanisation) et d'un substrat à tester. Les essais ont été effectués 3 répliquats pour chaque substrat. Avec les 15 flacons digesteurs on peut ainsi donc inoculer 3 x 4 échantillons dans une série, les 3 autres flacons sont réservés au témoin (inoculum seul). Pour lancer les tests, le ratio MO inoculum/MO substrat est fixé à 3,5/1. En effet, cette valeur du ratio a été adoptée pour avoir un compromis entre le temps de latence, la respiration endogène et le pouvoir tampon du substrat (Angelidaki *et al.*, 2004). Ce choix n'a aucun effet sur la valeur de potentiel méthane (Chen *et al.*, 1996; Raposo *et al.*, 2006).

Avant chaque essai, il est donc nécessaire d'effectuer un prélèvement de l'inoculum pour déterminer la matière sèche (MS) à 105°C et la teneur en matière organique (MO), il s'agit de la matière volatilisée par séchage de la matière sèche à 550°C pendant au minimum 4 heures. Les mêmes mesures sont réalisées sur le substrat. La quantité de matière organique présente dans cette quantité d'inoculum étant connue, on peut ainsi calculer les quantités de substrat nécessaires pour chaque échantillon afin de respecter le ratio. Ainsi, 400g d'inoculum sont pesés pour les témoins, et 400g d'inoculum + X g de substrat pour les essais. La température d'incubation est de 35°C. Un logiciel fourni avec l'appareil permet de contrôler le test pendant les 30 à 50 jours d'expérimentation. Le test prend fin quand le maximum de

production de gaz est atteint : la production journalière est différente de moins de 3% de celle de la veille.

A la fin du test, les données sont traitées dans une feuille de calcul Excel™ (Microsoft Excel, 2010) spécifique suivant le principe suivant : la production de méthane de chaque voie « substrat » est ramenée à la productivité en ml de gaz produit par g de MO du substrat (on soustrait l'inoculum), on moyenne les 3 répétitions si elles sont à $\pm 20\%$ et à l'aide d'un outil statistique de type XLStat™ (Addinsoft, Paris, France) on modélise la courbe selon la loi exponentielle :

$$B = B_0 \times (1 - e^{-kt})$$

avec B = production de méthane en litre de CH_4/kg de MO

B_0 = potentiel de production maximum (asymptote de l'exponentielle)

k = coefficient caractérisant la cinétique de la méthanisation

t = temps en jours

La Figure 5.1 illustre un exemple du résultat obtenu à partir du logiciel.

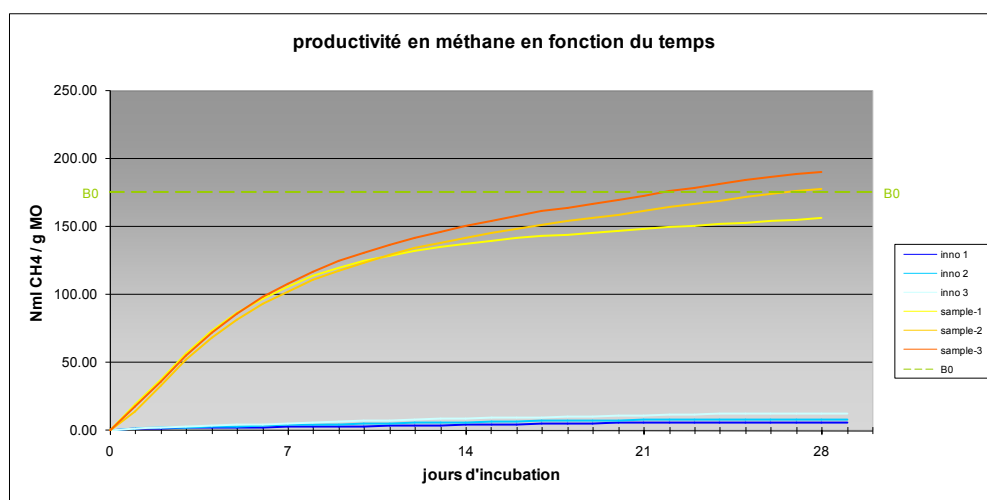


Figure 5.1 : Productivité en méthane en fonction du temps en sortie du logiciel de calcul

5.2.3 Analyses SPIR

Afin de procéder à l'acquisition des spectres SPIR, les échantillons ont été séchés à 40°C puis broyés à 1mm. Les échantillons broyés ont été scannés dans les régions du visible et du proche-infrarouge entre 400 et 2500 nm avec un spectromètre de laboratoire FOSS XDS (Foss NIRSystems, Silver Spring, MD, USA). Les mêmes procédures décrites dans le chapitre 2 ont été appliquées.

5.2.4 Etalonnage SPIR

Les données spectrales ont été traitées par le logiciel WINISI (Infrasoft Int., Port Matilda, (PA), USA). Les longueurs d'onde visibles (400-1098 nm) n'ont pas été utilisées pour ne pas rendre les modèles trop sensibles à d'éventuelles différences de couleur non dépendantes de la composition. Le prétraitement mathématique des spectres a été déterminé pour optimiser les performances des modèles. On a utilisé un traitement des spectres en dérivée d'ordre 2, avec normalisation des spectres et lissage sur 5 points de mesure (procédure WINISI SNVD 2, 5, 5, 1). Les équations d'étalonnages ont été établies par des régressions linéaires multiples (MLR) afin de choisir les longueurs d'ondes les plus informatives (Shenk *et al.*, 1991).

Afin de minimiser les erreurs spectrales ou les erreurs de laboratoire, les outliers ont été écartés lors de la procédure de calibration. Pour décrire les performances des étalonnages, les paramètres suivants ont été pris en compte : le coefficient de détermination (R^2), et les écarts type résiduels d'étalonnage (SEc) et de validation croisée (SEcv). Le ratio performance to deviation $RPD = ET/RMSEcv$ a été calculé comme critère synthétique de la qualité des modèles.

5.3 Résultats

5.3.1 Caractéristiques des MOEx

La MS des substrats utilisés varie entre 0,96 à 87 % de la matière brute. La plus faible valeur correspond à un lisier de porc tandis que la plus forte correspond à des fientes de volaille. Cette gamme de MS indique que les substrats testés sont à l'état liquide, pâteux ou solide au départ.

Les substrats ont des teneurs en MO de 40 à 91% de la MS. Le compost de déchets verts a la plus faible teneur en MO alors que la boue carnée de volaille présente la plus forte teneur.

Les BMP mesurés ont varié dans une gamme de 69 à 488 NmlCH₄.g⁻¹MO. La boue carnée de volaille a un potentiel de production de méthane 8 fois plus élevé que le compost de fumier de volaille. La Figure 5.2 montre les BMP des 19 MOEx étudiées.

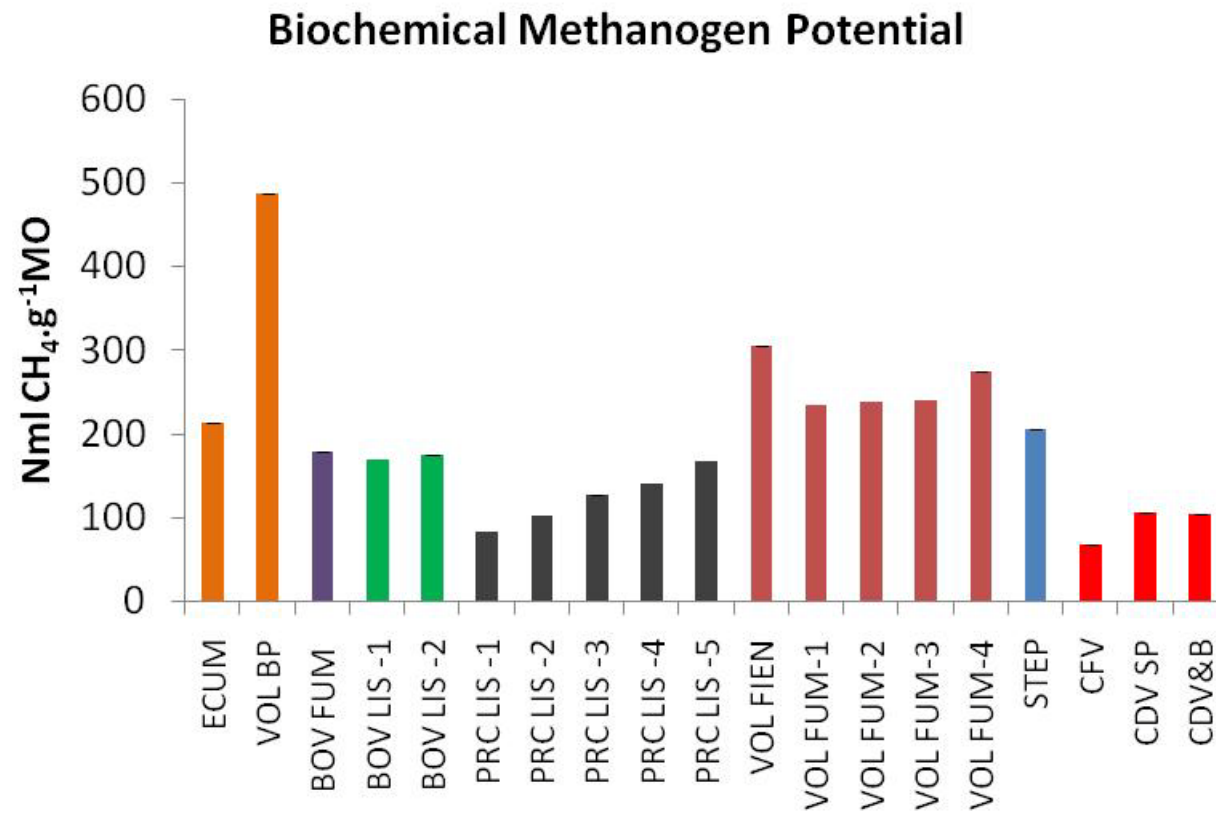


Figure 5.2 : BMP des MOEx étudiées

5.3.2 Performance des étalonnages SPIR

Le Tableau 5.1 présente les performances de l'étalonnage. 2 longueurs d'onde significatives ont servi à cet étalonnage. En effet les limites acceptées par une modélisation SPIR sont fixées à un nombre de longueur d'onde explicatif égal à 10% du nombre des échantillons à calibrer. En étalonnage, un RPD de 2,5 est obtenu. En validation croisée, avec la boue carnée de volaille et les écumes de sucrerie en ouliers, un RPD de 2,7 est calculé. Ces valeurs de ratio RPD indiquent un modèle de prédiction acceptable pour une approximation quantitative des BMP. Quant au SE, il est ici de 24,7 NmlCH₄.g⁻¹MO.

Tableau 5.1 : Paramètres du modèle de calibration SPIR

N	Outliers	#	BMP	Moyenne	ET	SE _c	R ² _c	SE _{cv}	R ² _{cv}	RPD
19	0	2	69-488	190	97	37,61	0,83	38,80	0,83	2,5
17	2	2	69-306	171	67	22,31	0,86	24,70	0,86	2,7

est le nombre de longueurs d'onde pris en compte par notre modèle

BMP, Moyenne, ET, SE_c, PRESS sont exprimés en NmlCH₄.g⁻¹MO

R²_c et R²_{cv} sont les coefficients de détermination respectifs de calibration et de cross-validation

SE_c est l'erreur standard d'étalonnage

SE_{cv} est l'erreur standard de cross-validation

RPD est le ratio entre ET et SE_{cv} indiquant la performance du modèle

5.4 Discussion

5.4.1 BMP des MOEx en milieu tropical

Les déchets de l'industrie agroalimentaire, comme les boues carnées de volaille notamment riches en graisses, permettent une production de biogaz élevée et sont souvent utilisés comme co-produits entrant dans le digesteur (Zdanevitch *et al.*, 2009).

En ce qui concerne les produits compostés, les BMP sont faibles. Ces MOEx sont déjà très minéralisées au cours du compostage (Bernal *et al.*, 1998; Berthe *et al.*, 2008). La partie la plus fermentescible de la MO a été métabolisée et seuls subsistent des composés peu ou pas biodégradables par méthanisation ((Bernal *et al.*, 2009).

Le Tableau 5.2 compare les BMP mesurés dans notre étude et ceux rapportés par d'autres auteurs. Les BMP des substrats en milieu tropical étudiés ici sont inférieurs à ceux de la bibliographie. En effet, en fonction des substrats utilisés, les rendements en méthane et la composition du biogaz peuvent varier (Bujoczek *et al.*, 2000; De Gioannis *et al.*, 2007; Segatto *et al.*, 2007). Ainsi, le potentiel méthanogène des matières entrantes est très variable, les déjections animales (lisiers, fumiers) ayant le potentiel le plus faible : en effet ces matières sont déjà issues d'une digestion biologique partielle dans l'intestin de l'animal (ruminants principalement). En revanche les déjections animales sont intéressantes pour la méthanisation à cause de leur flore bactérienne, très riche, et de la stabilité qu'elles apportent au processus de méthanisation (Steffen *et al.*, 1998).

Tableau 5.2: Comparaison des valeurs de BMP mesurées sur des MOEx tropicales avec d'autres études

MOEx	Nb.	BMP (NmlCH ₄ .g ⁻¹ MO)	Source
Ecumes de sucrerie	1	214	Notre étude
Résidus de canne à sucre (size:1)		177	(Nzila <i>et al.</i> , 2010)
Boues carnées de volaille	1	488	Notre étude
Déchets d'abattoir de volaille		550–670	(Salminen <i>et al.</i> , 2000)
Déchets carnés (viande)	14	180-610	(Doublet <i>et al.</i> , 2013)
Déchets agroindustriels	58	70-820	(Doublet <i>et al.</i> , 2013)
Fumier de bovin	1	180	Notre étude
		148	(Moller <i>et al.</i> , 2004, 2004)
		197 (3)	(Triolo <i>et al.</i> , 2011)
		184	(Omar <i>et al.</i> , 2008)
Lisier de bovin	2	173,5 (±3,5)	Notre étude
		243	(Steffen <i>et al.</i> , 1998)
	9	238 (42)	(Luna-delRisco <i>et al.</i> , 2011)
Lisier de porc	5	114,5 (±32,9)	Notre étude
		244-343	(Vedrenne <i>et al.</i> , 2008)
		175-350	(Steffen <i>et al.</i> , 1998)
		317	(Luna-delRisco <i>et al.</i> , 2011)
		356	(Moller <i>et al.</i> , 2004, 2004)
		417,2 (11,8)	(Triolo <i>et al.</i> , 2011)
Fientes de volaille	1	306	Notre étude
		410-430	(Webb <i>et al.</i> , 1985)
		283-548	(Bujoczek <i>et al.</i> , 2000)
		350-600	(Moletta, 2008)

Tableau 5.2 (suite)

Fumier de volaille	4	240,8 ($\pm 4,3$)	Notre étude
		250 (ml/gMS)	(Moletta, 2008)
Boues de station d'épuration	1	206	Notre étude
	30	30-370	(Doublet <i>et al.</i> , 2013)
Compost de fumier de volaille	1	69	Notre étude
Compost de déchets verts	1	107	Notre étude
Compost de déchets verts et de boues	1	105	Notre étude
Déchets solides stabilisés	31	5-280	(Doublet <i>et al.</i> , 2013)

5.4.2 Prédiction des BMP par la SPIR

Nos résultats ont donné des performances permettant une approximation quantitative des valeurs de BMP avec une PRESS de 24,7 NmlCH₄.g⁻¹MO. Les performances obtenues dans notre étude sont similaires à celles rapportées par d'autres auteurs. Nous pouvons citer Lesteur *et al.* (2011) qui rapportent un RPD de 2,4 et un SE_P de 28 NmlCH₄.g⁻¹MO avec les déchets municipaux solides et Raju *et al.* (2011) qui notent un RPD de 1,8 et SE_P de 37 NmlCH₄.g⁻¹MO avec les tontes de prairie. Ces auteurs ont travaillé sur des matrices de MOEx uniques. Quant à Doublet *et al.* (2013) qui a étudié la prédiction des BMP sur des matrices de MOEx variées, un RPD de 2,6 et un SEP de 40 NmlCH₄.g⁻¹MO sont rapportés. Même si nous avons un nombre limité d'échantillons très hétérogènes, nos performances ont été similaires à celles d'autres études.

5.5 Conclusion

La SPIR apparaît comme une méthode appropriée pour la prédiction rapide des BMP des substrats organiques en milieu tropical à long terme. Néanmoins, l'intégration d'une plus grande diversité de substrats organiques est encore nécessaire pour rendre le modèle plus robuste. A cet effet, les mesures de référence de BMP doivent être multipliées afin de développer un étalonnage plus performant.

**Chapitre 6. Potential for nitrous oxide (N_2O)
emissions from denitrification after soil amendment
with exogenous organic matter (EOM) from
agricultural and urban activities in tropical areas**

Avant-propos

L'oxyde nitreux (N_2O) est un gaz à effet de serre avec un potentiel de réchauffement climatique 298 fois plus élevé que celui du dioxyde de carbone (CO_2) sur 100 ans (Solomon *et al.*, 2007). Il est aussi impliqué dans la dissociation de l'ozone stratosphérique, qui protège la biosphère contre les effets nuisibles des rayons ultraviolets du soleil. C'est même la plus importante cause de cette dissociation de ce 21^{ème} siècle (Ravishankara *et al.*, 2009). La concentration atmosphérique de ce gaz N_2O a augmenté durant les dernières décennies à un taux moyen de 0,2% par an (Khalil *et al.*, 2002), d'où l'intérêt scientifique et public dans la quantification précise des émissions de N_2O et la détermination des moyens pour réduire sa production (Bernard, 2011).

L'agriculture et les modes d'usage des sols sont à l'échelle mondiale les sources les plus importantes de ce gaz (Solomon *et al.*, 2007). Ainsi, les sols agricoles contribuent à 58% des émissions de sources anthropiques de N_2O (Solomon *et al.*, 2007). L'augmentation des émissions de N_2O des sols est liée à l'augmentation des apports d'azote, due à l'intensification de l'agriculture. Ce gaz est en effet le produit de plusieurs transformations de l'azote dans les sols (Robertson *et al.*, 1987), dont les processus majeurs sont la nitrification et la dénitrification (Mosier *et al.*, 1998).

Du fait des valeurs agronomiques des matières organiques exogènes (MOEx), qui sont des matières organiques apportées au sol et qui correspondent souvent à des déchets pour leurs détenteurs, leur retour au sol constitue une voie logique de valorisation. Une valorisation qui présente non seulement l'avantage de mieux gérer les déchets organiques mais aussi de pallier la dégradation des sols agricoles due généralement à une faible restitution des matières organiques. Dès lors, afin d'inscrire la valorisation de ces MOEx dans un contexte de développement durable, s'assurer de leur bienfait est un objectif incontournable (Calbrix, 2005). Mais l'apport de MO dans le sol peut stimuler la dénitrification en favorisant un environnement anaérobie (Stevens *et al.*, 1974; Rice *et al.*, 1988) ainsi qu'en fournissant une source d'énergie (C organique) aux bactéries dénitrifiantes (Christensen, 1985). Ainsi cette voie de valorisation des MOEx peut promouvoir l'émission de N_2O des sols agricoles. Les scientifiques portent un intérêt croissant sur les études des corrélations entre l'apport de MOEx au sol et ses émissions de N_2O (Maag, 1990; Paul *et al.*, 1993; Velthof *et al.*, 2003; Dambreville *et al.*, 2004; Jäger *et al.*, 2011; Paul *et al.*, 1989).

En zone tropicale, comme à Madagascar et à La Réunion, très peu d'études sur les émissions de N_2O des sols ont jusqu'ici été entreprises (Chapuis-Lardy *et al.*, 2009; Rabenarivo, 2011) et encore moins intégrant l'effet des apports de MOEx aux sols tropicaux.

Aujourd'hui, la spectroscopie de réflectance dans le proche infrarouge est reconnu comme une approche fiable pour quantifier, rapidement et à moindre coût, certaines propriétés du sol. Les développements récents ont montré son intérêt pour prédire des propriétés biologiques des sols comme la biomasse microbienne, le potentiel de dénitrification ou encore l'activité enzymatique (Reeves *et al.*, 2000; Cohen *et al.*, 2005; Terhoeven-Urselmans *et al.*, 2008; Barthès *et al.*, 2010).

L'objectif de ce chapitre est donc de (i) étudier les effets d'apport de MOEx sur les activités enzymatiques dénitrifiantes (DEA) et le ratio of $N_2O/(N_2O+N_2)$ et (ii) de prédire les DEA en faisant appel à la SPIR.

Ce chapitre correspond à l'article en préparation :

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Potential for nitrous oxide (N_2O) emissions from denitrification after soil amendment with exogenous organic matter (EOM) from agricultural and urban activities in tropical areas

6.1 Introduction

The global direct N₂O emissions from fertilized agricultural soils are estimated at 0.9 (range: 0.18–1.6) TgN year⁻¹ for soils fertilized with mineral N fertilizers and 0.6 (range: 0.12–1.1) TgN year⁻¹ for soils fertilized with animal wastes (Mosier *et al.*, 1998), but the uncertainties in these estimates are large. N₂O is produced in soil during several microbial processes, which may occur simultaneously within different microsites of the same soil. It is necessary to better understand the regulation of the different microbial processes, with a view to developing more targeted management practices for mitigation of N₂O (Baggs, 2011).

Nitrifiers produce N₂O in two ways, by nitrification and nitrifier denitrification. In nitrification, N₂O is produced as a by-product of NH₃ oxidation. In nitrifier denitrification, N₂O is an intermediate of the reduction of NO₂⁻ to N₂ (Wrage *et al.*, 2001). Denitrifiers produce N₂O as an intermediate and possible end product of the reduction of NO₃⁻ to N₂. Besides these main sources, other sources like chemodenitrification or heterotrophic nitrification contribute substantially under some conditions to the production of N₂O (Chalk *et al.*, 1983; Papen *et al.*, 1989; Anderson *et al.*, 1993).

One of the main pathways in the N cycle is denitrification. Denitrification, which is traditionally considered to occur under anaerobic conditions (Morley *et al.*, 2008), is the reduction of nitrate (NO₃⁻) or nitrite (NO₂⁻) to nitric oxide (NO), then N₂O and di-nitrogen (N₂) gases. Four enzymes are required sequentially to reduce NO₃⁻ ion into N₂. Each enzyme uses a redox active metal cofactor, such as molybdenum for NO₃⁻ reduction, iron or copper for NO₂⁻ reduction, iron for NO reduction, and copper for N₂O reduction (Richardson *et al.*, 2009).

There are several enzymatic and microbial routes to N₂O production. However, the bacterial N₂OR, is the only known enzyme capable of reducing N₂O to N₂. The reaction, shown in Equation 1, is highly favoured thermodynamically (indicated by the large negative value of the free energy, ΔG°).



Animal manures may differ strongly in composition and as a result may differ in the emission of N₂O following application to soil (Velthof *et al.*, 2003). Fertilizer and organic amendment type may affect N₂O emission in several ways, i.e: (1) the type of N (NO₃⁻, NH₄⁺, and organic N) which affects N₂O production during nitrification and denitrification, (2) the presence of easily available C, which stimulates denitrification activity and O₂ consumption in the soil following its application, and (3) effects on biological, chemical and physical soil

processes because of changes in pH and the addition of other compounds (salt, water). Animal manures are a mixture of mineral N, easily mineralizable and resistant organic N and C compounds, salts and water. For example, the application of slurry to soil increases the content of NH_4^+ , and of easily mineralizable N and C in the topsoil. This in turn may increase nitrification and subsequently denitrification locally, which may also increase emission of N_2O . The organic C compounds in slurry provide readily available substrate for denitrifiers (Dendooven *et al.*, 1998; Paul *et al.*, 1989). Application of animal slurries to soils increases the emission of N_2O , but there are large differences between types of slurries due to differences in slurry composition (Velthof *et al.*, 2003).

There are numerous approaches to quantify denitrification, and all the existing approaches have some limitations (Groffman *et al.*, 2006). These difficulties in measuring denitrification arise from its spatial and temporal variability, methodological restrictions and difficulty in quantifying the dominant end product N_2 against its high ambient concentration in the atmosphere. The most commonly used approach for estimating denitrification involves measuring the production of N_2O from the soils in the presence of acetylene (C_2H_2) which inhibits N_2O reduction to N_2 (Balderston *et al.*, 1976; Yoshinari *et al.*, 1976). This makes the easily detected N_2O the sole product of denitrification. Soil samples are incubated in the presence and absence of C_2H_2 , and the difference in N_2O produced during the incubation is used to calculate the amount of N_2 produced during denitrification. The C_2H_2 inhibition technique has been applied successfully in studies which have led to an understanding of the spatial and temporal variability of denitrification (Groffman *et al.*, 1999). A slight modification of the C_2H_2 inhibition method is used to estimate denitrification enzyme activity (DEA). Soil samples supplied with excess moisture, C and NO_3^- together are incubated in the presence of C_2H_2 in anaerobic conditions (Tiedje *et al.*, 1989). The N_2O emitted gives an estimate of potential denitrification of soil and the ambient reductase enzyme activity. Although this laboratory measurement is a valuable indicator for discriminating soils with high potential for N_2O emissions, yet it is a time-consuming method because it involves the incubation of soil samples with addition of organic carbon and nitrate (Barthès *et al.*, 2010).

Near infrared reflectance spectroscopy (NIRS) is a rapid and non-destructive analytical technique involving diffuse reflectance measurement in the near infrared (NIR) region (1000–2500 nm). NIR spectra depend on the number and type of chemical bonds in the analyzed material (Foley *et al.*, 1998). NIRS is now widely used to predict soil carbon and nitrogen content (Cécillon *et al.*, 2007). Recent developments of NIRS in soil ecology have shown its

efficiency to predict soil biological properties including microbial biomass, potential nitrification, soil enzyme activities (Reeves III *et al.*, 2000; Terhoeven-Urselmans *et al.*, 2008). Attempts to use NIRS for determining potential denitrification have been rare and limited to small or homogeneous sample sets (Schimann *et al.*, 2007; Cécillon *et al.*, 2008). Barthès *et al.* (2010) assessed the potential of NIRS for characterizing potential denitrification over a large set of topsoil samples representing contrasting tropical environments and land uses. Rabenarivo (2011) studied the help of NIRS to predict soil biological activity and potential denitrification of Malagasy soils with different textures. However, there is still a lack of knowledge about the usefulness of NIRS to predict DEA from amended soils. Such information would be useful for scenarios dealing with the mitigation of N₂O production in agricultural amended soils.

The purpose of this work was (i) to study the effect of EOM type on denitrifying enzyme activity (DEA) and on the ratio of N₂O/(N₂O+N₂) emitted during this transformation and (ii) to predict DEA by using near infrared spectroscopy.

6.2 Material and methods

6.2.1 Soil description

Our experiment was carried out with two Réunion soils: an andic cambisol and a nitisol and two Malagasy soils a ferralsol and an arenosol-nitisol. The andic cambisol from Réunion was collected at Les Colimaçons in a medium elevation area on the western windward side of the island. This loamy (38% loam) soil had a pH of 6.1, a total N content of 0.55%, and a C content of 2.7%. The nitisol was from La Mare. This clayey soil (66% clay) had a pH of 5.6, a total N content of 0.22 % and a C content of 2.3 %. Malagasy ferralsol was a clayey (31% clay) ferralsol sampled at Lazaina, located in the North East of Antananarivo. This soil had a pH of 5.5, a total N content of 0.14%, and a C content of 1.87%. Malagasy arenosol-nitisol soil was a sandy (46% sand) soil collected in Ankarafantsika (West of Madagascar, near Mahajanga). This soil had a pH of 5.4, a total N content of 0.05 %, and a C content of 0.22 %. After air-drying, soils were sieved through a 2 mm mesh sieve.

6.2.2 Added EOM

Three categories of EOM were used for the experiments: 21 animal wastes, 6 agro-industrial wastes and 7 urban wastes. Table 1 summarizes their main characteristics. Biochemical fractions of EOM were determined using the Van Soest method (Van Soest *et al.*, 1991) as modified under the French standard XP U 44-162 (AFNOR, 2009). The soluble (SOL),

hemicellulose-like (HCEL) cellulose-like (CEL) and lignin+cutin-like (LIC) fractions were separated.

6.2.3 Incubation experiment and N₂O measurements

68 mixtures of soil and EOM were mixed for the incubation experiment: 15 Réunion EOM-Réunion soils and 19 Malagasy EOM-Malagasy soils. The same amount of EOM added into soil was equivalent to 33kgN.ha⁻¹ which corresponded to the recommended dose for Malagasy rice crop. The soil samples, equivalent to 30 g of dry soil and corresponding amounts of organic waste (0.05mgN.g⁻¹ soil), were mixed thoroughly. The 4 soils without added EOM were taken as control for each series.

The denitrifying enzyme activity (DEA) test measured the activity of denitrifying enzymes from data on N₂O accumulated over a short duration just after optimal conditions for denitrification have been achieved, i.e. without growth of denitrifying populations, and when N₂O reductase activity is inhibited as described by Lensi *et al.* (1991). Briefly, triplicates of mixtures soil-EOM were put in a 150-ml airtight vial. Before incubation at 28°C, each soil-EOM mixture was humidified at 100% of its water holding capacity with a nutritive solution containing potassium nitrate (0.2 mg N.g⁻¹ soil), glucose (1 mg C.g⁻¹ soil) and glutamic acid (1 mg C.g⁻¹ soil). Two series of incubation were conducted. The atmosphere of the vial was evacuated and replaced by a 90:10 helium-acetylene mixture to provide anaerobic conditions and the inhibition of the N₂O reductase activity (Yoshinari *et al.*, 1977). This measurement usually accounts for the soil potential to emit N₂O by denitrification.

The potential N₂O production from denitrification was evaluated by incubation of parallel samples without acetylene allowed to account for the reduction of N₂O in N₂. Both measurements were used to calculate the ratio N₂O/(N₂O+N₂). The N₂O efflux was measured in the headspace atmosphere of the vials using a gas chromatograph equipped with an electron capture detector (Varian Star 3400 CX, Varian Chromatography Group, Walnut Creek, CA, USA) and expressed as µg N-N₂O.g⁻¹.h⁻¹ dry soil.

The ratio N₂O/(N₂O+N₂) was calculated as follows:

$$\text{Ratio} = \frac{\text{Potential N}_2\text{O production}}{(\text{Potential N}_2\text{O production} + \text{DEA})}$$

The ratio between the final products from denitrification N₂O/(N₂O+N₂) indicated the capacity of denitrifiers to reduce N₂O to N₂ under optimal conditions for their functioning.

Table 6.1 : EOM characteristics.

EOM category, EOM nature, N contents, CtoN ratio and C added to soil (C added was the quantity of C when the equivalent of 33kgN.ha⁻¹ of EOM were mixed with soil) are presented in this table.

Category	Nature	Code	N (mg.g ⁻¹ dry matter)	C/N	C added (mgC.g ⁻¹ dry soil)
Animal	Composted dairy manure with bagasse	CoA	10.9	13.71	0.69
	Composted sheep manure and coffe cake	VGT	24.7	17.12	0.86
	Composted pig slurry	CPS-Co	20.7	15.27	0.76
		CPSc-SJ	34.6	9.05	0.45
	Composted poultry manure	CCM-Co	34.1	11.43	0.57
		CCM-Rep	21.6	12.15	0.61
	Dairy manure	DM-Bb	24.4	13.82	0.69
		DM-PSS	19.3	15.36	0.77
		DM-RUN	24.9	17.43	0.87
	Dairy slurry	DS-LiB	19.6	13.30	0.66
		DS-RUN	27.2	16.66	0.83
	Ovine manure	GM-RUN	29.8	11.71	0.59
		GM-Mdg	21.5	18.79	0.94
	Pig manure	PM-Mdg	11.5	17.49	0.87
	Pig slurry	PS-LiP	8.1	18.54	0.93
		PSc-SJ	19.8	17.12	0.86
	Poultry droppings	PID-P	51.1	6.43	0.32
	Poultry droppings	PID-V	23.9	9.33	0.47
	Poultry manure	PIM-Av	41.8	9.84	0.49
		PIM-Pon	40.6	8.82	0.44
	Rabbit manure	RM	12.4	10.73	0.54
Agroindustrial	Fishery waste	FSW	39.5	5.79	0.29
	Oil cake (Oil mill waste)	OMW	70.6	6.53	0.33
	Slaughterhouse sludge	PSS	53.6	11.96	0.60
	Slaughterhouse waste	SHW	99.2	4.07	0.20
	Sugar refinery waste	SCUM	15.4	19.06	0.97
	Zebu ground horn	ZGH	73.7	3.20	0.16
Urban	Composted fermentable waste	CFW-M	10.3	17.98	0.90
		CFW-V	6.2	21.35	1.07
	Composted green waste	CGW-SP	13.7	16.79	0.84
		CGWSS	27.6	9.86	0.49
		LPS-A	7.7	25.51	1.28
	Potting soil from landfill	LPS-I	6.4	17.22	0.86
		LPS-T	5.0	19.88	0.99
	Mineral fertilizer	NPK			

6.2.4 Statistical analysis

Statistical analyses were performed by using the XLSTAT Pro 12 software. Before doing analysis, distribution normality was tested. A Dunnett bilateral test was used to assess the difference between the control and each EOM. The t Student test was used to compare the effect of different EOM. The analysis of the variance (ANOVA) was used to detect the effect of EOM on DEA and potential N₂O production as well as the interactions between soil and EOM.

PCA were performed by taking into account DEA values ($\mu\text{g N-N}_2\text{O}\cdot\text{g}^{-1}\cdot\text{h}^{-1}\text{dry soil}$), C added to soil as EOM ($\text{mgC}\cdot\text{g}^{-1}\text{dry soil}$), N contents of EOM ($\text{g}\cdot\text{g}^{-1}\text{dry matter}$), C-to-N ratio, biochemical Van Soest fractions: SOL, HCEL, CEL, LIC ($\text{g}\cdot\text{g}^{-1}\text{TOM}$).

6.2.5 Modeling DEA using near infrared spectroscopy

6.2.5.1 Spectra acquisition

Sample reflectance in the NIR range was measured between 1100 and 2500 nm at 2-nm intervals with a Foss NIRSystems XDS spectrophotometer (Silver Spring, MD, USA). The scan was performed on a 5-g subsample (control soil and soil with EOM) (<1mm ground, oven-dried at 40°C) packed in a ring cup. Each spectrum, averaged from 32 co-added scans, was recorded as absorbance ($\log [1/\text{reflectance}]$). All spectral data analyses were conducted using the WinISI III-v.1.61 software (Infrasoft International, LCC, State College, PA, USA).

6.2.5.2 Calibration

Several mathematical pre-treatments were evaluated for spectrum pre-processing, in order to reduce baseline variations, enhance spectral features, reduce particle-size effect, remove linear or curvilinear trends of each spectrum, or remove additive or multiplicative signal effects (Geladi *et al.*, 1985; Barnes *et al.*, 1989; Reeves III *et al.*, 2002). The standard normal and variate with detrending (SNVD) pre-treatment was selected.

A principal component analysis was carried out on spectral data for calculating the Mahalanobis distance H , and samples with $H > 3$ were considered spectral outliers and eliminated from further investigations (Mark *et al.*, 1985).

Cross-validation was performed by using multiple linear regression. The calibration subset was divided into four groups (the sample number was given in Table 3 and 4), all but one being used for developing the model and one for prediction, the procedure being performed four times to use all samples for both model development and prediction. The residuals of all predictions were pooled to calculate the standard error of cross-validation (SE_{CV}). Calibration outliers (i.e. with residual > 2.5 times SE_{CV}) were removed and another cross validation was

performed, the procedure being carried twice. The number of factors after which final SE_{CV} no longer decreased meaningfully determined the optimal number of factors of the model. The model performance was evaluated according to coefficient of determination (R^2), and RPD_{CV} (ratio of standard deviation to SE_{CV}); SE_{CV} was expressed in absolute value (in $\mu\text{gN-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil). According to Chang et al. (2001), prediction models with $RPD > 2$ were considered accurate for soils properties calibration.

6.3 Results

6.3.1 Activity measurements

Table 6.2 summarizes the statistical analyses related to significant difference between soil receiving a given EOM and the control (no EOM) for both N_2O emissions measurements.

6.3.1.1 Denitrifying Enzyme Activity (DEA)

The DEA varied depending on the soil. DEA from Lazaina mixtures were as much as those from Les Colimaçons mixtures but were about 3 to 4 times more important than DEA with La Mare soil EOM mixtures and about 40 to 50 times more important than DEA from Ankarafantsika soil EOM mixtures. An ANOVA performed with all mixtures allowed to order soils as follows: DEA Lazaina (LZN) > DEA Les Colimaçons (COLI) > DEA La Mare (MARE) > DEA Ankarafantsika (ANK).

For Les Colimaçons mixtures, DEA ranged from 0.39 to 0.89 $\mu\text{g N-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil. One-way ANOVA showed a significant effect of EOM treatment on DEA with the following classification: CPS-Co > PSc-SJ > CCM-Co > CCM-Rep > CPS-SJ > GM-Run=VGT > DS-Run=CGW-SP > PIM-Av > PIM-Pon=DM-Run > CGWSS=PSS=SCUM > NPK > COLI. 11 of the 16 EOM generated significant higher DEA than in the control for Les Colimaçons soil.

For La Mare mixtures, DEA varied between 0.12 and 0.31 $\mu\text{g N-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil. Statistically, 13 of the 16 added EOM conducted to an effect on DEA when compared to the control ($p < 0.001$). NPK, PSS and VGT were the exceptions. ANOVA test allowed to classify EOM effect on DEA in the following order: PSc-SJ > CPS-Co > CGW-SP = CCM-Rep > CGWSS = DM-Run > DS-Run > GM-Run > SCUM > CPS-SJ > CCM-Co = PIM-Pon = PIM-Av > NPK = PSS = VGT = MARE.

For Ankarafantsika mixtures, a range from 0.01 to 0.02 $\mu\text{g N-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil was measured for DEA depending on the added EOM: PS-LiP > CFW-V > DM-PSS = RM > LPS-A > LPS-T = LiB > PID-V > PM-Mdg = CoA > CFW-M = DM-Bb = PID-P > GM-Mdg > FSW = OMW > VGT = SHW = ZGH = ANK (one-way ANOVA; $p < 0.05$). Adding EOM

in Ankarafantsika soil led to higher DEA for 15 of 20 treatments ($p < 0.05$) compared to values in the control.

For Lazaina mixtures, DEA varied between 0.70 to 1.52 $\mu\text{g N-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil. Added EOM can be ranked for their stimulating effect on DEA as follows: CFW-M > GM-Mdg=PID-V= CFW-V=LiB > CoA > PS-LiP > RM=DM-PSS=PID-P=LPS-T= LPS-A=FSW=PM-Mdg > LPS-I=DM-Bb > ZGH > Vgt > SHW=OMW = LZN. However, 14 of 20 EOM treatments were significantly different from the control according to bilateral Dunnett test ($p < 0.05$).

Table 6.2 : Level of probability (p) of the Dunnett bilateral tests used to compare a soil receiving a given EOM to its control treatment (same soil without EOM) for potential denitrification tests with and without acetylene. (NS: for a given soil, no significant difference between the control and the considered EOM treatments)

		p< 0.001	p<0.05	p<0.1	NS
With C ₂ H ₂	Madagascar Lazaina	- CFW-M, GM-Mdg, PID-V, CFW-V, DS-LiB, CoA	PS-LiP, RM, DM-PSS, PID-P, LPS-T, LPS-A, FSW, PM-Mdg		LPS-I, DM-Bb, ZGH, SHW, VGT, OMW
	Madagascar Ankarafantsika	- PS-LiP, RM, LPS-T, LPS-I, LPS-A, LiB, PID-V, PM-Mdg, CoA, CFW-M, CFW-V, DM-Bb, PID-P, DM-PSS	GM-Mdg		FSW, OMW, VGT, SHW, ZGH
	Reunion Colimaçons	- CPS-Co, PSc-SJ, CCM-Co, CCM-Rep, CPSc-SJ, GM-RUN, VGT	DS-RUN, CGW-SP, PIM-Av, PIM-Pon		DM-RUN, CGWSS, PSS, SCUM, NPK
	Reunion – La Mare	- PSc-SJ, CPS-Co, CCM-Rep, CGW-SP, CGWSS, DS-RUN, DM-RUN, CCM-Co, SCUM, CPSc-SJ, PIM-Pon, , PIM-Av			PSS, VGT, NPK
Without C ₂ H ₂	Madagascar Lazaina	- PID-V, CFW-M, CFW-V, DS-LiB, GM-Mdg, FSW, PID-P, DM-PSS	PS-LiP, PM-Mdg, LPS-T, RM, CoA, SHW, LPS-I	ZGH, LPS-A	DM-Bb, OMW, VGT
	Madagascar Ankarafantsika	- PS-LiP, RM, LPS-T, LPS-I, LPS-A, DS-LiB, PID-V, PM-Mdg, CoA, CFW-M, CFW-V, DM-Bb, DM-PSS	GM-Mdg, PID-P, FSW		OMW, VGT, SHW, ZGH
	Reunion Colimaçons	- PSc-SJ, CPSc-SJ, CCM-Rep, CCM-Co, CPS-Co	GM-RUN, VGT		DS-RUN, CGWSS, DM-RUN, CGW-SP, PSS, SCUM, PIM-Pon, NPK, PIM-Av
	Reunion – La Mare	- PSc-SJ, CPS-Co, CCM-Rep, CGW-SP, CGWSS	CPSc-SJ		DS-RUN, DM-RUN, CCM-Co, PSS, SCUM, VGT, PIM-Pon, NPK, PIM-Av

6.3.1.2 Potential N₂O production

For Les Colimaçons, the potential N₂O production varied between 0.45 and 0.94 $\mu\text{g N-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil. The control, PSc-SJ, CPS-Co and PIM-Av presented a significant difference when compared to the DEA.

Potential N₂O net production ranged between 0.11 and 0.28 $\mu\text{g N-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil for La Mare control and mixtures. DEA differed from potential N₂O net production for LisPc, CGW- SP ($p<0.05$), DS-Run, DM-Run and SCUM ($p<0.01$).

For Ankarafantsika, potential N₂O net production ranged between 0.01 and 0.014 $\mu\text{g N-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil. DEA and N₂O production differ significantly neither for control nor EOM-soil mixtures.

Potential N₂O net production ranged between 0.93 and 1.27 $\mu\text{g N-N}_2\text{O.g}^{-1}.\text{h}^{-1}$ dry soil for Lazaina. In general, potential N₂O measured was lower than for DEA excepted for SHW and FSW. Statistical significant difference in N₂O production between both activities (+C₂H₂ / - C₂H₂) was observed for CFW-A and CFW-M ($p<0.05$).

6.3.2 Ratio N₂O/(N₂O+N₂)

Comparisons of the DEA (measurement with C₂H₂) and the potential N₂O production (measurement without acetylene) for the 4 soils are presented in Figure 6.1. The calculated ratio per soil and EOM treatment is reported in Figure 6.2. The ratio N₂O/(N₂O+N₂) values varied between 0.40 to 0.66.

6.3.3 Relation between N₂O production and EOM composition

The results of principal components analyses as performed per soil are presented in Figure 6.3 to Figure 6.7.

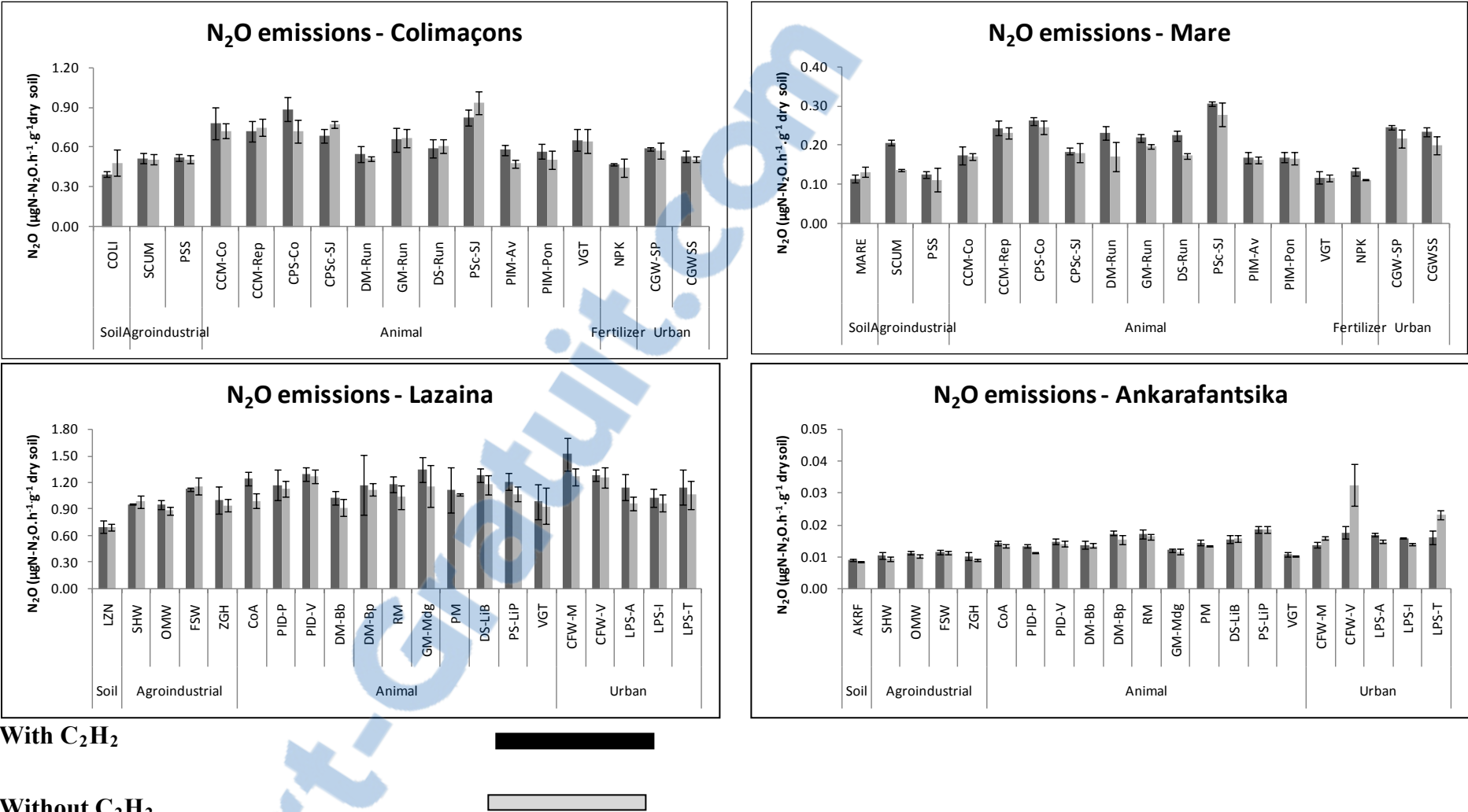


Figure 6.1 : N₂O fluxes with acetylene (DEA) and without acetylene (potential denitrification) tests

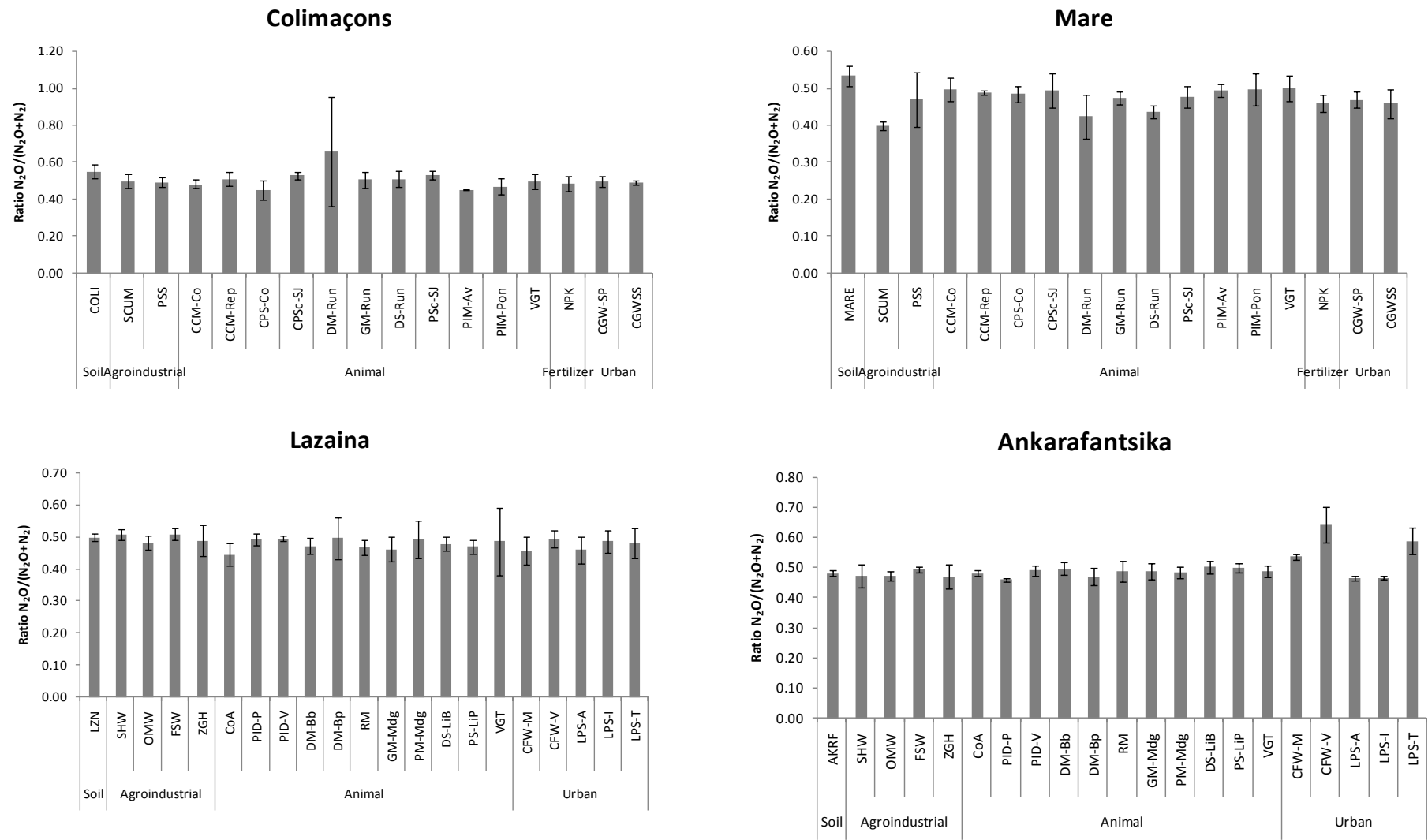


Figure 6.2 : Ratio $N_2O/(N_2O+N_2)$

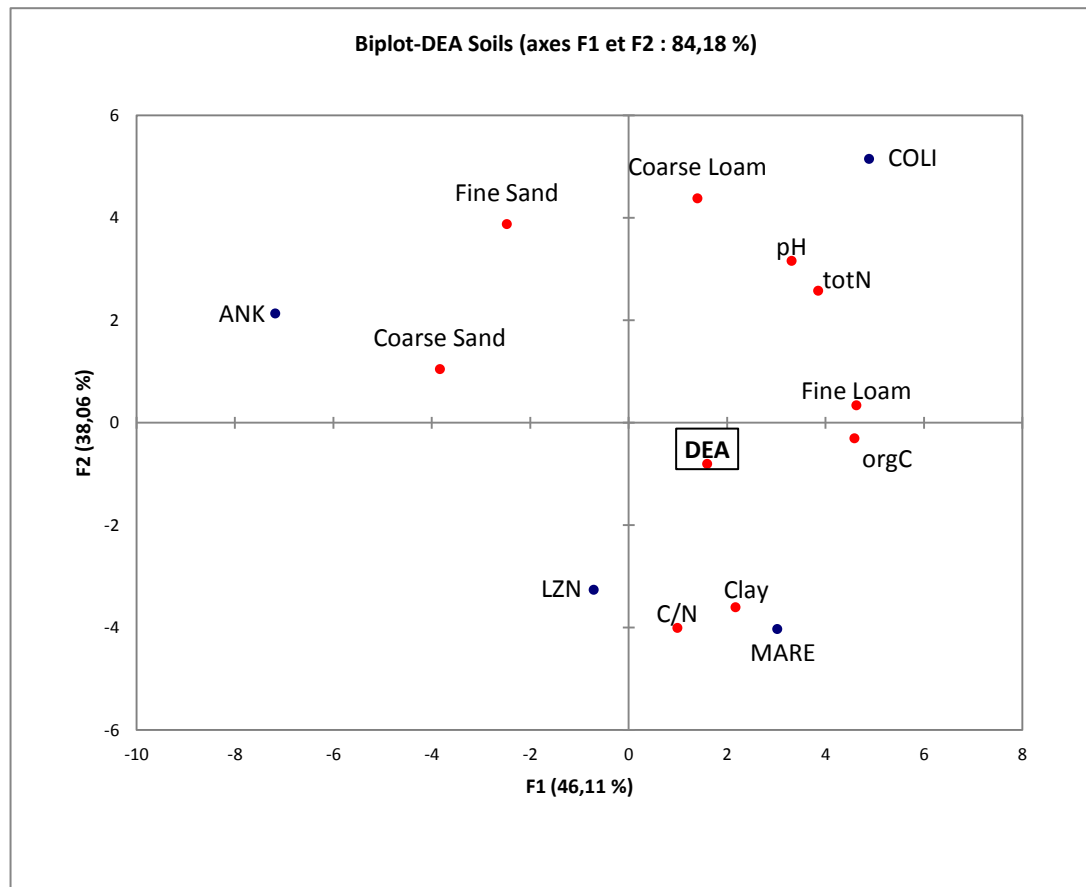


Figure 6.3 : Influence of soil characteristics on DEA

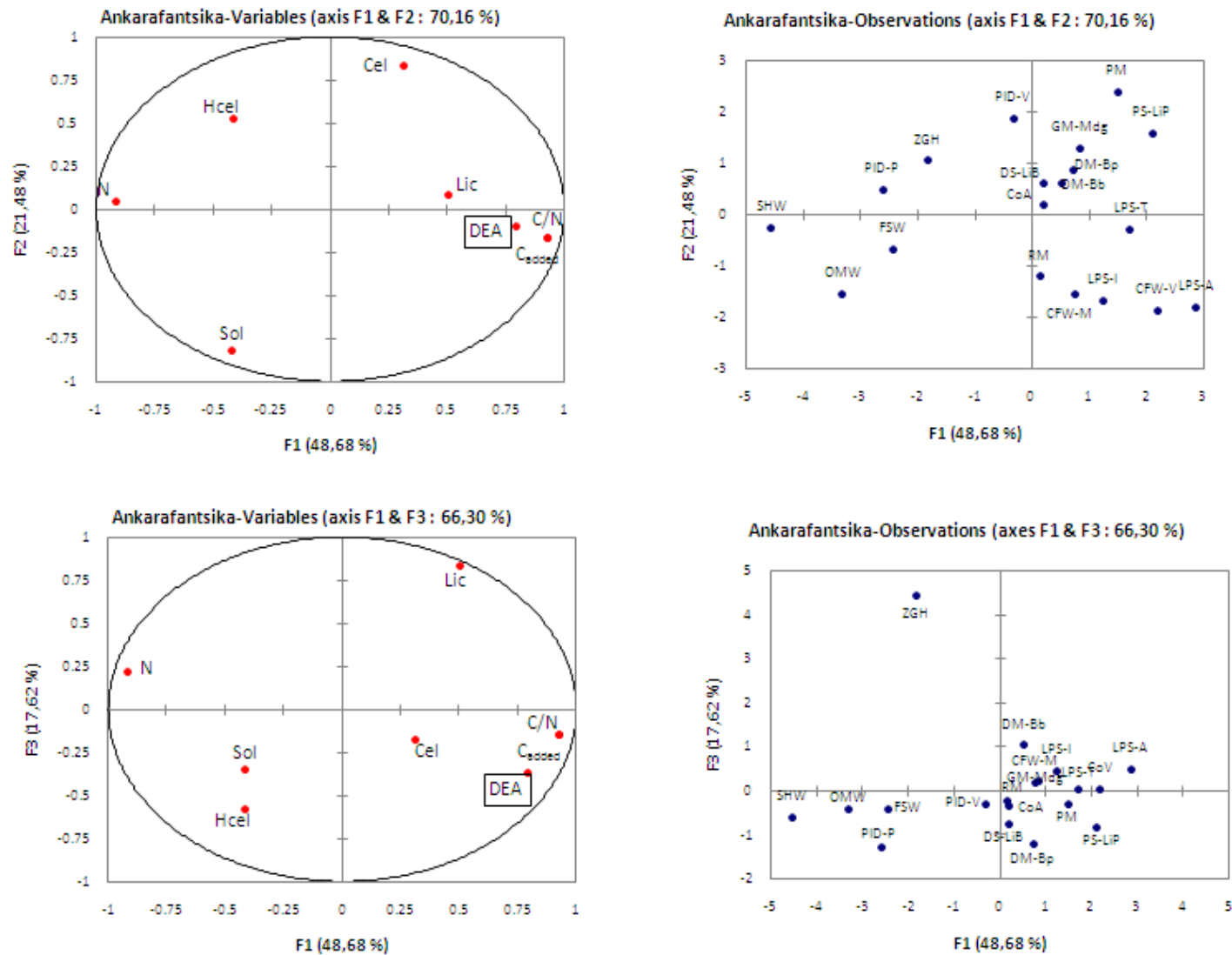


Figure 6.4 : Principal components analysis based on Ankarafantsika soil and EOM mixtures

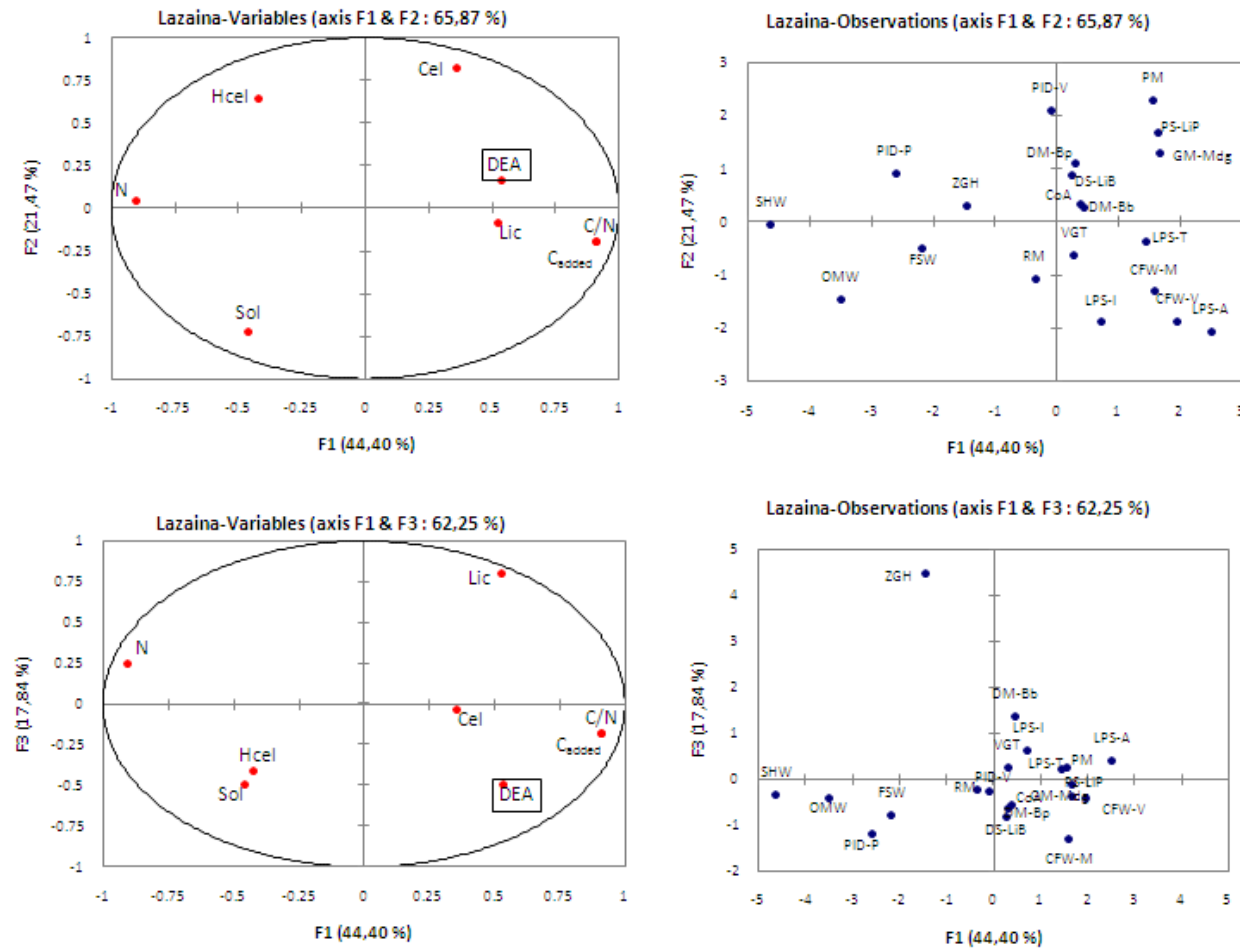


Figure 6.5 : Principal components analysis based on Lazaina soil and EOM mixtures

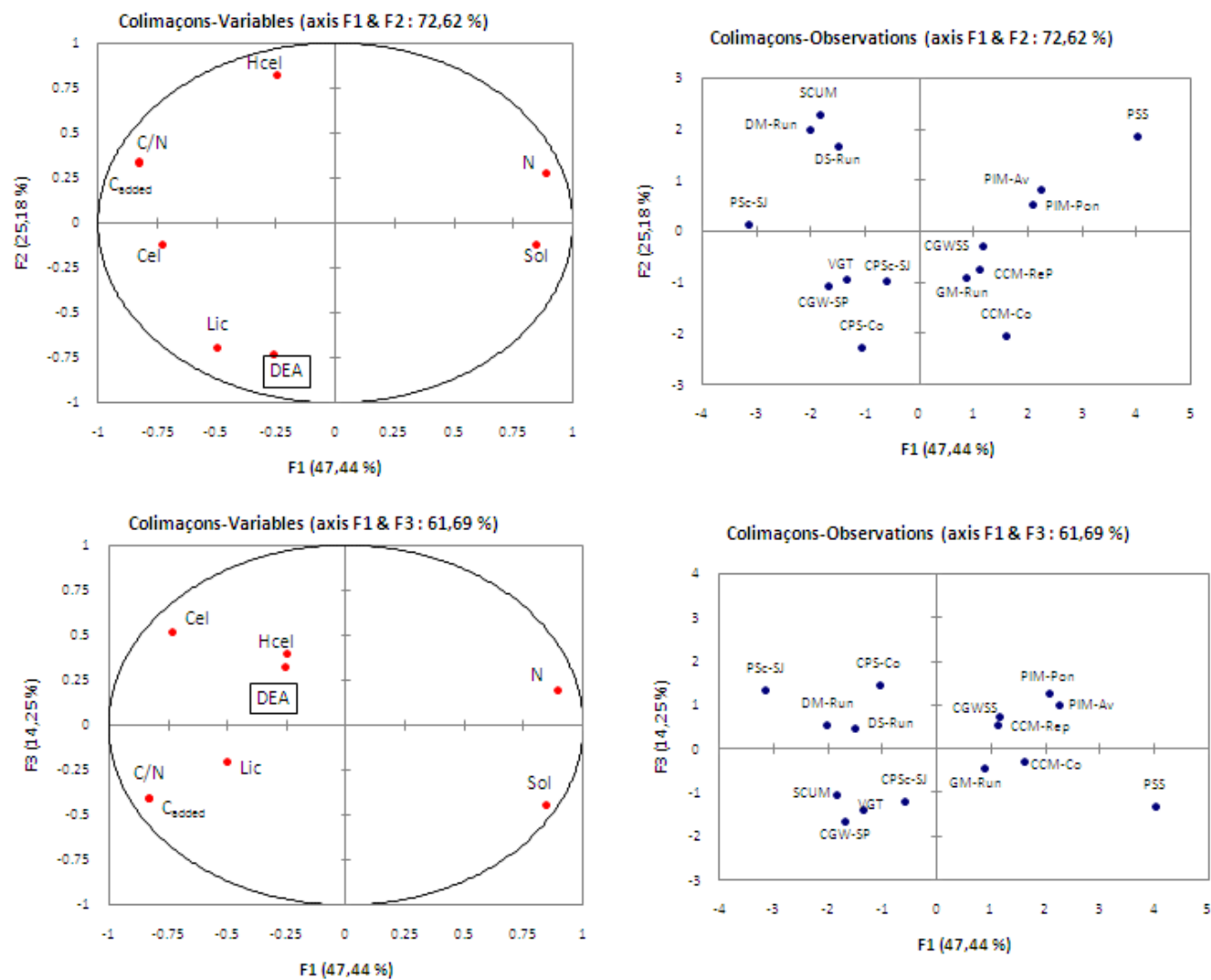


Figure 6.6 : Principal components analysis based on Colimaçons soil and EOM mixtures

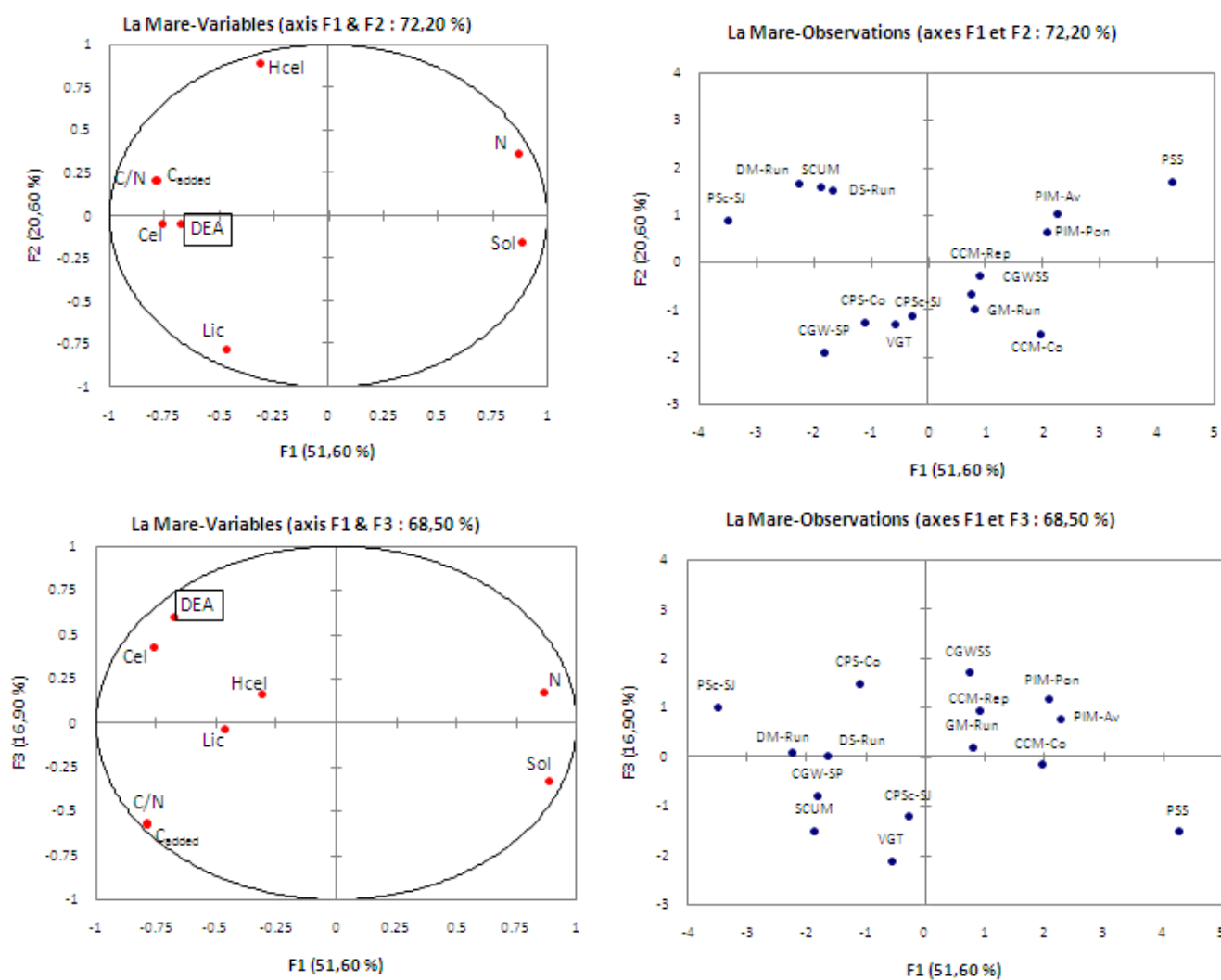


Figure 6.7 : Principal components analysis based on La Mare soil and EOM mixtures

6.3.3.1 PCA for Reunion EOM and soil mixtures

For Les Colimaçons, 87% of variance was expressed by the three first axes. N content and DEA were not correlated with axis 1 or axis 2. N content and DEA had the same direction only for axis 3 which represented 14.25% of variance. SOL fractions and DEA had the same direction only for axis 2 which represented 25.18% of variance. The ratio CtoN was only positively correlated to DEA in axis 1 (47.44% of variance).

For La Mare, 89% of variance was represented by the axis 1, axis 2 and axis 3. N content and DEA were neither correlated nor with axis 1 nor with axis 2. N content and DEA had the same direction only for axis 3 which represented 16.90% of variance. Sol fractions and DEA had neither the same direction nor in axis 1 nor in axis 2 and nor in axis 3. The ratio CtoN was only positively correlated to DEA in axis 1 (51.60% of variance).

For the 2 Reunion soils, EOM could be discriminated through the first axis. This distribution was related to N content, Sol fraction and the ratio CtoN of each EOM because these variables mainly contributed at the definition of this axis. The highest contribution of DEA was noticed respectively for axis 2 and for axis 3, for Les Colimaçons and La Mare.

6.3.3.2 PCA for Malagasy EOM and soil mixtures

For Lazaina, 84% of variance was expressed by the three first axes. N content and DEA were not correlated with axis 1 or axis 3. N content and DEA had the same direction only for axis 2 which represented 21.47% of variance. Sol fractions and DEA had the same direction only for axis 3 which represented 17.84% of variance. The ratio CtoN was only positively correlated to DEA in axis 1 and in axis 3 (62.25% of variance).

For Ankarafantsika, 88% of variance was expressed by the three first axis. N content and DEA were not correlated with axis 1 or axis 2 or axis 3. SOL fractions and DEA had the same direction for axis 2 and axis 3 which represented 39% of variance. The CtoN ratio was positively correlated to DEA in the three axes.

For the 2 Malagasy soils, EOM could be discriminated through the first axis. This distribution was related to N content, C added, the ratio CtoN and DEA of each EOM because these variables strongly contributed for the definition of this axis.

6.3.4 DEA prediction by NIR

Due to the number of sample in one dataset (~ 20 mixtures per soil), it was not possible to define calibration and independent validation set. Only results performed with cross-validation were reported.

6.3.4.1 DEA calibration based on EOM

The calibrations based on spectra acquired from EOM alone (without soil) were good for Ankarafantsika ($R^2_{cv}=0.85$ with an RPD of 2.6), allowed for approximate prediction for Lazaina ($R^2_{cv}=0.79$ with an RPD of 2.2) and poor for Les Colimaçons ($R^2_{cv}=0.32$ with an RPD of 1.3) and La Mare ($R^2_{cv}=0.37$ with an RPD of 1.3). Table 6.3 summarizes the details of cross-validation performance.

6.3.4.2 DEA calibration based on soil & EOM mixture

Table 6.4 presents the cross-validation performance of DEA calibration based on soil and EOM mixtures. Calibration were excellent for Ankarafantsika ($R^2_{cv}= 0.9$; $RPD_{cv} = 3.5$) mixtures, good for Les Colimaçons ($R^2_{cv}= 0.9$; $RPD_{cv} = 2.7$) and poor for La Mare ($R^2_{cv}=0.7$; $RPD_{cv} = 2$) and Lazaina ($R^2_{cv}=0.5$; $RPD_{cv} = 1.5$).

6.4 Discussion

6.4.1 Effect of soil on DEA

In our study, a large range of potential N_2O emissions was noticed as they varied between 0.01 and 1.6 $\mu N-N_2O.g^{-1}.h^{-1}$ dry soil. These values were high when compared to those reported by Barthès *et al.* (2010) in tropical soils (from 0 to 0.115 $\mu N-N_2O.g^{-1}.h^{-1}$ dry soil), and those reported by Baudoin *et al.* (2009) for Malagasy Highland soil (0.2 to 0.6 $\mu N-N_2O.g^{-1}.h^{-1}$ dry soil).

DEA seems to be explained by the soil organic C content and the fine loam soil texture as can be biplotted in Figure 6.3

Soil C content influences DEA at two levels: on the capacity of denitrification, considering its energy role (Lowrance *et al.*, 1988) but also on the development of the bacterial population (Myrold *et al.*, 1985). In microbial denitrification processes, soil C acts as an electron donor and N compounds are primary terminal electron acceptors (Brady *et al.*, 1999). Denitrification processes are dependent on the soil C availability (Senbayram *et al.*, 2012) as denitrifying bacteria are heterotrophic and hence they require a C source (Sainz Rozas *et al.*, 2001). Increased C availability acts as energy and electron source thereby increasing denitrification (Weier *et al.*, 1993).

Table 6.3 : Calibration and cross-validation statistics of DEA based on EOM only

Soil	N _c	Mean _c	SD _c	SE _c	R ² _c	RPD _c	N _{cv}	Mean _{cv}	SD _{cv}	SE _{cv}	R ² _{cv}	RPD _c	λ
Ankarafantsika	19	0.0142	0.0026	0.001	0.85	2.6	19	0.0142	0.0026	0.001	0.85	2.6	2
Lazaina	19	1.1577	0.1493	0.08	0.70	1.9	18	1.1474	0.1465	0.0653	0.79	2.2	2
Colimaçons	13	0.6623	0.1128	0.0892	0.32	1.3	13	0.6623	0.1128	0.0892	0.32	1.3	1
La Mare	13	0.2136	0.0499	0.0381	0.37	1.3	13	0.2136	0.0499	0.0381	0.37	1.3	1

N_c and N_{cv} were the number of samples used respectively for calibration and cross-validation, Mean_c and Mean_{cv} were the mean of DEA respectively for the calibration and cross-validation samples, SD_c and SD_{cv} were the standard deviation of DEA respectively for the calibration and cross-validation samples, SE_c and SE_{cv} were standard error of calibration and cross-validation, R²_c and R²_{cv} were determination coefficient respectively for calibration and cross-validation, RPD_c and RPD_{cv} were ratio of standard deviation (of calibration and cross-validation, respectively) to SE_c and SE_{cv}, respectively and λ was the number of considered wavelengths.

Table 6.4 : Calibration and cross-validation statistics of DEA based on soil and EOM mixtures

Soil	N _c	Mean _c	SD _c	SE _c	R ² _c	RPD _c	N _{cv}	Mean _{cv}	SD _{cv}	SE _{cv}	R ² _{cv}	RPD _c	λ
Ankarafantsika	21	0.0141	0.0028	0.0008	0.91	3.5	21	0.0141	0.0028	0.0008	0.91	3.5	3
Lazaina	19	1.1593	0.1493	0.0989	0.54	1.5	19	1.1593	0.1493	0.0989	0.54	1.5	2
Colimaçons	16	0.6121	0.1313	0.0483	0.86	2.7	16	0.6121	0.1313	0.0483	0.86	2.7	2
La Mare	15	0.1976	0.0588	0.0295	0.73	2.0	15	0.1976	0.0588	0.0295	0.73	2.0	2

N_c and N_{cv} were the number of samples used respectively for calibration and cross-validation, Mean_c and Mean_{cv} were the mean of DEA respectively for the calibration and cross-validation samples, SD_c and SD_{cv} were the standard deviation of DEA respectively for the calibration and cross-validation samples, SE_c and SE_{cv} were standard error of calibration and cross-validation, R²_c and R²_{cv} were determination coefficient respectively for calibration and cross-validation, RPD_c and RPD_{cv} were ratio of standard deviation (of calibration and cross-validation, respectively) to SE_c and SE_{cv}, respectively and λ was the number of considered wavelengths.

Fine textured soil had more DEA than equilibrate textured soil, such result has been reported by Pinay *et al.* (2000) and D'Haene *et al.* (2003) when measured potential N₂O emissions in temperate soil. In our experiment, DEA for the clayey Lazaina ferralsol reached the highest values while the sandy soil of Ankarafantsika presented the lowest DEA. Clayey soils generally produce larger in-situ N₂O fluxes than sandy soils as they retain more water and may be partially anaerobic due to the smaller textural pores (Laudone *et al.*, 2011). Additionally, smaller pores provide different micro-sites for bacteria, as inferred from the greater production of N₂O by denitrification in microaggregates (Sey *et al.*, 2008). A well aggregated soil, in contrast, contains large pores that are unsaturated, at least in part, at field capacity and so gas exchange is facilitated and oxygen maintained at a concentration unsuitable for anaerobic bacteria activity.

6.4.2 Effect of EOM on DEA

The N₂O emitted in DEA assays varied according to EOM applied to soil. Organic amendments provide energy for soil microorganisms which eventually increases the soil microbial biomass and denitrification rates because of decreased soil redox potential (Köster *et al.*, 2011), increased of available C and mineral N. There is a marked relationship between EOM application, soil microbial properties and N₂O emitted in DEA assays. Several studies have shown higher rates of N loss through denitrification from soils treated with EOM such as manure, composts, and plant residues when compared to unamended or mineral N treated-soils (Walker *et al.*, 2006; Dambreville *et al.*, 2006). In literature, depending on soil structure, effect of EOM on N₂O production can be explained by C-to-N ratio. The positive correlation between C-to-N ratio and DEA was in accordance with Millar *et al.* (2004) but contrasted with another studies by Kaiser *et al.* (1998) and Baggs *et al.* (2000) where emissions were shown to increase with greater N content, or lower C-to-N ratio. The accessibility of available C to microorganisms is an important factor in controlling denitrification, especially under field conditions. As mentioned before, denitrifying organisms use organic C compounds as electron donors for energy and for synthesis of cellular constituents. Therefore, denitrification is strongly dependent on the availability of organic compounds such as native soil organic matter, crop residues, etc. Since much of the total soil organic C is highly resistant to decomposition, it has been reported that denitrification correlates better with glucose equivalent C (Stanford *et al.*, 1975), water soluble C (Bijay-Singh *et al.*, 1988; Schloemer, 1991; Hill *et al.*, 2004) and mineralizable C (Bijay-Singh *et al.*, 1988; Hill *et al.*, 2004), which

are easily decomposable. In this study, the SOL fraction of Van Soest method was used as an estimation of the amount of readily available C. Possible explanations for the DEA decrease are adsorption to soil particles, C immobilization into soil microflora and respiration (Chaves Daguiar, 2006). Poor correlations were found between SOL fraction (available C) and potential N_2O emission, what may indicate that easily available C was not a limiting factor in this study. The rate of C supply is likely to be faster in the case of dissolved organic carbon when compared to other more stable C sources such as lignin and cellulose in soils (Myrold *et al.*, 1985)

6.4.3 Effect of EOM on $\text{N}_2\text{O}/\text{N}_2\text{O}+\text{N}_2$ ratio

The C_2H_2 concentration above 1kPa, as used in our DEA assay inhibits the last step of denitrification, i.e. the reduction of N_2O to N_2 . The measurement carried out without C_2H_2 allows to characterize the N_2O emitted through denitrification when the whole pathways is active, i.e. N_2O produced and emitted as it is *minus* N_2O further reduced and emitted as N_2 . Hence, the amount of N_2O in the DEA (+ C_2H_2 assay) should be more important than in the potential N_2O net production assay (- C_2H_2), resulting in a $\text{N}_2\text{O}/\text{N}_2\text{O}+\text{N}_2$ ratio lower than 1. Such results were observed for the all EOM in our experiment. Surprisingly, N_2O production seemed to be stimulated by addition of C_2H_2 for Les Colimaçons, 5 Reunion Island animal effluents and 2 Malagasy agro-industrial wastes. As noticed by Chronakova *et al.* (2009) the reason may be that the ratio between the products of denitrification, i.e., N_2O and N_2 , was not only controlled by mineral nitrogen. In fact, because nitrate is preferred over N_2O as an electron acceptor for denitrifiers at concentrations higher than $10 \mu\text{g.g}^{-1}$ (Philippot *et al.*, 2009), but also by several other factors including pH, carbon availability, oxygen partial pressure (Šimek *et al.*, 2002; Munch *et al.*, 2007; Philippot *et al.*, 2009) and bacterial factors, lack of nitrous oxide reductase to reduce N_2O into N_2 (Baudoin *et al.*, 2009; Philippot *et al.*, 2009). Although the role of pH in modulation of the denitrification pathway is still not well understood, there are some studies which showed a relative increase of N_2O production under lower pH and vice versa (Firestone *et al.*, 1980; Šimek *et al.*, 2002), which is consistent with our results. Hereafter, nitrous oxide reductase seems to be more sensitive to the primary environmental regulators, including low pH, than the other enzymes of the denitrification pathway (Cavigelli *et al.*, 2001). Soil available C has been shown to enhance denitrification while either decreasing (Weier *et al.*, 1993) or increasing (Dendooven *et al.*, 1996) the $\text{N}_2\text{O}/\text{N}_2$ molar ratio.

6.4.4 Classification of tropical EOM according to N₂O emissions

Emissions of N₂O varied according to added EOM. This was most likely due to the differences in the quality of the EOM (Palm *et al.*, 2000). As shown by our results, N₂O production is significantly different from the control soil in 73% of our mixtures (25 EOM out of 34). Some dairy manures (DM-Bb and DM-Run) did not presented a significant difference from control N₂O emissions. For such animal manure, some studies indicate that there is no clear or no effect of application technique on N₂O emission and denitrification from animal slurries applied to soil (Sommer *et al.*, 1996; Velthof *et al.*, 1997; Dendooven *et al.*, 1998; Velthof *et al.*, 2003). For another animal waste, such as pig effluents, poultry manure, ovine manure, injection of slurry enhances potential N₂O emissions from denitrification. These are in accordance with our expectation and have been already reported by another study (Flessa *et al.*, 2000). For urban wastes, significant increase in N₂O production was observed for 5 of 7 EOM in this category. For agroindustrial wastes, only FSW led to an increase in potential N₂O production by denitrification and DEA.

In our study, total added N was fixed at 0.05 mgN.g⁻¹ soil for all the EOM, only added C differed. For the Malagasy soils, composted animal manure (VGT) and potting soils induced the lowest potential N₂O production where as the highest N₂O production occurs when the soil received animal slurry, animal manure, composted animal waste and agro-industrial waste. For Réunion soils, chemical fertilizer induced high potential emissions of N₂O while agro-industrial waste and VGT did not affect potential N₂O production or DEA.

Composition of EOM differs greatly and hence varies in their effect on N₂O emission during soil application (Chadwick *et al.*, 2000). Mineral N was not measured in our experiment. All soil received the same extra amount of N although addition of EOM may generate difference in mineral N. For example, pig slurry has been shown to contain 2 to 3 times more water soluble C and 3 to 4 times more volatile fatty acids than cattle slurry (Kirchmann *et al.*, 1993) and hence application of pig slurry resulted in higher N₂O emission (7.9 mg N/m²) than cattle slurry application (3.6 mg N/m²) (Velthof *et al.*, 2003). Similarly, López-Fernández *et al.* (2007) noticed that pig slurries contain higher amounts of ammoniacal-N and lower organic N compounds than municipal waste composts. Hence, application of liquid slurry adds NH₄⁺-N, which undergoes rapid nitrification when mixed with aerated soils resulting in higher N₂O emissions when compared to that from composts. Likewise, decomposition rates of crop residues vary with crop types. For example, wheat straw decomposes more slowly than pea straw (Soon *et al.*, 2002) and hence differs in N₂O emission factor (Dobbie *et al.*, 2003).

The rate, type and timing of applications of EOMs are important management factors in determining N loss as N_2O from the soils (Xu *et al.*, 2000; Weitz *et al.*, 2001; Eckard *et al.*, 2010).

6.4.5 Usefulness of near-infrared spectroscopy to predict DEA

In this study, the prediction of DEA was tested according two approaches (i) considering only EOM spectra and (ii) taking into account the EOM-soil mixtures spectra. We showed that results were not the same for the 2 approaches. Both procedures can be considered as original. Indeed, other studies generally focuses only on spectra from soil with different texture (Barthès *et al.*, 2010; Rabenarivo, 2011), neighbouring chronosequences representing gradients of reforestation (Schimann *et al.*, 2007), soil and earthworm spectra (Cécillon *et al.*, 2008). We noticed that DEA calibration models by NIRS best performed using spectra from soil - EOM mixtures rather than from EOM alone for Ankarafantsika and Les Colimaçons, which were coarse-textured soils (considering their clay content lower than 28%). On the opposite, DEA calibration was more accurate by NIRS based on spectral analysis of EOM rather than soil - EOM mixtures for the fine-textured soil of Lazaina (clay > 28%). Calibration of DEA was poor either based on EOM only, or based on soil - EOM mixtures for La Mare, which was a fine-textured soil too (clay > 28%). These results seemed to indicate that NIRS predictions were not dependant on soil textures, although Barthès *et al.* (2010) suggested that better prediction were explained by soil texture. Poorer prediction obtained with EOM and soil mixture spectra only could be explained by the adsorption of EOM with fine particles reducing the availability of C and N components. In fact, spectral regions that contributed most to NIRS prediction of potential denitrification could be attributed to organic nitrogenous compounds, amide containing ones especially, and carbonaceous compounds (Barthès *et al.*, 2010). Another studies hypothesized that denitrification potential was in dependence of upon soil OC content (Burford *et al.*, 1975; Enwall *et al.*, 2005) and by the fact that amides represent the predominant form of soil organic N (Schulten *et al.*, 1998) and an important component of microbial biomass (Lehmann *et al.*, 2008).

If compared our cross-validation results with those reported in literature, using global calibration for soil DEA prediction, Cécillon *et al.* (2008) and Rabenarivo (2011) obtained poor results on a bigger set (cross-validation $R^2 = 0.38$, RPD = 1.3 for 50 topsoil and earthworm cast samples from forest plots affected by wildfire, and prediction $R^2 = 0.41$, SEP = 114 %, RPD = 1.3; calibration $R^2 = 0.85$, $SE_{CV} = 59\%$ and RPD = 2.2 for 185 malagasy

soils, respectively), while Schimann *et al.* (2007) reported good results on reforestation chronosequences which were from neighbouring and homogeneous site.

6.5 Conclusion

Our contribution allowed a first appreciation of the potential for N₂O production from denitrification when applying EOM in four common soil types of the south western Indian Ocean area. Soil organic carbon and texture affected potential N₂O emissions when regarding soil control. For soil and EOM mixtures, DEA was explained by soluble fractions (SOL) from Van Soest method for sandy soil with low organic carbon and by EOM C-to-N ratio for the others. Depending on what samples were used in the prediction, EOM only or soil and EOM mixtures, DEA can be acceptably predicted by using near infrared spectroscopy.

Chapitre 7. Putative role of trace elements and soil chemical properties in the induction or mitigation of rhizotoxicity in tropical soils amended with organic wastes

Avant-propos

La gestion des déchets organiques (ou Matières Organiques Exogènes, MOEx) peut poser problème à la Réunion où, contrairement à d'autres régions, l'exportation n'est pas possible. Néanmoins, ces déchets peuvent être des ressources valorisables. Leur retour au sol est une voie de valorisation au double avantage : utiliser le potentiel agronomique des MOEx tout en procédant à leur élimination.

Cependant, des risques de pollution des sols liés à l'épandage de MOEx peuvent exister. La présence de micropolluants métalliques (éléments trace métallique, ETM) dans ces MOEx constitue un facteur limitant leur utilisation en agriculture. Bien qu'ils ne soient présents qu'en faible quantité, les ETM peuvent être potentiellement toxiques.

Quoique la concentration totale en ETM dans les MOEx et dans les sols suite à l'apport de MOEx n'indique que très partiellement leur toxicité (Zhang *et al.*, 2001). Seule l'étude de la fraction biodisponible des ETM, quantité assimilable par les organismes variant selon la spéciation des ETM, dans les différents mélanges sol-MOEx permet d'évaluer la toxicité potentielle de ces ETM (Thakali *et al.*, 2006; Doelsch *et al.*, 2010).

Ce chapitre se focalisera sur l'étude de la biodisponibilité des ETM pour les plantes, i.e. la phytodisponibilité. Un test biologique normalisé (ISO 11269-1, 2012), basé sur l'inhibition de l'élongation racinaire, sera utilisé pour évaluer la phytotoxicité des ETM dans divers mélanges sol-MOEx représentatifs du contexte du recyclage agricole à la Réunion. A l'issue du test, plusieurs techniques physico-chimiques ont été mises en œuvre pour évaluer la disponibilité des ETM dans les mélanges sol-MOEx. Ces mesures de disponibilité ont été par suite mises en regard des mesures d'élongation racinaire de manière à évaluer la phytotoxicité des ETM.

Les objectifs de ce chapitre sont d'évaluer (i) l'occurrence de la phytotoxicité des ETM dans des sols tropicaux amendés par des MOEx matérialisée par l'élongation racinaire de l'orge et (ii) le rôle respectif des ETM et des propriétés de la solution du sol dans l'induction ou la réduction de cette phytotoxicité des ETM.

7.1 Introduction

The current growth of the world population is at the origin of the increase of the production of waste. According to the OECD, waste production increased by 35 % per capita from 1980 till 2005. As mentioned by *Clapp et al.* (2007) resources must be recycled to ensure sustainable development and this especially applies to organic wastes. From a waste management standpoint, agricultural recycling is a way of making effective use of organic waste of different origins: agricultural (slurry, manure) (Moreno-Caselles *et al.*, 2005), urban (compost, sewage sludge (Doelsch *et al.*, 2006)), and agroindustrial (vinasse from fermentation industries (Tejada *et al.*, 2005)). The agronomically efficient and environmentally safe use of any EOM requires adequate control of their chemical quality (Doelsch *et al.*, 2009) but also of their potential pollutants. Among these pollutants, trace elements (TE) (i.e. metals and metalloids) have been closely examined due to their toxicity to humans, animals and plants.

Although, the use of organic wastes, so called Exogenous Organic Matter (EOM), has many benefits for agricultural soils, there are several factors that significantly limit the applicability of this strategy. After spreading EOM, the chemical and biological conditions of the soil can be substantially altered during mineralization of this EOM through changes in organic matter (OM) stock and dynamics, water flows, or in the physicochemical properties (pH, Eh, etc.) in the soil solution (Stevenson, 1994; Sanchez-Martin *et al.*, 2007; Doelsch *et al.*, 2009). On the one hand, the solid components in EOM added to soils provide new exchange sites for cations as well as other binding sites. Metals are retained in either easily or difficultly recoverable forms (Petrizzelli *et al.*, 1994; Sadovnikova *et al.*, 1996). In this respect, Harter and Naidu (1995) observed that organic matter in soils is the most important component concerning metal retention. On the other hand, organic amendments can increase solubility of metals by producing ligands that chelated the metals, thereby blocking their sorption and promoting leaching through formation of soluble metal complexes (Madrid *et al.*, 1998). Furthermore, organic matter can modify the pH, influencing the nature and extent of metal retention by both solid and soluble organics.

TE have become one of the most serious anthropogenic stressors for plants and other organisms (Seregin *et al.*, 2001). It is well recognized that risk assessment of TE in soils needs to take into account metal bioavailability. Metal bioavailability is strongly influenced by soil properties. Organisms such as plants also can modify their rhizosphere environment, thus affecting TE bioavailability (Barber, 1984; McLaughlin, 2002). Therefore, bioavailability

is a concept that is easily understood but difficult to measure (Zhao *et al.*, 2006). Micò *et al.* (2008) reported that metal toxicity is assumed to be caused by free metal ions i.e. the bioavailable TE and toxicity of substance depends on the sensitivity of the test organism as well as the properties of the soil in which the organism inhabits.

To date, phytotoxicity of trace elements were almost exclusively characterised in hydroponic system (i.e. without soil) or in soils spiked with soluble salts of trace element (Kinraide *et al.*, 2004; Thakali *et al.*, 2006). This kind of investigation can however hardly provide relevant references in organic waste-amended soils as side effects such alterations of soil properties are expected in the latter (Smolders *et al.*, 2012). In addition, the question of a specific fate of TE in tropical soils is still a matter of debate as tropical soils usually exhibit peculiar physical-chemical properties (e.g. lower pH, higher Fe oxyhydroxides content) and rather few investigations were performed in comparison with temperate soils (Rieuwerts, 2007). Therefore, an ecotoxicological approach using biological tests can be recommended in order to ease the determination of the effects of TE contaminated soils on the root elongation (Rooney *et al.*, 2006; Thakali *et al.*, 2006; Micò *et al.*, 2008). The ISO/DIS 11269-1 (2010) described this method.

Only few studies have focused on TE speciation in tropical volcanic soils (Doelsch *et al.*, 2008) or TE speciation patterns after application of EOM on tropical volcanic soil (Doelsch *et al.*, 2010), but even fewer have attempted to TE phytotoxicity via root elongation. The present study therefore aimed at assessing (i) the occurrence of phytotoxicity in two tropical soils amended with ten organic wastes and (ii) the respective role of trace elements and soil chemical properties in the induction or the mitigation of phytotoxicity.

7.2 Material and methods

7.2.1 Soils and exogenous organic matter

Two soils from Réunion were incubated as control and with ten organic wastes, including five organic fertilizers, four organic amendments from Réunion and one potting soil from Madagascar, at three different rates 1, 3 and 9 times the normal dose. This recommended dose was depending on the EOM nature, organic fertilizers were added into soil with an equivalent of 200kgN.ha⁻¹ organic amendments were mixed into soil with an equivalent of 30t.ha⁻¹ of fresh amendments and the potting soil with the ratio of 1% of soil as normal dose.

7.2.1.1 Soils samples

For this study, soil samples from Réunion were collected from the CIRAD experimental fields. The sample from Nitisol was collected in a lowland area from the northern windward

coast, while the sample from Cambisol was collected in a medium elevation on the western windward side of the island. The following were determined: pH, clay content, soil organic matter (SOM), calcium carbonate and cationic exchange capacity (CEC), water holding capacity. Soil pH was measured in 1:5 v/v (soil/distilled water) extract, then shaken for 5 mn and measured after 1h. Table 7.1 shows the soils' physical and chemical characteristics.

7.2.1.2 EOM samples

EOM used in this work can be classed into two categories: organic fertilizer or organic amendment according to the French normalization (NFU 42-001 and NFU44-051). As organic fertilizer, we had a bovine slurry (DS), a pig slurry (PS), a poultry dropping (PD), a poultry manure (PIM) and a sewage sludge (SS). As organic amendment, we had a bovine manure (BM), a composted pig slurry (CPS), a composted poultry manure (CCM) and a composted green waste (CGW). A potting soil (LPS) from Malagasy landfill was also taking into account in this work. Table 7.2 presents the main characteristics of studied EOM.

Table 7.1: Physico-chemical characteristics of soils

Parameters	Units	Colimaçons	La Mare
orgN	g.kg ⁻¹	3.92	1.63
orgC	g.100g ⁻¹ dm	4.01	1.95
totP	mg.kg ⁻¹ dm	157.85	270.83
totCa	mg.kg ⁻¹ dm	559.80	1072.60
totMg	mg.kg ⁻¹ dm	82.36	259.12
totK	mg.kg ⁻¹ dm	13.28	379.69
totNa	mg.kg ⁻¹ dm	40.23	34.25
CEC	meq.100g ⁻¹ dm	6.114	9.059
pH (H ₂ O)		5.05	5.70
pH (KCl)		4.25	4.46
Clay	%	13.60	38.70
Fine silt	%	31.60	35.80
Coarse silt	%	18.90	8.00
Fine sand	%	20.10	7.80
Coarse sand	%	13.00	9.70

dm: dry matter basis, org N : organic nitrogen, org C : organic carbon, totP: total phosphorus, totCa: total calcium, totMg: total magnesium, totK: total potassium, totNa: total sodium, CEC: cation exchange capacity

7.2.1.3 Trace Elements contents

Studied TE concerned copper (Cu), nickel (Ni), chromium (Cr), zinc (Zn), cadmium (Cd) and lead (Pb). Table 7.3 reports their contents in soil and in EOM.

7.2.2 Phytotoxicity assays

7.2.2.1 Rhizotoxicity measurement

Considering root sensitivity to TE toxic effect, rhizotoxicity was chosen as the phytotoxic endpoint and was assessed by performing a root elongation test.

To conduct this study, a phytotoxicity assay using barley (*Hordeum vulgare* L.) as described by ISO/DIS 11269-1 (2010) was carried out. It is based on the determination of effects of contaminated soils on the root elongation of terrestrial plants. Pre-germinated seeds were exposed to the test material under controlled conditions. After the growth period, the lengths of the roots and shoots of the test plants were compared with those of the control plants. Statistically significant differences in the root and shoot lengths of seedlings grown in any test medium compared to the controls are indicative of an effect.

Table 7.2 : EOM physico-chemical characteristics

Categories	Nature	Code	dm	pH(H ₂ O)	orgN	orgC	TOM	P ₂ O ₅	K ₂ O	CaO	MgO
			(%)	pH	(% dm)	(% dm)	(% dm)	(% dm)	(% dm)	(% dm)	(% dm)
Organic fertilizer	Bovine slurry	DS	13.12	10.04	3.47	39.82	74.01	2.58	6.29	3.39	2.12
	Porcine slurry	PS	2.81	7.78	2.34	37.45	66.28	5.51	8.49	5.99	2.62
	Poultry Droppings	PID	86.97	7.40	3.70	35.04	66.60	2.63	2.25	10.95	1.39
	Poultry Manure	PIM	58.30	6.53	4.18	41.10	83.40	3.88	4.68	2.86	1.43
	Sewage sludge	SS	26.00	5.66	7.31	40.19	80.38	5.00	0.38	1.15	0.38
Organic amendment	Bovine manure	DM	31.30	9.01	2.49	43.43	80.74	1.54	4.52	1.68	1.12
	Composted porcine slurry	CPS	30.56	7.95	1.98	33.89	65.04	7.64	0.90	5.46	4.10
	Composted poultry manure	CCM	50.01	9.94	3.41	38.98	76.29	4.47	6.12	4.43	1.47
	Composted green waste	CGW	60.50	8.08	1.37	22.95	39.85	0.63	0.97	3.43	2.04
	Potting Soil	LPS	ND	8.25	0.50	10.01	13.93	0.72	0.46	3.35	0.44

dm: dry matter, orgN: organic nitrogen, orgC: organic carbon, TOM: total organic matter, P₂O₅: total phosphorus, K₂O: total potassium, CaO, total calcium, MgO: total magnesium

Table 7.3 : Trace element contents in soils and in EOM

Categories	Code	Zn (mg.kg ⁻¹ dm)	Cu (mg.kg ⁻¹ dm)	Ni (mg.kg ⁻¹ dm)	Cr (mg.kg ⁻¹ dm)	Pb (mg.kg ⁻¹ dm)	Cd (mg.kg ⁻¹ dm)
Soils	Coli	224.68	79.48	89.25	131.10	12.65	0.18
	Mare	226.88	117.98	37.75	59.51	5.50	0.23
Organic fertilizer	DS	305.70	50.30	9.60	8.88	1.29	ND
	PS	962.02	559.02	14.30	9.30	1.32	0.34
	PID	244.21	49.04	16.28	14.90	17.64	0.15
	PIM	380.00	82.00	9.00	3.00	1.00	1.00
	SS	403.86	135.35	20.57	21.90	13.68	0.36
Organic amendment	DM	143.20	23.90	6.46	5.75	0.48	0.30
	CPS	833.80	164.06	28.25	33.50	0.86	0.49
	CCM	570.90	126.79	12.75	26.75	0.58	0.58
	CGW	251.35	100.28	166.50	161.00	694.60	0.39
Potting soil	LPS	698.03	421.37	47.63	191.20	627.48	0.73

Dm: dry matter basis

7.2.2.2 Incubation

Four replicates of each mixture were considered. Pots are incubated in controlled environmental chamber during four days. Climatic conditions in the growth chamber were fixed as suited (day/night): 14/10 h, 22 C, 70% of relative humidity and 3000 lux of photosynthetically active radiation. After the growth period, each pot was laid on its side and pressed manually with care to remove soil out of the pot. Plants and soil were separated, and then each plant was washed.

7.2.2.3 Plant measurements

At harvest, the whole root system of each plant was carefully removed from soil and gently cleaned. A photography of the root system of each plant was taken and the root length was subsequently determined using the picture analysis software (Image J) . After length measurements, root and shoot samples were oven-dried at 60°C for dry biomass determination.

To enable the comparison between the two soils, the relative root length (*RRL*) was determined according to Kinraide *et al.* (2004):

$$RRL (\%) = 100 \times (RL - RL_{\min}) / (RL_{\max} - RL_{\min})$$

where, *RL* is the root length for a given treatment, *RL_{min}* and *RL_{max}*, the minimal and maximal root length measured among the different treatments

7.2.2.4 Chemical analyses of soil solution

After the harvest of plants, soil was repacked and watered up to 100 % of the maximal water holding capacity. Soil solution was recovered within the following day by centrifugation and filtration. Electrical conductivity, pH, total concentrations of trace elements (i.e. Cd, Cr, Cu, Ni, Zn and Pb) were subsequently determined.

7.2.2.5 Statistical analysis

For comparing the means, standard deviations and coefficients of variation were calculated. Statistical analysis was performed by one-way analysis of variance (ANOVA) using XL STAT (Addinsoft, Paris, France). ANOVA was applied separately to data of the Cambisol and the Nitisol. Means were compared by a Tukey's test and a Dunnett's test. Multiple linear regression (MLR) was build in order to materialize the relationship between soil solution parameters (pH, pIS, free TE (pCu, pNi, pCr, p Zn, pCd, pPb), added TE (logCu, logNi, logCr, log Zn, logCd, logPb), added OM (logOM), added P (logP) and the rhizotoxicity (*RRL*). Three series of MLR were elaborated using: i) the 2 soils together, ii) the Cambisol only, and iii) the Nitisol only. All correlations were developed by using a stepwise method.

All the procedures, including equation construction and statistics, were executed using XLSTAT Software (Addinsoft, Paris, France).

7.3 Results

7.3.1 Plant measurements

Figure 7.1 presented the scattergrams for Relative Root Length, Root Biomass, Shoot Length and Shoot Biomass.

7.3.1.1 Relative Root Length (RRL)

Figure 7.2 showed the RRL in the different treatment.

For the Cambisol, if compared the soil control and different treatments, the RRL for soil and EOM mixtures were upper than in the soil control for the majority of the treatments (24/30) except for the PID-1, CCM-3, CCM-9, SS-1, SS-3, SS-9. Whatever, the Dunnett test showed that a significant difference was noted only for CGW-3 ($p = 0.049$), TPS-3 ($p = 0.032$) and LPS-9 ($p = 0.008$). When an intra-rate comparison was carried out for each EOM, significant differences were seen only for CCM and LPS. For the other EOM, rates had no effect in the RRL.

For the Nitisol, the comparison of RRL between soil control and different treatments allowed to note that (i) all the treatments had a RRL lower than the soil control and (ii) differences were significant for CPS-9, PID-9, PM-9, CCM-3, CCM-9, and SS-9. Except for CGW and LPS, increasing rates of EOM presented an effect in the RRL: the more the rate was, the less was the RRL. However, intra-rate differences were significant only for CPS, CCM, and SS.

7.3.1.2 Root biomass

Figure 7.3 represents the root biomass weight.

The root biomass for the soil control and the different treatments were presented in Figure 3. Root biomass varied between 0.0063 and 0.0597 g for the Cambisol. Differences between treatments and soil control were significant only for the CCM-9. Root biomass was upper than the soil control for 14 treatments, equal for 2 treatments, and lower for the other. Intra-rate comparison showed significant differences for DM, PS and CCM.

The range of root biomass was between 0.0128 and 0.061 g for the Nitisol. For all treatments, root biomass in the soil control was the higher value. Whatever, significant differences were only noted for CPS-9 and CCM-9. Rates 1, 3, and 9 were significantly different for PS and CCM.

7.3.1.3 Shoot length

Shoot length measurements were reported in Figure 7.4

For the Cambisol, shoot lengths measured in the soil control and the treatments varied between 3.2 to 9.5 cm. Significant difference was only observed for the CCM treatments linked to the rate levels and the soil control for CCM-9.

Shoot length values went from 6.2 to 11.2 cm for the plant grown with the Nitisol. Although the shoot length for the various treatments were upper (4/30) or lower (26/30) than shoot length of the control, no significant difference either with regard to the control or compared with the intra-doses effects was revealed.

7.3.1.4 Shoot biomass

Figure 7. 5 shows the shoot biomass weight.

No significant difference has been noted for the shoot biomass whether this is assessed on soil control, the Cambisol or the Nitisol.

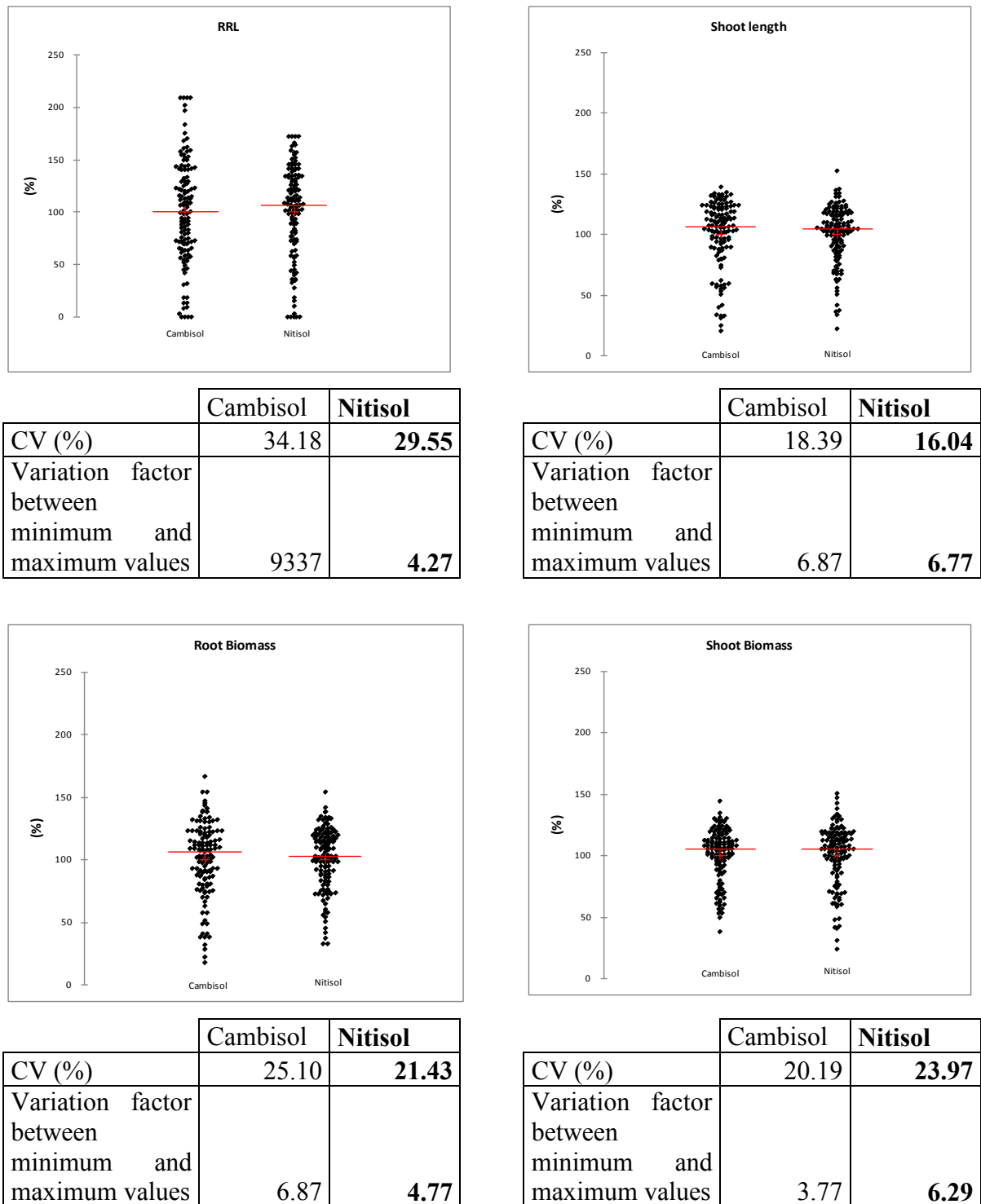


Figure 7.1: Scattergrams representing the distribution of RRL, root biomass, shoot length and shoot biomass depending on the 2 soils: Cambisol and Nitisol

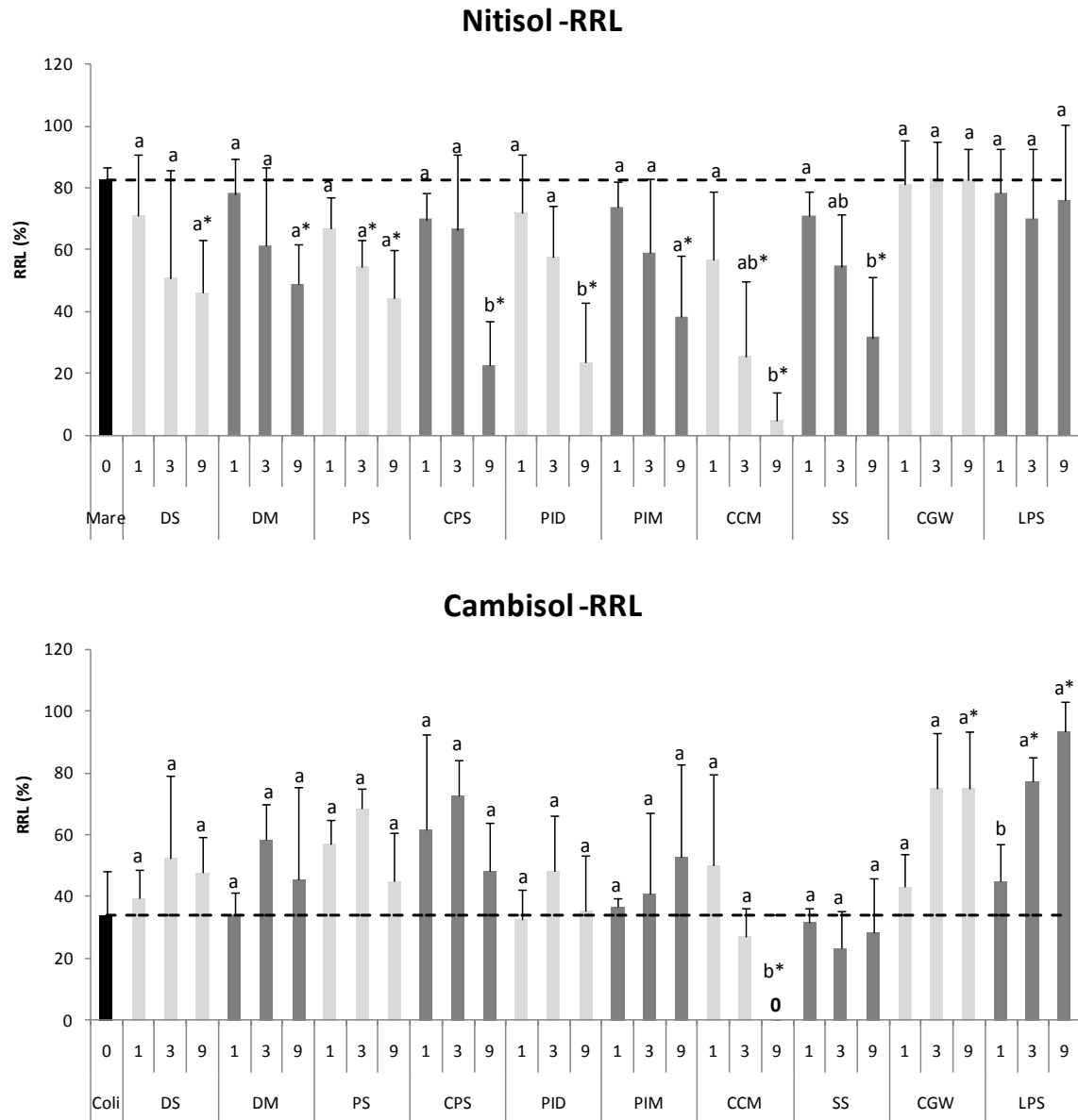


Figure 7.2 : Relative root length of 4-day barley seedlings grown in the soil. The soil was either not amended (control soil, Mare for Nitol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

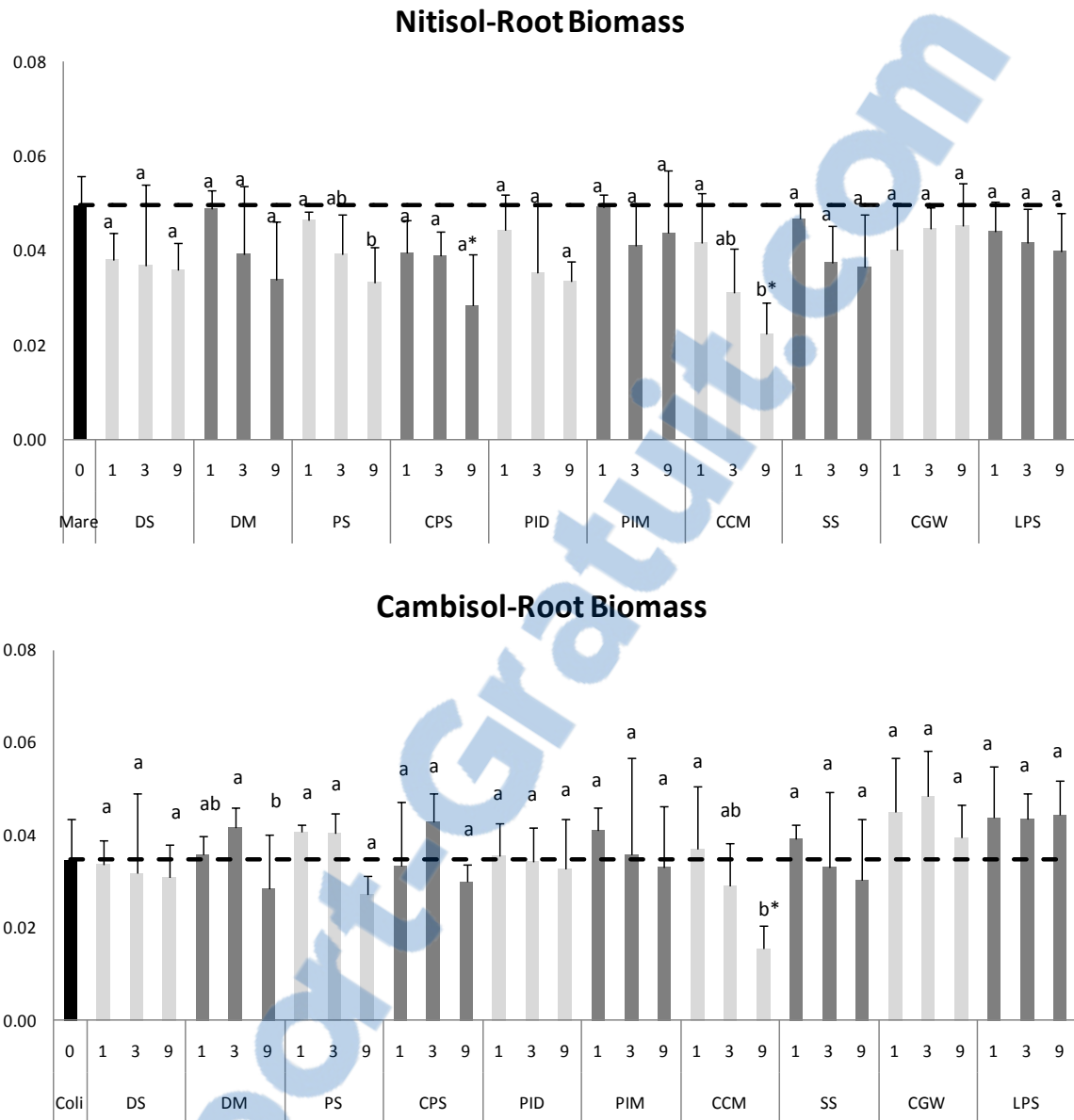


Figure 7.3 : Root biomass of 4-day barley seedlings grown in the soil.

The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

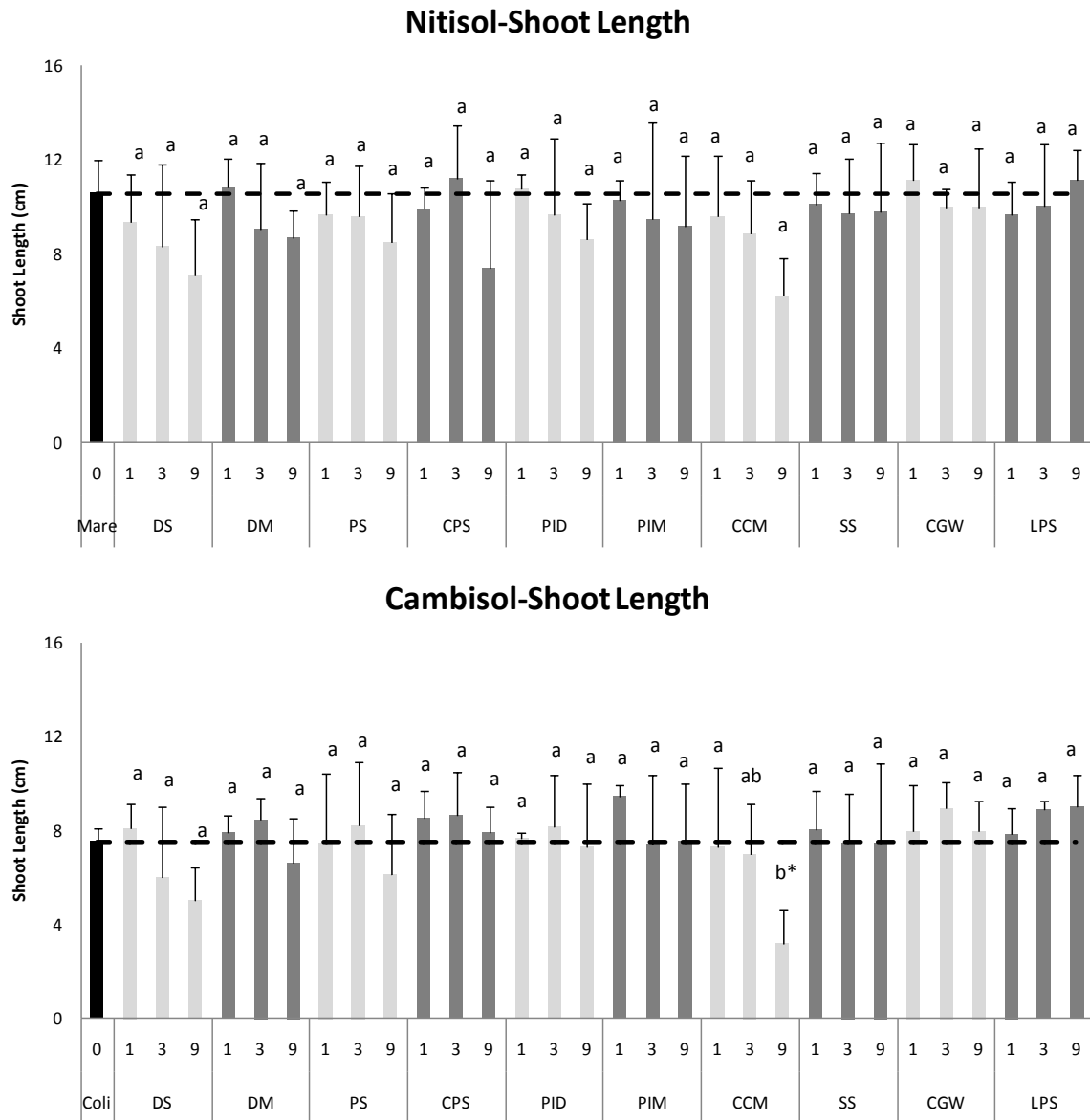


Figure 7.4 : Shoot length of 4-day barley seedlings grown in the soil.

The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

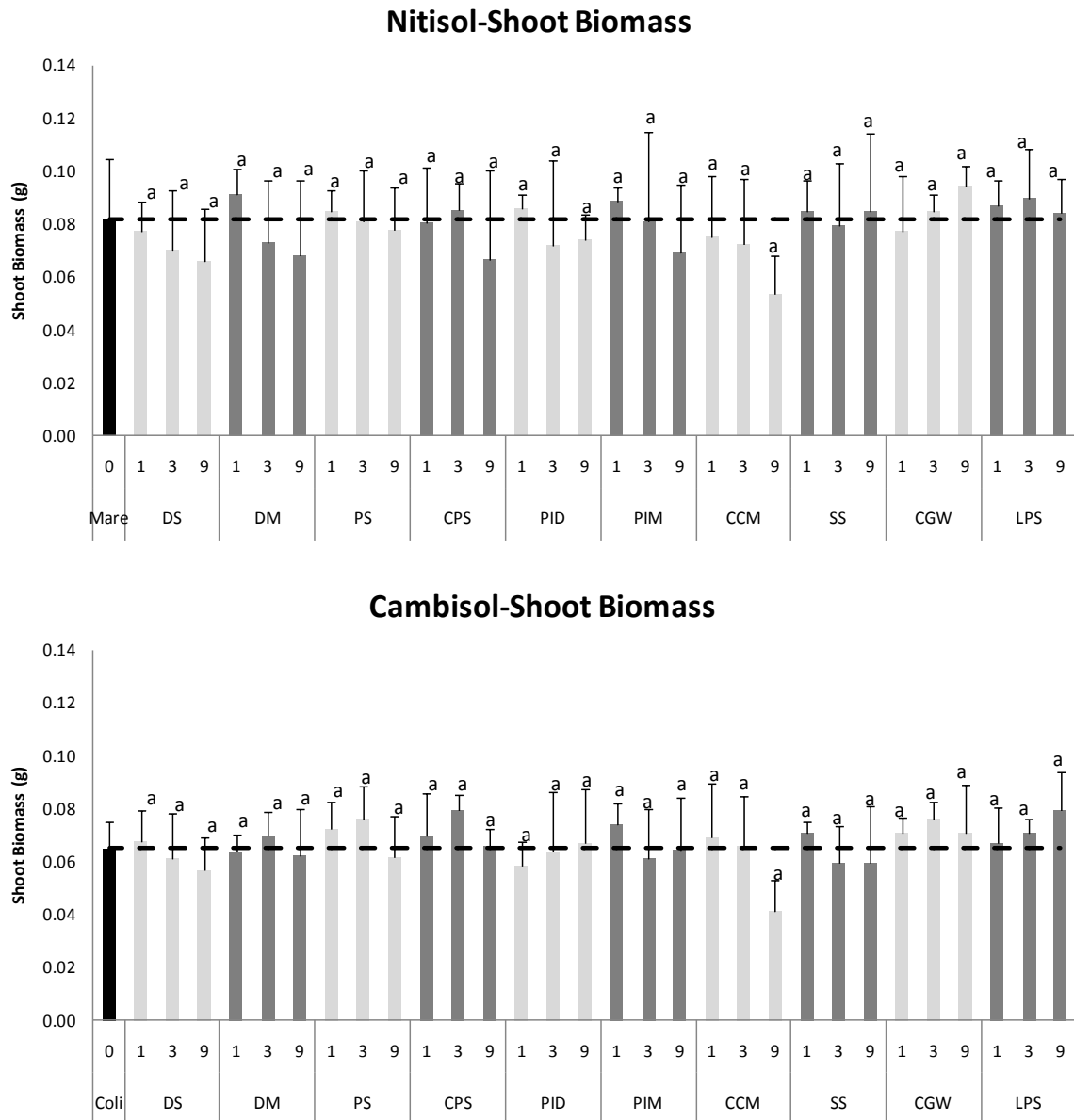


Figure 7. 5 : Shoot biomass of 4-day barley seedlings grown in the soil.

The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

7.3.2 Soil solution measurements

Figure 7.6 to Figure 7.13 showed the soil pH, Ionic Strength (pIS), extractable Cu (pCu), extractable Ni (pNi), extractable Cr (pCr), extractable Cd (pCd), extractable Zn (pZn) and extractable Pb (pPb) concentrations after the pot experiments. It exhibited that each soil solution measured here varied among different EOM treatments.

The soil pH increased after EOM treatments except for PIM-1 in The Cambisol, PID-1, CGW-1 and CGW-9 in The Nitisol. Compared with the control, the increase of soil pH in the treatments at rate 3 and rate 9 was more significant than the treatments at rate 1 for the majority of tested EOM. As for the same EOM treatments but with different concentrations of HM, the soil pH did not change at a significant level of $P < 0.05$ for SS and CGW in The Cambisol, for PS, CPS, CCM and CGW in the Nitisol.

Besides the soil pH, the soil IS, especially in the treatments of the PS, CPS and CCM, increased markedly wherever in the Cambisol or in the Nitisol. The difference of soil IS among the same manure treatments with different concentrations of TE was significant in most cases except for PIM and SS.

The soil extractable Cu concentration increased sharply for CPS (6 to 116 ppb) and CCM (15 to 527 ppb) in the Cambisol and for DS (11 to 98 ppb), CPS (12 to 157 ppb), PID (16 to 140 ppb) and CCM (36 to 635 ppb) in the Nitisol. The soil extractable Ni concentration increased clearly from rate 1 to rate 9 for CCM in the Cambisol and for CPS and CCM in the Nitisol. Compared with the soil control, the increase of soil extractable Ni concentration was significant for PS, CPS and CCM at rate 9 in the two soils and for DS and PID at rate 9 in the Nitisol. The soil extractable Cr concentration in soil control was not significantly different in most cases. At rate 1, added EOM had no effect in Cr concentration; at rate 3, PID had effect only in The Nitisol and CCM influenced Cr both into the 2 soils; at rate 9, PID and CCM presented significant difference for the 2 soils and PS is different only for the Nitisol.

The soil extractable Zn concentration increased markedly for CCM at rate 9 in the 2 soils. Depending on the EOM nature, the extractable Zn concentration decreased or increased according to the application rates. The soil extractable Cd concentration differed between treatments. With the Cambisol, effects of EOM rate could be observed for 6 of 10 studied EOM. With the Nitisol, these effects were noticed only for 2 EOM.

The soil extractable Pb concentration depended on the treatments. As can be seen here, the difference were neither significant nor intra-rate nor with the control most of time.

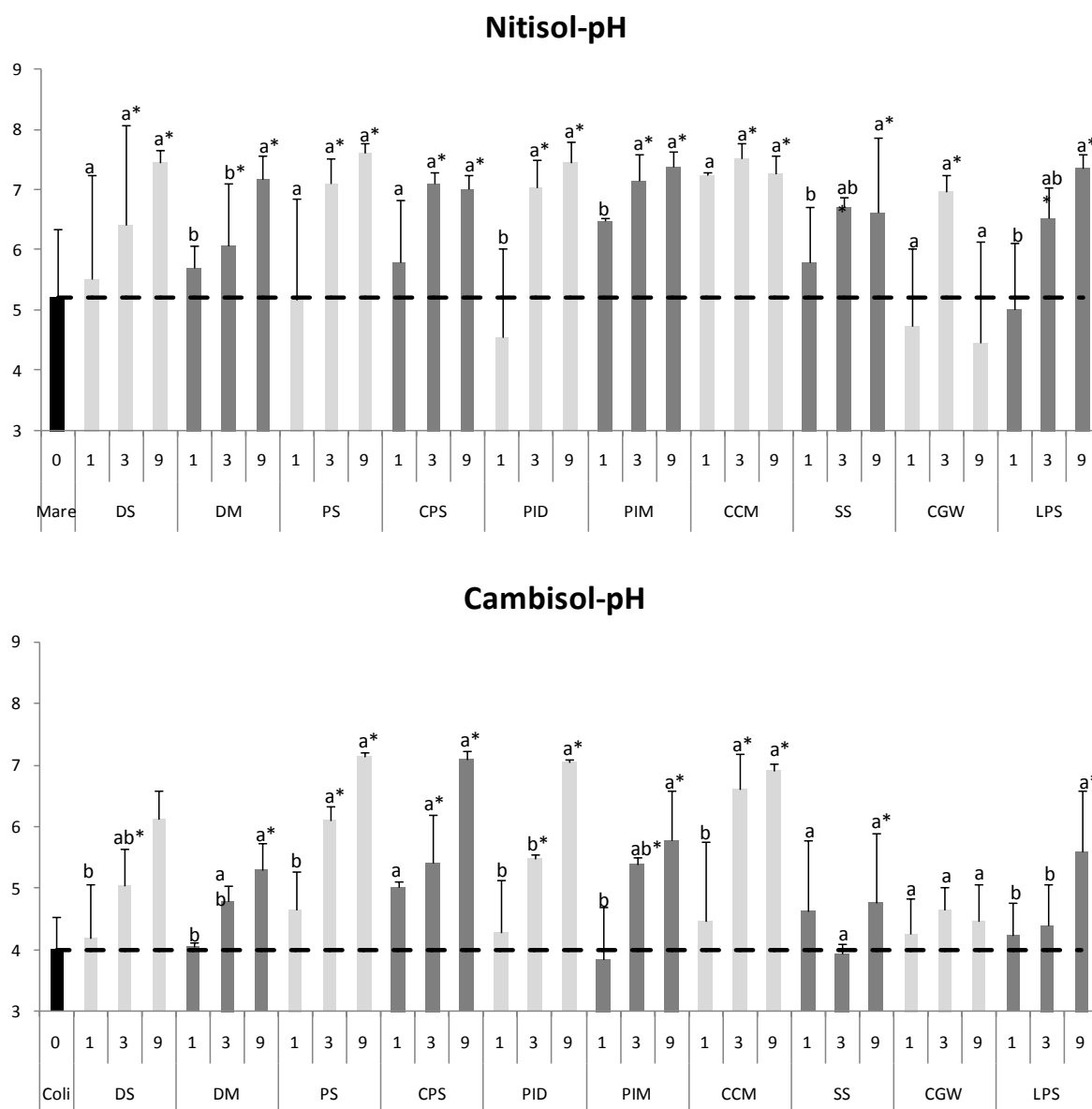


Figure 7.6 : pH of soil solution after 4-d barley grown in the soil

The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

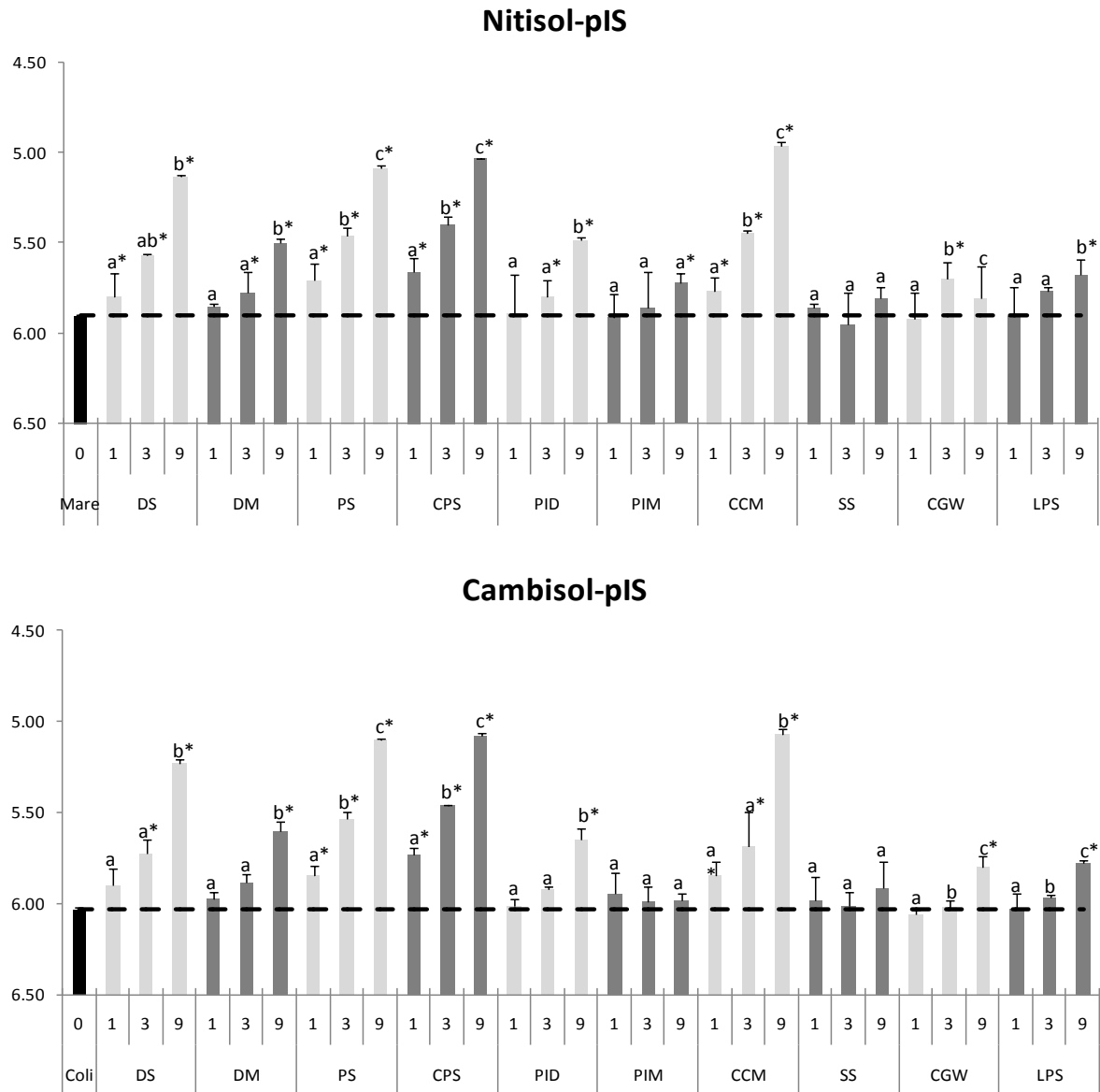


Figure 7.7 : Ionic strength of soil solution after 4-d barley grown in the soil

The soil was either not amended (control soil, Mare for Nitrosol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

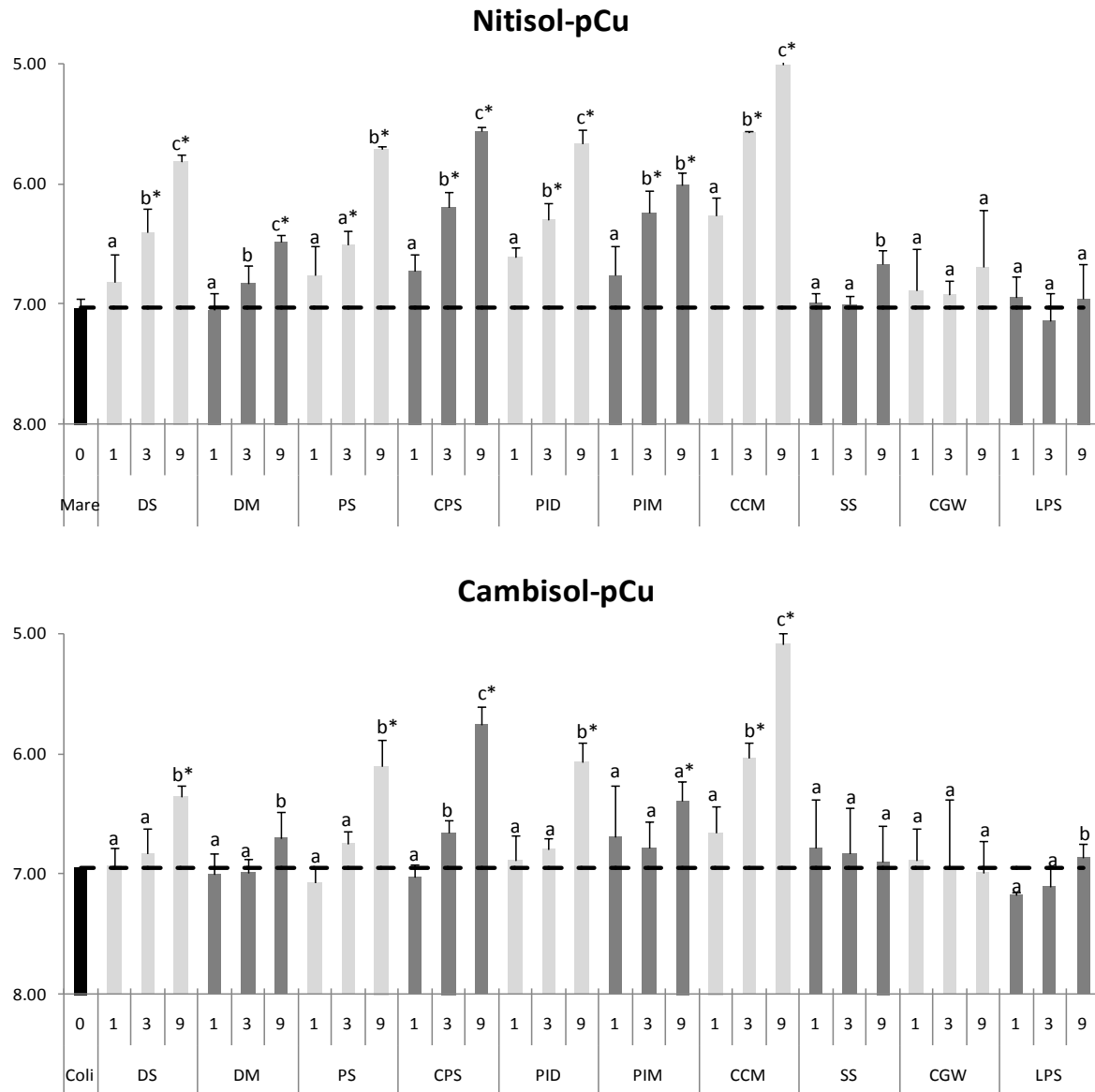


Figure 7.8 : Extractable Cu in soil solution after 4-d barley grown in the soil

The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

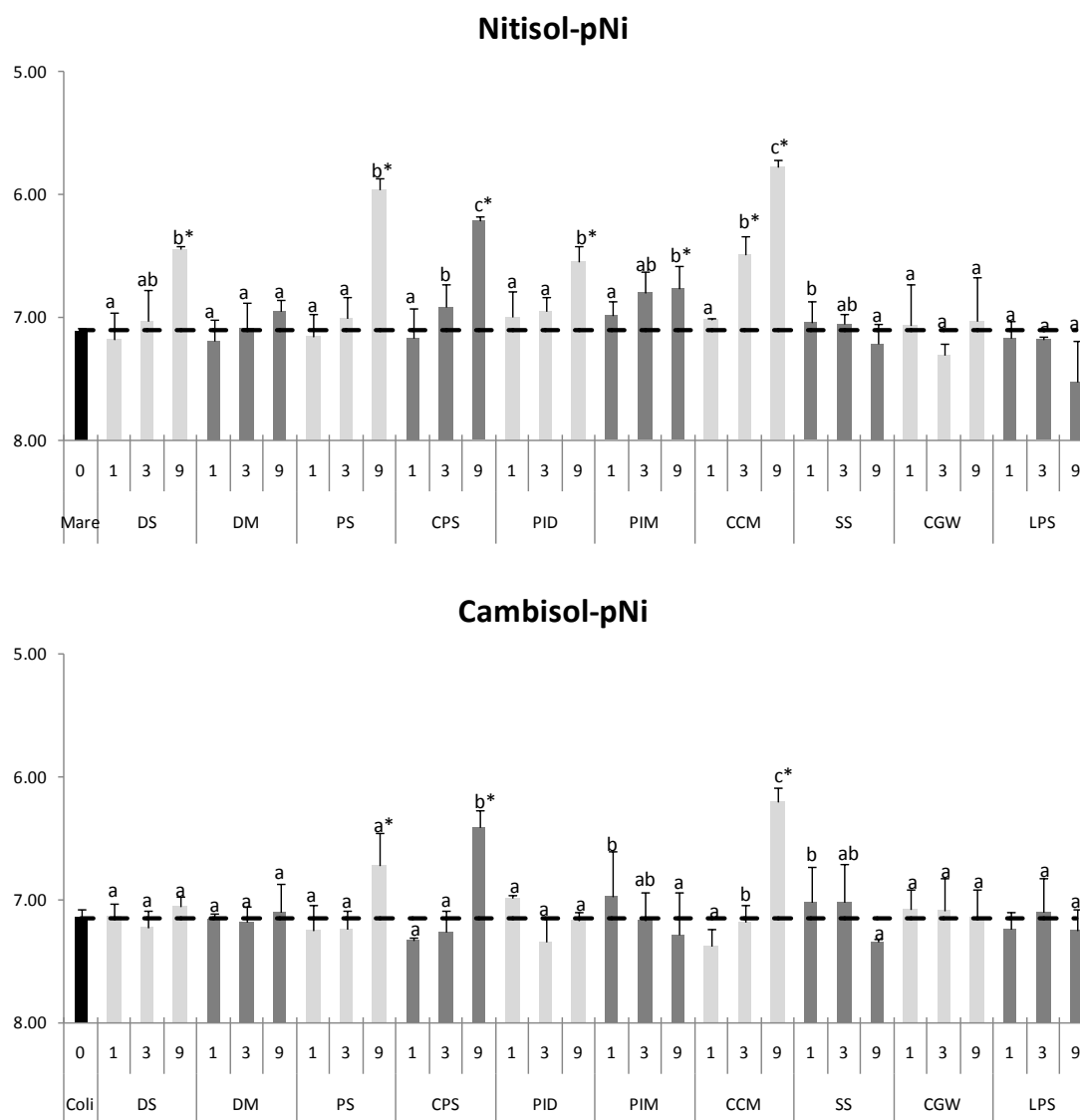


Figure 7.9 : Extractable Ni in soil solution after 4-d barley grown in the soil

The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

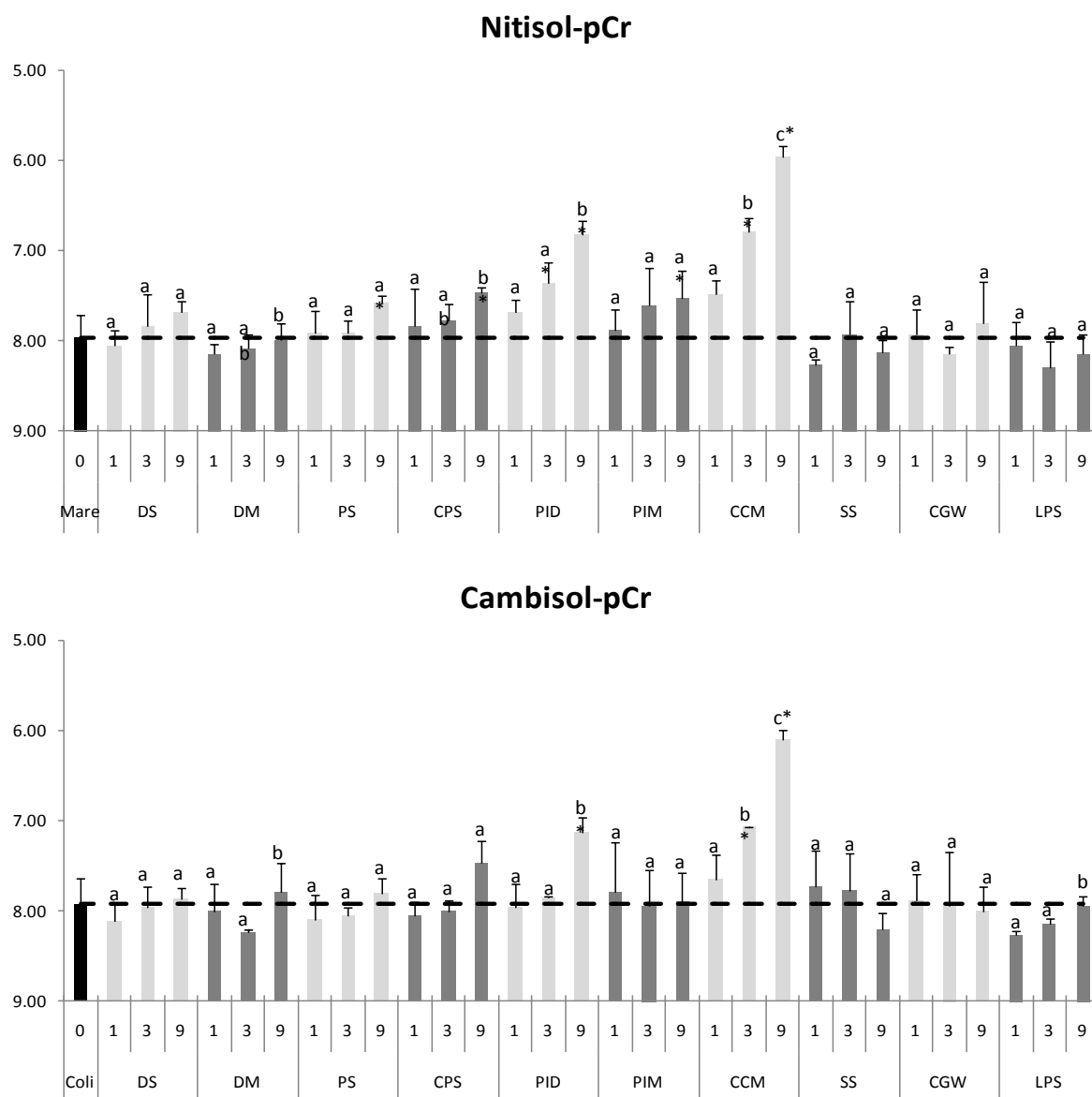


Figure 7.10 : Extractable Cr in soil solution after 4-d barley grown in the soil
The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

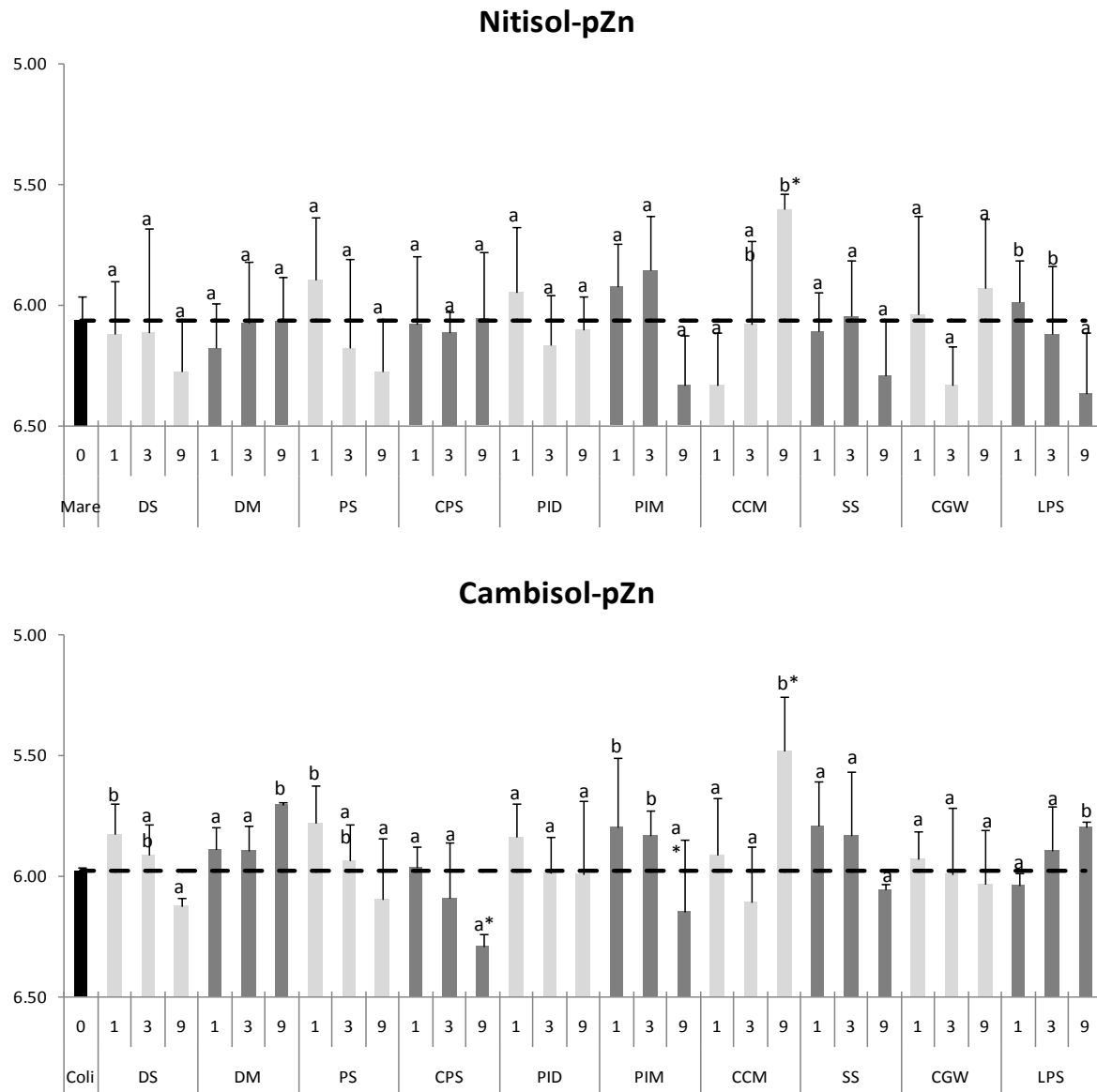


Figure 7.11 : Extractable Zn in soil solution after 4-d barley grown in the soil
 The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

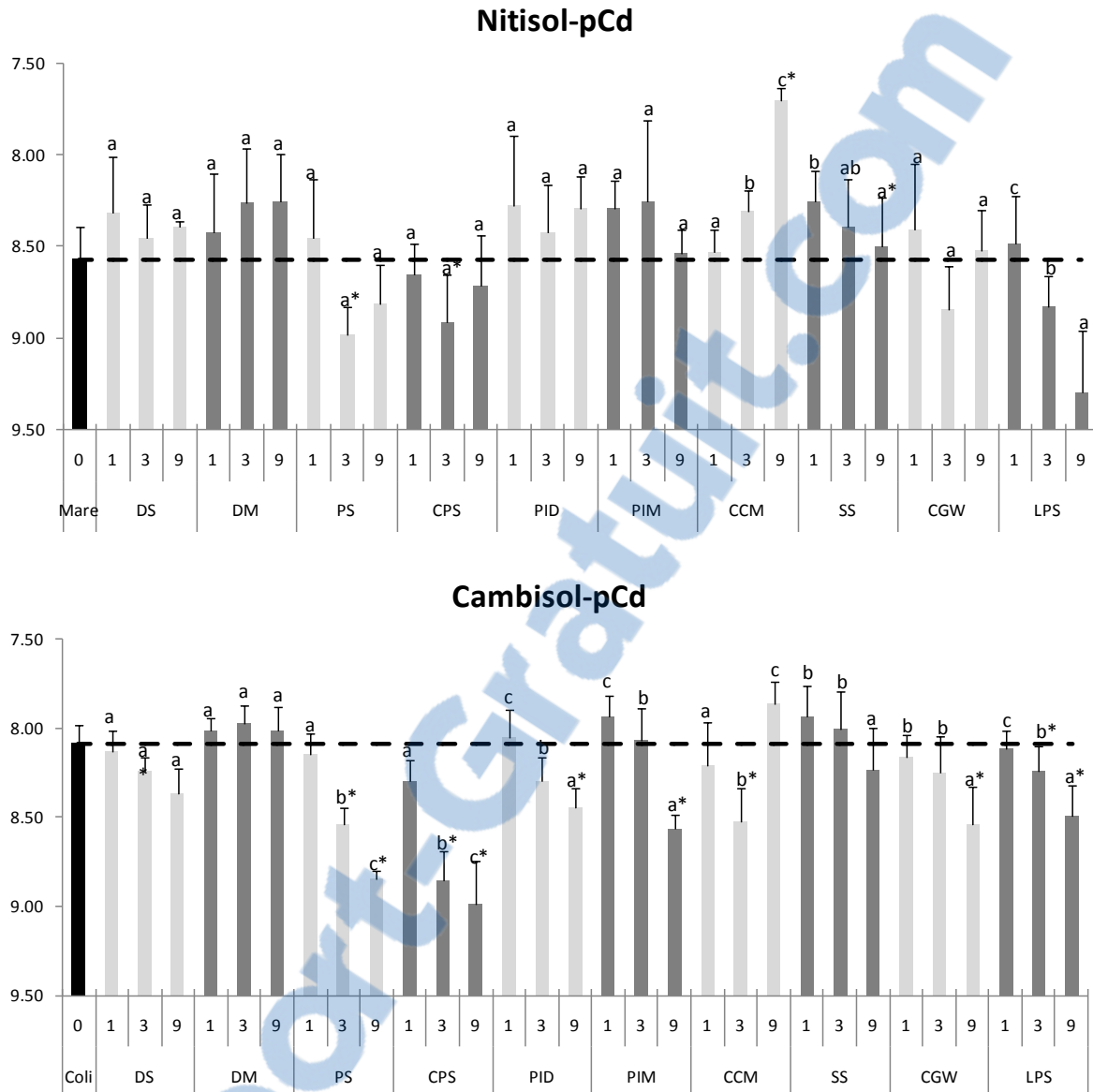


Figure 7.12 : Extractable Cd in soil solution after 4-d barley grown in the soil
The soil was either not amended (control soil, Mare for Nitisol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

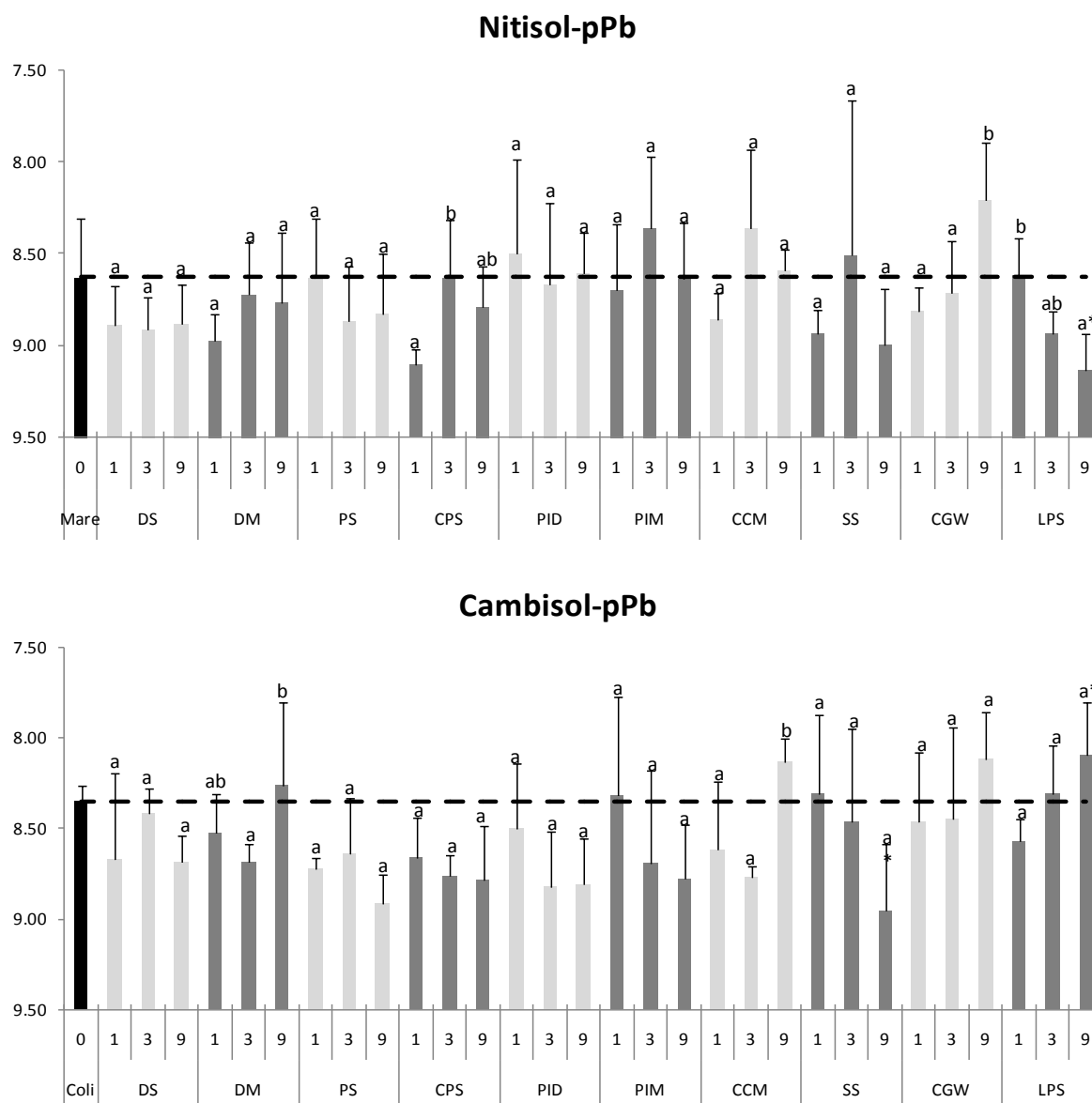


Figure 7.13 : Extractable Pb in soil solution after 4-d barley grown in the soil
 The soil was either not amended (control soil, Mare for Nitol and Coli for Cambisol) or amended at three different rates (1, 3 and 9) with dairy slurry (DS), dairy manure (DM), pig slurry (PS), pig slurry compost (CPS), poultry dropping (PID), poultry manure (PIM), composted chicken manure (CCM), sewage sludge (SS), composted green waste (CGW) or landfill potting soil (LPS). Stars stand for significant difference between amended and non-amended soils, while different letters for a given organic waste stand for significant difference between application rates ($P \leq 0.05$)

7.3.3 Relationship between soil solution parameters

Soil solution parameters included: pH, pIS, extractable TE (pCu, pNi, pCr, pZn, pCd, pPb), added TE (logCu, logNi, logCr, log Zn, logCd, logPb), added MO (logMO), added P (logP). Correlations between those parameters were shown in Table 7.4 for the Cambisol and Table 7.5 for the Nitisol.

The application of organic wastes to the two soils also greatly impacted the chemistry in the soil solution (Figure 7.6 to Figure 7.13). The electrical conductivity and pH significantly increased with the application of EOM to the two soils as well as with the rate of application. It is noteworthy that these increases were greater for the seven EOM from livestock farming activities than for the three EOM from urban activities.

The impact of these chemical changes on trace elements concentration in soil solution depended on the trace elements concerned. The concentration of Cr, Cu and Ni significantly increased with the addition of EOM, which is presumably due to the very strong affinity of these trace elements for organic matter. Alternatively, Cd and Zn concentration significantly decreased with the addition of the most of EOM, which is presumably due to the strong effect of the increase of pH. The concentration of Pb exhibits a more contrasted pattern with concomitant increase or decrease depending on the organic waste applied and the application rate. This is presumably due to the competitive effect of increasing pH, on one hand, that lead to decrease Pb concentration and of DOC binding capacity, on the second hand, that lead to increase Pb concentration.

Table 7.4: Pearson correlation coefficients (r) between soil solution characteristics on the Cambisol.

pH, pIS, extractable TE (pCu, pNi, pCr, pZn, pCd, pPb), added TE (logCu, logNi, logCr, log Zn, logCd, logPb), added MO (logMO), added P (logP). The correlations are significant ($P < 0.001$) from $r = 0.21$, for more relevant interpretations, only r values > 0.5 are in bold.

Cambisol	pH	pIS	pCr	pNi	pCu	pZn	pCd	pPb	logZn	logCu	logNi	logCr	logPb	logCd	logOM	logP
pH	1.00															
pIS	-0.64	1.00														
pCr	-0.34	0.46	1.00													
pNi	-0.23	0.52	0.71	1.00												
pCu	-0.58	0.68	0.88	0.72	1.00											
pZn	0.36	-0.13	0.39	0.39	0.12	1.00										
pCd	0.60	-0.43	0.12	0.09	-0.16	0.69	1.00									
pPb	0.27	-0.03	0.45	0.44	0.21	0.61	0.32	1.00								
logZn	0.65	-0.68	-0.29	-0.21	-0.45	0.26	0.65	0.02	1.00							
logCu	0.54	-0.54	-0.19	-0.15	-0.31	0.21	0.61	-0.02	0.96	1.00						
logNi	0.36	-0.37	-0.14	-0.14	-0.19	0.28	0.57	-0.16	0.75	0.77	1.00					
logCr	0.31	-0.32	-0.17	-0.13	-0.15	0.21	0.47	-0.18	0.74	0.77	0.96	1.00				
logPb	0.02	0.11	0.10	0.04	0.18	0.15	0.26	-0.23	0.36	0.50	0.80	0.82	1.00			
logCd	0.55	-0.56	-0.27	-0.18	-0.44	0.24	0.52	-0.08	0.90	0.81	0.74	0.70	0.37	1.00		
logOM	0.68	-0.75	-0.42	-0.29	-0.63	0.25	0.51	0.04	0.76	0.58	0.53	0.44	0.02	0.78	1.00	
logP	0.73	-0.80	-0.42	-0.29	-0.65	0.24	0.58	0.15	0.83	0.68	0.40	0.35	-0.12	0.72	0.89	1.00

Table 7.5 : Pearson correlation coefficients (r) between soil solution characteristics on the Nitisol

pH, pIS, extractable TE (pCu, pNi, pCr, pZn, pCd, pPb), added TE (logCu, logNi, logCr, log Zn, logCd, logPb), added MO (logMO), added P (logP). The correlations are significant ($P < 0.001$) from $r = 0.21$, for more relevant interpretations, only r values > 0.5 are in bold.

Nitisol	pH	pIS	pCr	pNi	pCu	pZn	pCd	pPb	logZn	logCu	logNi	logCr	logPb	logCd	logOM	logP
pH	1.00															
pIS	-0.38	1.00														
pCr	-0.20	0.55	1.00													
pNi	-0.19	0.75	0.81	1.00												
pCu	-0.35	0.73	0.90	0.89	1.00											
pZn	0.42	0.22	0.48	0.53	0.38	1.00										
pCd	0.33	0.19	0.49	0.52	0.39	0.71	1.00									
pPb	0.07	-0.02	0.36	0.29	0.33	0.45	0.17	1.00								
logZn	0.41	-0.68	-0.38	-0.44	-0.51	-0.03	0.27	-0.06	1.00							
logCu	0.32	-0.55	-0.24	-0.32	-0.34	0.01	0.37	-0.03	0.96	1.00						
logNi	0.15	-0.37	-0.17	-0.14	-0.19	0.06	0.34	-0.04	0.75	0.78	1.00					
logCr	0.08	-0.32	-0.15	-0.09	-0.12	0.03	0.30	0.02	0.73	0.77	0.95	1.00				
logPb	-0.11	0.12	0.13	0.22	0.24	0.16	0.35	0.04	0.32	0.47	0.77	0.80	1.00			
logCd	0.41	-0.56	-0.31	-0.37	-0.45	-0.03	0.19	-0.08	0.89	0.82	0.72	0.68	0.31	1.00		
logOM	0.54	-0.76	-0.55	-0.61	-0.72	-0.10	-0.08	-0.13	0.73	0.55	0.49	0.37	-0.07	0.75	1.00	
logP	0.56	-0.80	-0.55	-0.63	-0.75	-0.12	0.02	-0.10	0.83	0.67	0.40	0.32	-0.16	0.71	0.89	1.00

7.3.4 Relationship between rhizotoxicity and soil solution measurements

The multiple linear regressions in order to explain the relationship between RRL and soil solutions parameters gave the following results:

- Two soils together:

$$\log \text{RRL} = -0.372\text{pPb} + 0.346 \text{pCd} + 0.243 \text{pCr} - 0.088 \log \text{P}; R^2=0.630$$

- The Cambisol only:

$$\log \text{RRL} = -0.103*\text{pFI} + 0.06*\text{pH} - 0.348*\text{pPb} + 0.311*\text{pCd} + 0.156*\text{pNi} + 0.221*\text{pCr} - 0.209*\text{pZn} + 0.107*\text{pCu}; R^2=0.586$$

- The Nitisol only:

$$\log \text{RRL} = -0.337\text{pPb} + 0.420 \text{pCd} + 0.531 \text{pCr} - 0.263 \log \text{Cu} - 0.283 \log \text{OM}; R^2=0.867$$

7.4 Discussion

7.4.1 Relevance of root length as indicator of plant phytotoxicity

As our plant measurements results showed, relative root elongation presented the most variability (highest variation factor) and allowed to observe more significant difference between EOM treatments than other parameters (root biomass, shoot length, shoot biomass). In this study, RRL was relevant as indicator of plant phytotoxicity. One of the main ways of plant exposure in TE contaminated soil corresponds to the contact of root with soil solution: roots are the first organ of plant exposed to metals (Bravin, 2008). The TE accumulation in root is favorable to the phenomena of rhizotoxicity which can be visible by a brownish color and a thickening of roots, a decrease of root elongation and an increased number of poorly developed lateral roots (Kopittke *et al.*, 2006; Kopittke *et al.*, 2007).

7.4.2 Induction and mitigation of rhizotoxicity by EOM application

A dual effect of the application of organic wastes on the two tropical soils studied was observed. In the Nitisol, the application of EOM induced a rhizotoxicity as the composted chicken manure and composted pig slurry at rate 9 caused the worst effect. In the Cambisol, EOM application induced a rhizotoxicity as the composted chicken manure at rate 9, and can mitigate this phenomenon such as the composted green waste at rate 9. The rhizotoxicity induction may be associated to the TE added by EOM application. The rhizotoxicity mitigation can be explained by the decreased aluminium toxicity in the acidic soils which tends to improve plant growth.

7.4.3 Alteration of soil solution chemistry by organic waste application

The soil pH increased after organic manure treatments, which is ascribed that the pH of all three manures were higher than that of the garden soil. Previous report also showed that basic organic matter increased soil pH (Diaz-Barrientos *et al.*, 2003).

The higher EC of the OM may be related to the manufacturing process of organic manure. Wong *et al.* (1999) also found that the manure compost significantly increased soil EC and ascribed it to the introduction of large quantities of soluble salts, such as Mg^{2+} , Ca^{2+} , Cl^- and HCO_3^- ions from the manure compost. Similar results were observed in the previous studies conducted by Hao *et al.* (2003).

It can be ascribed to two aspects. On the one hand, the increasing soil total Zn concentration introduced by the PIM treatments was higher than that by the CCM and EOM treatments; on the other hand, Zn in pig manure usually exists mainly as inorganic ions, and is more mobile (L'Herroux *et al.*, 1997), but showed a high retention in the OM fraction when a poultry litter extract was used to leach metals from a Zn, Cd and Pb contaminated soil (Li *et al.*, 1997) or when farmyard manure was used as amendment of Zn contaminated soils (Rupa *et al.*, 2003).

7.4.4 Impact of soil solution chemistry on the induction or mitigation of rhizotoxicity

Considering the multiple changes observed in the chemistry of the soil solution, no single chemical parameter can be related to the alteration of the RRL in amended soils compared to the non-amended soils (results not showed). However, the decrease in RRL observed for 7 out of 10 organic wastes in the Nitisol should be related to the increase in Cu, Cr and Ni concentration, and in salinity (i.e. related to the increase in electrical conductivity). Correlation analyses did not enable to ascertain which parameter(s) is/are the main one(s). Considering the very low pH measured in the non-amended Cambisol (pH = 4), the increase in the RRL in the application of almost all the organic wastes is most likely related to the mitigation of aluminium rhizotoxicity by the increase in pH observed in amended soil. In the Cambisol amended with the poultry manure compost at the higher application rate, the mitigation of Al rhizotoxicity was nevertheless exceeded by the induction of a rhizotoxicity. This rhizotoxicity would be explained by the same parameter(s) than those controlling the rhizotoxicity observed in the Nitisol.

7.5 Conclusion

The most striking result concern the dual effect of the application of organic wastes on the two tropical soils studied, either by alleviating rhizotoxicity presumably due to aluminium in the most acidic soils (i.e. the Cambisol) or alternatively by inducing a rhizotoxicity (in the two soils). The EOM-induced rhizotoxicity also greatly varied between EOM. However, the correlation analyses between soil solution chemical parameters and the RRL did not enable to characterise the processes controlling the occurrence of rhizotoxicity. The implementation of advance modelling such as the electrostatic model developed by Kinraide *et al.* (2004) that accounts for both major and trace element speciation and interaction with plant roots should support a better understanding of the main geochemical drivers of rhizotoxicity.

Chapitre 8. Tentative de classification des MOEx en milieu tropical par la méthode multicritère SIRIS en vue d'orienter leur usage agronomique et/ou énergétique

8.1 Introduction

Les matières organiques exogènes (MOEx) sont diverses de par leurs caractéristiques intrinsèques liées à leur mode de gestion mais également à cause de leur potentiel à être valorisées en nouveau « produit ». Ces MOEx incluent les résidus organiques issus des activités agricoles, urbaines et industrielles ainsi que les produits issus de leur traitement (Marmo *et al.*, 2004). La deuxième vie de ces MOEx est envisageable via leur valorisation agricole en tant qu'amendements ou engrais pour les sols ou bien via leur valorisation énergétique en tant que biomasse.

Cette valorisation agronomique et/ou énergétique des MOEx rend nécessaire la mise en place d'une typologie permettant de les classer. Idéalement, les outils nécessaires à ce classement doivent être pertinents, simples à utiliser, fiables, peu onéreux et faciles à interpréter. Dans la pratique, l'établissement de cette typologie est difficile car elle met en jeu des critères scientifiques variés que l'on doit obligatoirement hiérarchiser dans le but de répondre à des objectifs précis. Les critères les plus importants sont ensuite agrégés d'une façon plus ou moins formelle afin de faciliter l'utilisation de cette information hétérogène. Ces opérations peuvent être réalisées grâce à l'emploi de méthodes multicritères qui permettent de construire d'une façon optimale des outils opérationnels d'aide à la décision. Les méthodes mathématiques d'analyse multicritère ont pour but la résolution des problèmes d'aide à la décision multicritère. Elles constituent une étape importante du processus de décision, qui suit celle d'identification et de définition du problème, et aboutissent au choix d'une ou plusieurs solutions optimale(s) parmi un ensemble discret de solutions, via une procédure de sélection (Roy, 1985).

C'est la raison pour laquelle les méthodes multicritères ont trouvé des applications dans de nombreux domaines de l'environnement, dont la gestion des rivières (Hermans *et al.*, 2007), des ressources en eau (Joubert *et al.*, 2003) ou des crues (Kenyon, 2007), l'estimation des risques environnementaux de sites contaminés (Critto *et al.*, 2007), la gestion des déchets d'équipements électriques et électroniques (Roussis *et al.*, 2008), ou celles de boues de traitement des eaux usées (Bellehumeur *et al.*, 1997).

Dans cette étude, la méthode multicritère SIRIS (Système d'intégration du risque par interaction de scores) (Vaillant *et al.*, 1995) a été utilisée pour élaborer une typologie des MOEx afin de faciliter les choix d'usages des MOEx selon différents scénarios de valorisation agronomique et énergétique. À partir de certaines caractéristiques intrinsèques, prédites par la

spectrométrie proche infrarouge, de chaque MOEx, l'évaluation multicritère SIRIS est appliquée pour juger de l'adéquation d'usages de cette MOEx et ceci en tenant compte des contraintes négatives liées à ce choix. L'objectif de notre démarche est donc de fournir une aide pour décider de la valorisation des MOEx.

8.2 Matériel et méthodes

8.2.1 Méthode SIRIS

La méthodologie SIRIS est une méthode mathématique dite « hiérarchique de rang » (Vaillant *et al.*, 1995). L'idée générale des méthodes hiérarchiques est d'établir un système d'inéquations entre les critères et leurs modalités, plutôt qu'un système d'équations. La Figure 8.1 illustre les inéquations construites à partir de 3 critères ayant 3 modalités chacun (« f » : favorable ; « m » : intermédiaire ; « d » : défavorable).

Si en postulat de base, on considère les critères dans l'ordre d'importance suivant : Critère 1 > Critère 2 > Critère 3, alors la pénalité associée à la modalité défavorable du critère 1 est supérieure à celle de la modalité défavorable du critère 2, elle-même supérieure à celle du critère 3. Pour un même critère, la pénalité associée à la modalité défavorable doit évidemment être supérieure à la pénalité de la modalité intermédiaire, elle-même supérieure à la pénalité de la modalité favorable. Enfin, la pénalité associée à la modalité favorable est nulle, et ce quel que soit le critère.

Il n'y a donc, sur cette base, pas lieu de préciser le niveau exact de contribution (le poids) de chacun des critères, puisqu'il repose sur un système d'inégalité découlant de la hiérarchisation des critères.

Critère 1	>	Critère 2	>	Critère 3
f	=	f	=	f
^		^		^
m	>	m	>	m
^		^		^
d	>	d	>	d

Figure 8.1 : Base d'un système combinatoire hiérarchique

En fonction du choix de valorisation d'une MOEx, un ensemble de critères pouvant regrouper une ou plusieurs caractéristiques de MOEx est pris en compte. Tous ces critères n'ont pas le même poids. La hiérarchisation des critères peut être différente d'une méthode multicritère à l'autre (Roy, 1985; Ben Mena, 2000), c'est pourquoi elle peut sembler plus ou moins arbitraire pour les personnes qui n'ont pas l'habitude d'employer ces techniques. Pour pallier ce problème, nous avons décidé d'utiliser la méthode SIRIS (Vaillant *et al.*, 1995) pour laquelle la hiérarchisation consiste uniquement à positionner les critères les uns par rapport aux autres sans qu'il soit nécessaire d'introduire des pondérations contrairement à certaines approches. Les différents critères sont classés par ordre décroissant d'importance. Avec la méthode SIRIS, il est possible de considérer que deux critères ont la même importance.

Dans notre démarche, nous avons donc choisi de grouper les critères qui décrivent le même type d'information et de traiter ces groupes distinctement plutôt que d'établir une seule hiérarchie sur l'ensemble des critères retenus. C'est ce que nous avons fait dans cette étude en hiérarchisant séparément les critères de valorisation agronomique, les critères de valorisation énergétique.

8.2.1.1 Organisation hiérarchique des critères

Face à une MOEx que l'on cherche à valoriser, la mise en œuvre de la méthode SIRIS repose sur un consensus autour :

- De la sélection de critères jugés ayant une responsabilité dans le scénario de valorisation considéré. Les deux scénarios pris en compte sont le scénario agronomique et le scénario énergétique ;
- De la hiérarchisation des différents critères retenus et de leurs interactions synergiques ;
- De la définition de seuils pour chaque critère.

Des regroupements de critères au sein d'une même classe sont possibles, dès lors que l'on considère que ces critères possèdent le même niveau d'importance et que, par ailleurs, il n'existe pas d'interactions synergiques entre eux. Les seuils des critères encadrent des intervalles de valeurs auxquels sont attribués des codes : les modalités.

8.2.1.2 Déclassement par pénalisation

Faisant référence à la description de Le Gall (2012), l'un des grands principes de la méthodologie SIRIS est qu'elle repose sur un système de déclassement par pénalisation. Pour cela, toutes les combinaisons de critères sont envisagées, depuis la situation idéale où tous les critères présentent des modalités favorables, jusqu'à la situation la plus critique, où tous les

critères présentent des modalités défavorables. Notons que ces deux situations extrêmes peuvent être purement théoriques et ne pas exister.

C'est en partant de la situation idéale que la méthode SIRIS procède à un déclassement, et ce à chaque fois qu'un critère présentera une modalité défavorable. Pour cela une pénalisation ou score est associée à chaque modalité. L'importance de la pénalisation dépend de l'ordre des critères ainsi que du niveau de la modalité. Au final, la somme des pénalités associées à chaque modalité de critère rencontré donne un rang.

8.2.1.3 Orientation d'usage de MOEx

Dans les conditions idéales, il est ainsi possible de construire une échelle de « rang » basée à la fois sur les critères de valorisation agronomique et sur les critères de valorisation énergétique. Etant donné que les critères d'évaluation pour ces deux types d'usages ne sont pas les mêmes, il n'est pas possible de définir un score global pour départager les différents scénarios. Par la suite, une MOEx donnée sera « notée » par un score agronomique (Score A) et un score énergétique (Score E).

8.2.2 Données sur les MOEx

Notre base de données comprend 2199 échantillons de MOEx collectés et analysés dans le contexte de différents programmes de recherches. Cette collection de MOEx couvre une large gamme de MOEx fraîches et transformées. Selon les origines des MOEx, nous avons 50% d'effluents de volaille, 19% d'effluents de bovin, 17% d'effluents porcins, 9% d'effluents urbains, 3% d'effluents agro-industriels, 1% d'effluents d'ovins et 1% d'effluents mixtes (mélanges de différents types d'effluents). 1199 MOEx ont été collectées à La Réunion et 1000 MOEx proviennent de Madagascar.

8.2.2.1 Caractéristiques mesurées au laboratoire

Sur une partie des MOEx (cf Chapitre 2), des données de références mesurées au laboratoire sont disponibles. Ces analyses concernent les dosages des :

- C organique et N organique, selon la méthode Dumas décrites par les normes NF ISO 13878 (ISO 1998) et 10694 (ISO 1995)
- P et K totaux qui sont dosés de la manière suivante. Il est nécessaire de transformer les matières organiques des MOEx en matières minérales. Après séchage et broyage, les échantillons sont calcinés à 520°C ce qui permet de détruire la matière organique et d'oxyder les composés minéraux non volatiles. Les cendres obtenues (matières minérales) sont mises en solution dans de l'acide chlorhydrique. Le phosphore est

dosé en flux continu par colorimétrie et le potassium est dosé par spectrométrie d'absorption atomique.

D'autres part, une série d'expérimentations spécifiques ont été conduites sur un lot de MOEx représentative des catégories de MOEx :

- Pour les potentiels dits « positifs » : suivi de la minéralisation du carbone et de l'azote en conditions contrôlées pour évaluer le potentiel agronomique (Chapitre 3); détermination du pouvoir calorifique et du potentiel méthanogène en vue d'apprécier le potentiel énergétique (Chapitres 4 et 5);
- Pour les potentiels dits « négatifs » dans le cadre du scénario de valorisation agronomique : détermination du potentiel de dénitrification des MOEx (Chapitre 6) et phytotoxicité des ETM suite à l'apport des MOEx au sol (Chapitre 7)

8.2.2.2 Caractéristiques prédites par la spectrométrie proche infrarouge

Les spectres dans le proche infrarouge des 2199 MOEx étudiées ont été acquis. Les données spectrales et les analyses de référence mesurées au laboratoire ont constitué deux matrices de données. A l'aide d'outils chimiométriques, ces matrices ont permis l'élaboration d'équations d'étalonnage des caractéristiques des MOEx. Cet étalonnage permet de prédire l'ensemble de notre base de données via les spectres SPIR. La démarche ainsi que les équations de prédiction sont rapportées dans le chapitre 2 de ce manuscrit.

Ce sont les caractéristiques prédites par la SPIR qui ont été utilisées par la suite comme données d'entrée de notre évaluation multicritère.

8.3 Résultats

8.3.1 Classification des MOEx suivant le scénario de valorisation agronomique

8.3.1.1 Organisation hiérarchique des critères

Les critères choisis ainsi que leur organisation hiérarchique dans le cadre d'une valorisation agronomique sont les suivants :

- La valeur fertilisante des MOEx matérialisée par leur teneur en éléments fertilisants (A1) : azote (N), phosphore total (P_2O_5) et potassium total (K_2O).
- La valeur amendante des MOEx évaluée par l'indice de stabilité de la matière organique (ISMO) (A2).

Les critères A1 et A2 ont été retenus car ils représentent les 2 fonctions principales que doivent les MOEx une fois apportée au sol. En effet, la valeur fertilisante d'une MOEx indique sur sa capacité pour la nutrition des cultures et la valeur amendante détermine sa potentialité à maintenir la fertilité du sol (AFNOR, 2011).

8.3.1.2 Définition des pénalités

La définition des pénalités est présentée dans le Tableau 8.1

8.3.1.3 Calcul des pénalités

Le calcul des pénalités est présenté dans le Tableau 8.2

Suivant les scores obtenus (Score A) par chaque MOEx, la classification suivante est proposée :

- Score 0 et 1 : engrais organo-minéral, tel défini par la normalisation NF U 42-001 (1981)
- Score 2 et 3 : engrais organique, tel défini par la normalisation NF U 42-001 (1981)
- Score 4 à 6 : amendement organique, tel défini par la normalisation NF U 42-051(2006)
- Score 9 : support de culture

8.3.1.4 Externalités négatives liées à la valorisation agronomique

Les externalités négatives retenues pour la valorisation agronomique des MOEx sont :

- Le potentiel de dénitrification via les émissions de N_2O , critère qui n'est pas quantitatif mais dont une appréciation qualitative est considérée. En effet, le Chapitre 5 de notre étude nous a permis de conclure que la dénitrification potentielle d'une MOEx dépend du sol auquel la MOEx est apportée. Ainsi, les MOEx qui ont des potentiels de dénitrification significativement différents du potentiel de dénitrification du sol seul sont considérées comme à risque.
- La phytotoxicité des ETM apportés par les MOEx, critère non quantitatif également mais dont une appréciation qualitative est considérée. Faisant écho au Chapitre 6 de ce manuscrit, les MOEx qui ont engendrées des diminutions de l'élongation racinaire sont à utiliser avec précaution.
- L'épandabilité des MOEx, critère lié à la siccité des MOEx pouvant impacter sur la nécessité de traitements avant l'épandage sur les sols.

8.3.1.5 Classification suivant le scénario de valorisation agronomique des MOEx

En prenant en compte les scores A obtenus pour chacune des MOEx, la répartition suivante a été obtenue :

- 13% ont été identifiés comme engrais organo-minéraux potentiels. Dans cette catégorie, on dénombre 253 effluents d'élevage (dont 193 effluents de volaille), 9 effluents d'agro-industrie (dont 8 déchets d'abattoir) et 22 effluents urbains.

- 45% sont classés comme potentiels engrais organiques. 936 effluents d'élevage (dont 596 effluents de volaille et 246 effluents de porcin), 9 effluents d'agro-industrie (dont 5 résidus d'abattoir), et 49 effluents urbains (dont 32 de déchets de décharge) y sont répertoriés.
- 40% sont classés en tant qu'amendements organiques. Le nombre d'effluents d'élevage, originaires de l'agro-industrie et de la ville de cette classe sont respectivement de 692 (dont 299 effluents de volaille et 285 effluents de bovins), 37 (dont 26 issus d'abattoir) et 124 (dont 89 déchets verts).
- 2% sont classés comme de supports de cultures. C'est le cas pour 18 effluents de bovin (sur 29 effluents d'élevage), 11 déchets de décharge (terreaux et composts de déchets verts).

Concernant les critères d'externalités négatives :

- en terme d'émissions de N_2O , les effluents d'élevage ont été identifiés comme acteurs potentiels au vu du chapitre 5 de notre manuscrit et confirmant d'autres auteurs (Flessa *et al.*, 2000; Velthof *et al.*, 2011) ;
- sur le plan phytotoxicité des ETM, seuls les composts de fumier de volaille apportés à une dose neuf fois supérieure à la dose recommandée présentent un effet négatif sur les racines (cf Chapitre 6) ;
- en matière d'épandabilité, les engrais organo-minéraux et organiques sont des produits secs, donc facilement épandables tandis que les amendements organiques peuvent être pour 17% des MOEx étudiées ici pâteuses ou même liquides donc nécessitent une opération supplémentaire avant l'épandage.

Tableau 8.1 : Liste des critères retenus pour le scénario agronomique et leur hiérarchisation

Critère retenu	Favorable	Intermédiaire	Défavorable	Seuils
A1 : Eléments fertilisants : N, P ₂ O ₅ , K ₂ O exprimés en % Matière Brute	N ou P ₂ O ₅ ou K ₂ O > 3 N+P ₂ O ₅ +K ₂ O >7	N ou P ₂ O ₅ ou K ₂ O > 3 3 < N+P ₂ O ₅ +K ₂ O <7	N+P ₂ O ₅ +K ₂ O <3	Définis sur la base de la norme sur les engrais (AFNOR, 1981) et les amendements (AFNOR, 2006)
A2 : Indice de Stabilité de la Matière Organique (ISMO) exprimé en ‰ Matière Organique	ISMO > 600	200 < ISMO < 600	ISMO < 200	Définis à partir de la répartition des ISMO établis par Lashermes <i>et al.</i> , (2009)

Tableau 8.2 : Echelle SIRIS de scores pour un système à 2 critères (A1, A2) présentant 3 modalités et avec A1 > A2

	A1	A2	Score-A
f = 0		f = 0	0
		m = 1	1
		d = 2	2
m = 2		f = 0	2
		m = 1	3
		d = 3	5
d = 5		f = 0	5
		m = 2	7
		d = 4	9

8.3.2 Classification des MOEx suivant le scénario de valorisation énergétique

8.3.2.1 Organisation hiérarchique des critères

Les critères retenus ainsi que leur organisation hiérarchique du plus important au plus faible dans le cadre d'une valorisation énergétique sont les suivants :

- La siccité des MOEx (E1). Ce critère est considéré comme le plus important du fait qu'elle conditionne la mise en incinération une MOEx et le choix de procédé pour la méthanisation. Liquide ou pâteuse ou sèche, une MOEx engendrerait un éventuel surcoût de préparation pour un usage donné.
- Le rapport C/N (E2). Ce critère matérialise la disponibilité de l'azote pour les microorganismes dans les MOEx en vue d'une méthanisation (Moletta, 2008). En effet, un C/N élevé témoigne d'une insuffisance d'azote qui diminue la potentialité des bactéries à assimiler tout le carbone présent dans le milieu. Et un C/N faible peut conduire à la formation d'ammonium qui pourrait inhiber la méthanogenèse.
- Le pouvoir calorifique (E3). Ce critère entre en jeu pour la mise en combustion des MOEx.

8.3.2.2 Définition des pénalités

Les pénalités sont définies dans le Tableau 8.3.

8.3.2.3 Calcul des pénalités

Le calcul des pénalités est effectué suivant le Tableau 8.4.

Suivant les scores obtenus, score E, par chaque MOEx, la classification suivante est proposée :

- Score 0, 1 ou 3 : combustion
- Score 5, 7 ou 9 : méthanisation
- Score 12 : aucune des 2 voies énergétiques (ni combustion ni méthanisation)

8.3.2.4 Classification des MOEx suivant le score E

En prenant en compte les scores des critères énergétiques obtenus par chacune des 2199 MOEx, nous avons 23% des MOEx pour lesquelles la méthanisation est la meilleure voie selon nos critères et 77% peuvent être destinées à la production de chaleur par combustion.

Le Tableau 8.5 regroupe en détail la répartition suivant les origines de MOEx étudiées.

Tableau 8.3 : Liste des critères retenus pour le scénario énergétique et leur hiérarchisation

Critères retenus	Favorable	Défavorable	Seuils
MS	MS > 35	MS < 35	Siccité de la MOEx MS > 35% MB (Chabalier <i>et al.</i> , 2006; Moletta, 2008)
C/N	C/N entre 20 et 30	C/N < 20 ou C/N > 30	Critère C/N pour la méthanisation (Moletta, 2008)
Pouvoir calorifique	PCS > 5MJ/kg	PCS < 5MJ/kg	Critère PCS pour la combustion (Ngnikam <i>et al.</i> , 2002)

Tableau 8.4 : Echelle SIRIS de scores pour un système à 3 critères (E1, E2, E3) présentant 2 modalités et avec E1 > E2 > E3

E1	E2	E3	Score-E
f=0	f = 0	f = 0	0
		d = 1	1
	d = 3	f = 0	3
		d = 2	5
d= 5	f = 0	f = 0	5
		d = 2	7
	d = 4	f = 0	9
		d = 3	12

Tableau 8.5 : Répartition des MOEx suivant les usages énergétiques potentiels

		Combustion		Méthanisation	
		Nombre	%	Nombre	%
Agro-industrie	Abattoir	13	48.1	14	51.9
	Boues laiterie	0	0.0	5	100.0
	Boues process volaille	0	0.0	13	100.0
	Autres	8	57.1	6	42.9
Elevage	Bovin	134	33.2	270	66.8
	Porcin	237	62.4	143	37.6
	Volaille	1084	99.5	5	0.5
	Caprin	6	21.4	22	78.6
	Autres	7	77.8	2	22.2
Urbain	STEP	0	0.0	7	100.0
	Déchets verts	107	100.0	0	0.0
	Décharge	66	93.0	5	7.0
	Autres	17	77.3	5	22.7
Mixte	Mixte	21	91.3	2	8.7

8.4 Discussion

8.4.1 Potentiel agronomique et énergétique des MOEx

La répartition des MOEx suivant le scénario agronomique et le scénario énergétique nous interpelle sur le fait que la valorisation des MOEx n'est pas limitée à un usage unique. C'est le cas pour les effluents d'élevage qui sont généralement valorisés par un retour au sol alors qu'ils pourraient être de bons substrats pour la méthanisation ou de la biomasse pour produire de la chaleur ou de l'électricité. En effet, les caractéristiques des MOEx leur confèrent différents potentiels que nous avons identifiés dans cette étude et qui méritent d'être documentés et approfondis en termes de mise en œuvre.

8.4.2 Orientation d'usage d'une MOEx donnée

Deux exemples sont considérés pour illustrer l'usage que pourrait avoir une MOEx donnée.

8.4.2.1 Exemple d'un fumier de bovin de Madagascar

Dans notre étude, un fumier de bovin collecté dans un centre de formation en agriculture et élevage sis à Bevalala, Madagascar est pris comme exemple. Ce fumier a un score A de 3 et un score E de 5 le prévalant pour une valorisation comme engrais organique ou bien pour une valorisation énergétique comme source de biogaz. Les données journalières sur les quantités de matière brute produites sur ce site sont en moyenne de 7 ± 3 kg/tête, avec les 12 génisses et 3 mâles, une production annuelle de 37800 ± 16200 kg de fumier. Pour cette exploitation, le fumier produit est stocké sous un hangar avant son épandage dans les rizières et/ou les

cultures maraîchères autour du centre. Pour la riziculture, cette quantité pourrait couvrir 4 ha à raison d'un apport de 10 t.ha^{-1} de fumier.

D'après notre classement, ce fumier a également un intéressant potentiel pour la production du biogaz : $180 \text{ Nm}^3 \text{CH}_4 \cdot \text{g}^{-1} \text{MO}$ soit $64,80 \text{ Nm}^3 \text{CH}_4 \cdot \text{g}^{-1} \text{MB}$. Annuellement, un potentiel de 2450 Nm^3 de CH_4 pourrait être produit sur ce site. Selon Moletta (2008), 1 m^3 de CH_4 serait équivalent à 9,7 kWh d'électricité ou encore 2,1 kg de bois. Donc théoriquement, les propriétaires de ce centre pourront avoir jusqu'à 24 MWh d'électricité ou l'équivalent de 430 kg de bois en optant pour la méthanisation de leur fumier.

Pour trancher sur la valorisation optimale de leur fumier, des questions sur la gestion de l'espace pour le stockage des fumiers, le coût des installations de digesteurs, la rentabilité économique, l'acceptation sociale, les aspects environnementaux sont à prendre en compte. Sur un territoire où les sols sont riches en matière organique, l'intérêt de la valorisation agronomique des fumiers est faible tandis que sur un territoire très enclavé la valorisation énergétique de ces derniers semble plus prégnante.

8.4.2.2 Exemple des déchets verts de la Réunion

Les déchets verts constituent d'importants gisements dans les plateformes réunionnaises. Un déchet vert issu du site du Port évalué par notre démarche ici a été coté à 5 en score agronomique et à 1 en score énergétique c'est-à-dire que ce déchet vert est potentiellement un amendement organique mais peut aussi alimenter une unité de génération de chaleur.

À la Réunion, 23500 t de broyats déchets verts sont acheminés à cette plate-forme chaque année (TCO, 2010). Les exploitants prévoient une valorisation de ces déchets par compostage avant leur vente en tant qu'amendements organiques pour les sols agricoles. Ceci confirme le résultat de notre scoring orientant l'usage de ces déchets verts comme amendements organiques. Environ 8000 t de compost pourrait être produit sur ce site et amender jusqu'à 270 ha de sols agricoles à raison de 30 t.ha^{-1} .

Toutefois, ces déchets verts présentent aussi un potentiel énergétique intéressant car ils ont en moyenne une énergie brute de $16,5 \pm 1,7 \text{ MJ.kg}^{-1}$. En tenant compte de la production annuelle de déchets verts et de cette valeur d'énergie brute, les déchets verts du Port pourraient fournir jusqu'à 108 GWh.an^{-1} équivalent aux besoins en électricité d'une ville de 72000 habitants.

Pour une meilleure orientation de ces déchets verts, d'une part les contraintes liées à la gestion de l'espace pour la plateforme de compostage et à l'homologation du compost fini sont à évoquer pour une valorisation agricole, et d'autre part, les opérations liées au séchage des déchets verts sont importantes pour la valorisation énergétique. En effet, comme signalé

par le TCO dans son rapport (TCO, 2010), la surface de la plateforme de compostage est limitée et ne peut stocker à terme qu'une quantité restreinte de compost. Quant à l'homologation du compost fini, elle fait écho à l'adéquation de ce compost aux normes des amendements organiques (AFNOR, 2006), notamment les métaux lourds. Au-delà de la faisabilité théorique, une évaluation de rentabilité socio-économique de chaque scénario est à prendre en compte pour prendre la décision finale.

8.5 Conclusion

Une typologie adaptée pour les MOEx collectées à Madagascar et à la Réunion permet d'avoir un outil pour orienter leur valorisation en tant que nouvel intrant agricole ou nouvelle source énergétique. N'ayant pas les données mesurées au laboratoire pour l'ensemble de notre base de données, la spectroscopie proche infrarouge nous a permis d'obtenir les informations relatives à la classification et à l'établissement des scores des MOEx. La visualisation de répartition des MOEx dans les différents scénarios permet d'apprécier *a priori* les potentiels agronomique et énergétique des MOEx d'origines diverses. Toutefois, les aspects économiques qui ne sont pas forcément les mêmes à La Réunion et à Madagascar compte tenu des coûts de l'énergie par exemple restent à prendre en compte dans cette balance pour une meilleure orientation d'usages.

Conclusion générale

La gestion des déchets organiques apparaît aujourd'hui comme une solution aux préoccupations du monde actuel sur les sujets de l'accroissement de la population et de la diminution des ressources alimentaires et énergétiques. Les déchets organiques, connues sous l'appellation de Matières Organiques Exogènes (MOEx) liées à différentes activités (élevage, agro-industrie, ville) sont de plus en plus considérés comme les « nouvelles ressources » de demain. Via leur valorisation agronomique, les MOEx constituent de « nouveaux intrants agricoles » pour la fertilisation et l'amendement des sols, mais, via également leur valorisation énergétique, les MOEx sont des « nouvelles biomasses » pour la génération de chaleur et d'électricité. Cependant, l'utilisation raisonnée des MOEx requiert une maîtrise de leurs caractéristiques intrinsèques et de leur devenir suivant la voie de valorisation considérée ainsi qu'une prise en compte de leurs impacts environnementaux (Chen *et al.*, 2008)

La problématique de la thèse a consisté à proposer un ensemble de méthodes pour aboutir à une typologie des MOEx afin d'orienter judicieusement leur valorisation agronomique et/ou énergétique.

L'objectif principal de la thèse était de (i) d'identifier les caractéristiques intrinsèques sur la base d'une méthode rapide et fiable, (ii) de déterminer des indicateurs pour évaluer la potentialité de l'usage d'une MOEx, ainsi que des indicateurs de du risque environnemental de l'usage potentiel (iii) d'intégrer l'ensemble ces informations pour établir une évaluation multicritère de leur valorisation.

Les travaux ont été basés sur une collection constituée de 2199 échantillons de MOEx collectés à Madagascar et à La Réunion MOEx.

Dans un premier temps, des analyses conventionnelles au laboratoire ont été réalisées sur une partie des échantillons. A partir de ces mesures et l'obtention d'un spectre PIR dans le même temps, des modèles de prédiction de ces caractéristiques ont été établies. Les principaux résultats étaient (i) de bonnes prédictions pour le carbone, l'azote organique, le phosphore, le potassium et la cellulose (ii) des prédictions approximatives pour les soluble, lignine, le magnésium et le zinc et (iii) des prédictions non valides pour l'hémicellulose, le calcium, le cuivre, le nickel, le chrome, le plomb et le cadmium. La SPIR comme méthode innovante peut être appliquée à notre démarche. Les caractéristiques chimiques et biochimiques des MOEx prédites par la SPIR ont servi par la suite à l'élaboration des critères pour l'orientation d'usages des MOEx. Les spectres PIR ont alors été acquis pour l'ensemble des MOEx de notre collection.

Ensuite, il a été proposé d'évaluer les potentiels « agronomiques » et « énergétiques » ainsi que les impacts environnementaux à travers des indicateurs spécifiques. Etant donné la lourdeur des expérimentations (mise en oeuvre, suivi, durée), tous les tests ont porté sur un ensemble représentatif de l'ensemble de notre base de données allant de 10 à 36 MOEx. Les objectifs étaient alors (i) de suivre les dynamiques de minéralisation du carbone et de l'azote des MOEx une fois apportée au sol, et (ii) de valider un modèle de transformation des MOEx : le modèle TAO (Transformation des Apports Organiques) pour prédire le comportement de l'ensemble des MOEx de notre base. 19 MOEx malgaches et 17 MOEx réunionnaises de différents types ont été sélectionnées et mises à incuber respectivement dans deux types de sols : 1 ferralsol de Madagascar, 1 cambisol de La Réunion. Les dynamiques de minéralisation de C et N sont dépendantes des caractéristiques intrinsèques des MOEx et non de leur origine car des effluents de même nature pouvaient avoir des transformations différentes une fois appliquée au sol. Nous avons montré que le modèle TAO défini par Thuriès *et al.* (2002) et Pansu *et al.* (2003), validé sur des MOEx d'Afrique de l'Ouest (Kaboré *et al.*, 2011) convient également pour la prédiction des comportements des MOEx tropicales. La capacité de la SPIR à prédire les deux compartiments du modèle TAO a été démontrée. Toutefois, le fait de faire une liaison entre les fractions biochimiques des MOEx et la taille des compartiments de TAO n'a pas été fructueux pour les MOEx étudiées. Une forte influence de la texture du sol est avancée pour expliquer cela car TAO a été élaboré sur des sols sableux contrairement à notre étude conduite sur des sols etc.

Pour le pouvoir calorifique des MOEx, notre étude a été articulée comme suit (i) tester douze modèles de prédictions de pouvoir calorifique de biomasses diverses de la bibliographie, (ii) développer de nouveaux modèles de prédictions de pouvoir calorifique à partir de leurs caractéristiques chimiques et biochimiques et (iii) développer de nouveaux modèles de prédictions de pouvoir calorifique à partir de leur réponse spectrale SPIR. Le principal résultat à retenir est que les meilleures prédictions ont été obtenues avec le modèle SPIR, en effet $SE_{PC} (NIRS) = 0.33 < SE (MLR-9) = 0.72 < SE_P (PC-7) = 0.83$. Pour les équations publiées, les précisions sont limitées car la nature des échantillons qui ont servi à établir ces modèles diffèrent des nôtres (Sheng *et al.*, 2005; Nhuchhen *et al.*, 2012). Pour les équations basées sur les caractéristiques chimiques et biochimiques des MOEx, les prédictions sont plus précises par rapport aux équations de la littérature mais elles ne sont vraiment exploitables que si les données de référence sont disponibles au préalable. En effet, l'acquisition des données de

référence reste toujours longue et onéreuse. Pour les équations basées sur les spectres SPIR, d'excellentes prédictions ont été enregistrées. Nos performances sont égales à celles rapportées par Bastianelli *et al.*, (2010) ou Smith *et al.*, (2001) pour les effluents de volaille et par Gillon *et al.*, (1999) pour les déchets verts. Nous avons conclu que les spectres et la composition chimique des MOEx apportent le même niveau d'informations pour la prédiction de pouvoir calorifique.

Pour le pouvoir méthanogène des MOEx, nous avons d'abord déterminé les BMP des MOEx avant d'élaborer une équation de prédiction par la SPIR. Les BMP des MOEx tropicales sont généralement plus faibles comparées à celles existantes dans la bibliographie. Par exemple pour les boues carnées de volaille, les BMP seraient comprises entre 550 et 670 NmlCH₄.g⁻¹MO selon Salminen *et al.*, (2000) et le BMP mesuré sur notre échantillon n'était que de 488 NmlCH₄.g⁻¹MO. De même pour les lisiers de porc, nous avons eu un BMP de 141 NmlCH₄.g⁻¹MO. en moyenne, alors que des valeurs entre 230 à 620 NmlCH₄.g⁻¹MO sont suggérées par Hejnfelt *et al.* (2009). Nos déterminations de BMP confirment qu'il n'y a pas d'intérêt à méthaniser des produits déjà compostés. Pour les prédictions SPIR, d'excellentes performances sont obtenues (RPD = 11, SE = 6,15 NmlCH₄.g⁻¹MO) et sont compatibles avec celles rapportées dans la littérature (Lesteur *et al.*, 2011; Doublet *et al.*, 2013). Toutefois, le modèle SPIR établi reste à optimiser au vu du nombre limité d'échantillons qui a servi à son étalonnage.

Quant aux impacts environnementaux que pourraient avoir les MOEx comme intrants agricoles, deux aspects (i) les émissions de N₂O et (ii) la phytotoxicité aux ETM des MOEx ont été évalués dans ce travail

A partir des 4 types de sol choisi pour cette expérimentation et des 34 MOEx considérées, les mesures d'activité dénitrifiante potentielle ont été obtenues. Ces résultats ont révélés (i) l'importance de l'« effet sol » sur les activités dénitrifiantes, (ii) l'« effet MOEx » significatif par rapport au témoin pour 25 sur les 34 MOEx étudiées et (iii) des émissions N₂O moins importantes pour les terreaux et les déchets verts par rapport aux autres types d'effluents. En effet, les émissions de N₂O seraient fonction du carbone facilement dégradable et des différentes formes de N (Burton *et al.*, 1985; Rice *et al.*, 1988) et que les substances facilement dégradables stimuleraient plus la dénitrification (Dambreville, 2007). Ces hypothèses n'ont pas pu être vérifiées dans notre étude dues aux caractéristiques « argileux » des sols d'incubation des MOEx qui adsorbent fortement leurs matières organiques, ainsi les

effets des MOEx sur la dénitrification sont masqués par les propriétés des sols (effet sol > effet MOEx).

Pour évaluer la phytotoxicité des ETM lors du recyclage agricole des MOEx, nous avons mis en relation la teneur en ETM des MOEx avec un critère mesurable sur la plante pour expliquer leur phytotoxicité. Le résultat le plus pertinent concerne le double effet de l'apport des MOEx sur les deux sols tropicaux étudiés, l'un ou l'autre en atténuant la rhizotoxicité vraisemblablement en raison de la toxicité aluminique dans les sols les plus acides (i.e. le cambisol) ou autrement en induisant la rhizotoxicité (dans les 2 sols). Les rhizotoxicités induites par les MOEx sont très variables entre elles. Cependant, les analyses de corrélation entre des paramètres de caractéristiques chimiques des MOEx et des solutions du sol avec l'élongation racinaire n'ont pas permis de mettre en évidence les processus contrôlant la présence de rhizotoxicité.

Pour terminer et intégrer l'ensemble des données acquises, il a été proposé une classification des MOEx par une évaluation multicritère de leur aptitude de valorisation. La méthode SIRIS (System of Integration of Risk with Interaction of Scores) (Vaillant *et al.*, 1995) a été choisie pour notre évaluation multicritère pour pallier aux problèmes de pondération des critères. Le classement des MOEx est fait essentiellement avec les données de référence prédites par la SPIR que ce soit pour les caractéristiques chimiques et biochimiques que pour les potentiels agronomiques et énergétiques des MOEx. Deux échelles de scores sont ensuite déterminées suivant une valorisation agronomique ou une valorisation énergétique des MOEx. Les résultats obtenus indiquaient que pour la plupart des MOEx, elles présentaient un indicateur non exclusif d'un usage. Il est donc clair que pour une valorisation optimale, outre les aspects scientifiques et théoriques, les aspects sociaux, économiques, agro-environnementaux doivent tenir également une place décisive dans la politique de gestion de la « seconde vie » des MOEx.

Ces travaux de thèse ont montré pour la première fois la faisabilité de l'évaluation multicritère utilisant la SPIR comme outil analytique d'un important panel de MOEx tropicales (>2000 MOEx) en vue d'orienter leur valorisation suivant un scénario agronomique et/ou énergétique. Toutefois, la méthodologie que nous avons adoptée accuse certaines limites qui méritent d'être repoussées dans le cadre de futurs travaux.

Parmi les limites imposées à la réalisation et à l'interprétation des résultats de nos travaux, nous pouvons citer :

- L'acquisition *a posteriori* des spectres de MOEx ne nous permettant pas l'identification au préalable des MOEx proches d'un point de vue spectrale (et chimiquement). En effet, dans la construction d'une base spectrale, il est essentiel d'avoir des spectres assez différents et une large gamme de valeurs au niveau des analyses de référence. Ceci permet d'avoir un étalonnage plus précis et plus robuste.
- La précision des modèles de prédiction qu'il convient encore d'affiner due au décalage entre le nombre d'analyses de référence et le nombre d'échantillons étudiés nous empêchant d'avoir une matrice carrée pour les étalonnages SPIR et la caractérisation des potentiels.
- Le facteur « sol » qui n'a pas été suffisamment pris en compte pourtant ce facteur « sol » masquait certains effets de la MOEx ajoutée notamment sur les émissions de N₂O et la mobilité des ETM
- L'absence d'analyses économique et sociale des scénarios de valorisation proposés nous réservant de trancher sur l'orientation d'usage optimale d'une MOEx donnée.
- Le développement d'indicateurs plus précis permettant de quantifier la potentialité d'une MOEx par rapport à un usage. On peut citer la notion d'équivalent en azote, pour sa valeur fertilisante, ou bien l'équivalent en kWh produit pour sa valeur énergétique

Ainsi, dans le cadre de futures investigations et de la suite de nos recherches, il serait intéressant de :

- Innover les procédures d'analyses de laboratoire par l'utilisation de la SPIR pour les analyses de routine ;
- Effectuer des modélisations de « comportement » de couples « Sol-MOEx » par la SPIR notamment dans le suivi de la minéralisation du C et du N des MOEx apportées au sol, la prédiction des émissions de N₂O, ... ;
- Conduire une évaluation environnementale qui tient compte des coûts/bénéfices liés à la meilleure valorisation des MOEx tropicales.

Références bibliographiques

- Aduraa (2007). Atelier de restitution du projet ADURAA : Analyse de la durabilité de l'agriculture dans l'Agglomération d'Antananarivo.
- AFNOR (1981). Engrais - Dénominations et spécifications. NF U 42-001.
- AFNOR (2006). Amendements organiques-Dénominations, spécifications et marquage. Organic soil improvers - Designation, specification and marking Paris, France, AFNOR NF U 44-051.
- AFNOR (2009). Amendements organiques et supports de culture. Caractérisation de la matière organique par la minéralisation potentielle du carbone et de l'azote. Paris, AFNOR. XP U 44-163.
- AFNOR (2009). Amendements organiques et supports de culture - Fractionnement biochimique et estimation de la stabilité biologique. Soil improvers and growing media - Characterization of organic matter by biochemical fractioning and estimation of its biological stability. Paris, France, AFNOR XPU 44-162.
- AFNOR (2011). Guide d'interprétation pour les méthodes de caractérisation de la matière organique des amendements organiques (XP U 44-162 et XP U 44-163). GA U 44-168. France, AFNOR: 20.
- Aiken, G. E., D. H. Pote, S. F. Tabler and T. C. Tabler (2005). "Application of Near-Infrared Reflectance Spectroscopy to Estimate Chemical Constituents in Broiler Litter." *Communications in Soil Science and Plant Analysis* 36(17-18): 2529-2539.
- Akaike, H. (1973). Information theory and an extension of the maximum likelihood principle. Second international symposium on information theory. B. N. Petrov and F. Csaki. Budapest, *Academiai Kiado*: 267-281.
- Albrecht, R., R. Joffre, R. Gros, J. le Petit, G. Terrom and C. Périsol (2008). "Efficiency of near-infrared reflectance spectroscopy to assess and predict the stage of transformation of organic matter in the composting process." *Bioresource Technology* 99: 448-455.
- Albrecht, R., R. Joffre, J. Le Petit, G. Terrom and C. Perissol (2009). "Calibration of chemical and biological changes in cocomposting of biowastes using near-infrared spectroscopy." *Environmental Science Technology* 43: 804-811.
- Ambus, P., L. K. Kure and E. S. Jensen (2002). "Gross N transformation rates after application of household compost or domestic sewage sludge to agricultural soil." *Agronomie* 22: 723-730.
- Anderson, I. C., M. Poth, J. Homstead and D. Burdige (1993). "A comparison of NO and N₂O production by the autotrophic nitrifier *Nitrosomonas europaea* and the heterotrophic nitrifier *Alcaligenes faecalis*." *Applied and Environmental Microbiology* 59: 3525-3533.
- Angelidaki, I., M. Alves, D. Bolzonella, L. Borzacconi, J. L. Campos, A. J. Guwy, S. Kalyuzhnyi, P. Jenicek and J. B. van Lier (2009). "Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays." *Water Science and Technology* 59(5): 927-934.
- Angelidaki, I. and W. Sanders (2004). "Assessment of the anaerobic biodegradability of macropollutants." *Rev Environ Sci Biotechnol* 3: 117-29.
- Angers, D. A. and S. Recous (1997). "Decomposition of wheat straw and rye residues as affected by particle size." *Plant and Soil* 189(2): 197-203.
- Angers, D. A., S. Recous and C. Aita (1997). "Fate of carbon and nitrogen in water-stable aggregates during decomposition of (CN)-C-13-N-15-labelled wheat straw in situ." *European Journal of Soil Science* 48(2): 295-300.
- ARER (2013). "La méthanisation par voie sèche." from <<http://www.arer.org/La-methanisation-en-voie-seche.html?espace=Monde%20agricole>>.
- ATEE (1998). "Biogaz: Les voies de valorisation." *Energie plus*. 213: 7p.
- Baggs, E. M. (2011). "Soil microbial sources of nitrous oxide: recent advances in knowledge, emerging challenges and future direction." *Current Opinion in Environmental Sustainability* 3: 321-327.

- Baggs, E. M., R. M. Rees, K. A. Smith and A. J. A. Vinten (2000). "Nitrous oxide emission from soils after incorporating crop residues." *Soil Use Management* 16: 82-87.
- Balderston, W. L., B. Sherr and W. J. Payne (1976). "Blockage by acetylene of nitrous oxide reduction in *Pseudomonas perfectomarinus*." *Applied and Environmental Microbiology* 31: 504 - 508.
- Balesdent, J., C. Chenu and M. Balabane (2000). "Relationship of soil organic matter dynamics to physical protection and tillage." *Soil & Tillage Research* 53(3-4): 215-230.
- Barber, A. A. (1984). *Soil Nutrient Bioavailability*. John Wiley, New York.
- Barnes, R. J., M. S. Dhanoa and S. J. Lister (1989). "Standard normal variate transformation and detrending of near-infrared diffuse reflectance spectra." *Applied Spectroscopy* 43: 772-777.
- Barthès, B. G., D. Bruneta, A. Braumana, N. Fromin, R. Lensi, A. Volanta, J.-P. Laclau, D. Blaveta and L. Chapuis-Lardy (2010). "Determination of potential denitrification in a range of tropical topsoils using near infrared reflectance spectroscopy (NIRS)." *Applied Soil Energy* 46: 81-89.
- Bastianelli, D., L. Bonnal, H. Juin, S. Mignon-Grasteau, F. Davrieux and B. Carr (2010). "Prediction of the chemical composition of poultry excreta by near infrared spectroscopy." *Journal of Near Infrared Spectroscopy* 18(1): 69-77.
- Baudoin, E., L. Philippot, D. Chèneby, L. Chapuis-Lardy, N. Fromin, D. Bru, B. Rabary and A. Brauman (2009). "Direct seeding mulch-based cropping increases both the activity and the abundance of denitrifier communities in a tropical soil." *Science Biology and Biochemistry* 41: 1703-1709.
- Beauchamp, E. G. (1997). "Nitrous oxide emission from agricultural soils." *Canadian Journal of Soil Science* 77(113-123).
- Bellehumeur, C., L. Vasseur, C. Anseau and B. Marcos (1997). "Implementation of a Multicriteria Sewage Sludge Management Model in the Southern Québec Municipality of Lac-Mégantic, Canada." *Journal of Environmental Management* 50(1): 51-66.
- Bellon-Maurel, V., E. Fernandez-Ahumada, B. Palagos, J.-M. Roger and A. McBratney (2010). "Critical review of chemometric indicators commonly used for assessing the quality of the prediction of soil attributes by NIR spectroscopy." *Trends in Analytical Chemistry* 29(9): 1073-1081.
- Ben Mena, S. (2000). "Introduction aux méthodes multicritères d'aide à la décision." *Biotechnologie, agronomie, Société et Environnement* 4(2): 83-93.
- Beraud, J., P. Fine, U. Yermiyahu, M. Keinan, R. Rosenberg, A. Hadas and A. Bar-Tal (2005). "Modeling carbon and nitrogen uptake by wheat." *Journal of Environmental Quality* 34: 664-675.
- Bernal, M. P., J. A. Albuquerque and R. Moral (2009). "Composting of animal manures and chemical criteria for compost maturity assessment. A review." *Bioresource Technology* 100(22): 5444-5453.
- Bernal, M. P., C. Paredes, M. A. Sanchez-Monedero and J. Cegarra (1998). "Maturity and stability parameters of composts prepared with a wide range of organic wastes." *Bioresource Technology* 63(1): 91-99.
- Bernard, M. E. (2011). *Nitrous oxide emissions and denitrification potential of fertilized grassland soils in western Norway*. McGill, McGill University. Master of Science: 149.
- Berthe, C., E. Redon and G. Feuillade (2008). "Fractionation of the organic matter contained in leachate resulting from two modes of landfilling: An indicator of waste degradation." *J. Hazard. Mater.* 154: 262-271.
- Bijay-Singh, J. C. Ryden and D. C. Whitehead (1988). "Some relationships between denitrification potential and fractions of organic carbon in air-dried and field-moist soils." *Soil Biol Biochem* 20: 737-741.
- Blackmer, A. M. and J. M. Bremner (1978). "Inhibitory effect of nitrate on reduction of N₂O to N₂ by soil microorganisms." *Soil Biology and Biochemistry* 10: 187-191.

- Blanchard, C. (2000). Caractérisation de la mobilisation potentielle des polluants inorganiques dans les sols pollués. Ecole doctorale de chimie de Lyon. Lyon. doctorat: 241p.
- Bonneau, M., F. Beline, J. Y. Dourmad, M. Hassouna, C. Jondreville, L. Loyon, T. Morvan, J. M. Paillat, Y. Ramonet and P. Robin (2008). "Elements of waste from pigs : knowledge and control." *Productions Animales* 21(4): 325-343.
- Brady, N. C. and R. R. Weil (1999). *The nature and properties of soils*. New Jersey, Prentice Hall.
- Bravin, M. N. (2008). Processus Rhizosphériques déterminant la biodisponibilité du cuivre pour le blé dur cultivé en sols à antécédent viticole. *Systèmes Intégrés en Biologie, Agronomie, Géosciences, Hydrosociences et Environnement*. Montpellier, Centre Internationale d'études supérieures en sciences agronomiques. Doctorat: 210.
- Brock, E. H., Q. M. Ketterings and M. McBride (2006). "Copper and zinc accumulation in poultry and dairy manure-amended fields." *Soil Science* 171(5): 388-399.
- Brunet, D., B. G. Barthès, J. L. Chotte and C. Feller (2007). "Determination of carbon and nitrogen contents in Alfisols, Oxisols and Ultisols from Africa and Brazil using NIRS analysis: effects of sample grinding and set heterogeneity." *Geoderma* 139: 106-117.
- Bruun, S., J. Luxhøi, J. Magid, A. D. Neergaard and L. S. Jensen (2006). "A nitrogen mineralization model based on relationships for gross mineralization and immobilization." *Soil Biology and Biochemistry* 38: 2712-2721.
- Bruun, S., B. Stenberg, T. A. Breland, J. Gudmundsson, T. M. Henriksen, L. S. Jensen, A. Korsæth, J. Luxhøi, F. Palmason, A. Pedersen and T. Salo (2005). "Empirical predictions of plant material C and N mineralization patterns from near infrared spectroscopy, stepwise chemical digestion and C/N ratios." *Soil Biology and Biochemistry* 37(12): 2283-2296.
- Buffière, P., D. Loisel, N. Bernet and J. P. Delgenes (2006). "Towards new indicators for the prediction of solid waste anaerobic digestion properties." *Water Science Technology* 53: 233-41.
- Bujoczek, G., J. Oleszkiewicz, R. Sparling and S. Cenkowski (2000). "High Solid Anaerobic Digestion of Chicken Manure." *Journal of Agricultural Engineering Research* 76(1): 51-60.
- Burford, J. and J. M. Bremner (1975). "Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter." *Soil Biol. Biochem.* 7: 389-394.
- Burton, D. L. and E. G. Beauchamp (1985). "Denitrification rate relationships with soil parameters in the field." *Commun. SoilSci. Plant Anal.* 16: 539-549.
- Cadish, G. and K. E. Giller (1997). *Driven by Nature*. Wallingford, UK, CAB International.
- Calbrix, R. (2005). Impacts des intrants organiques et des conduites culturales sur la biomasse microbienne et la diversité des bactéries telluriques. Université de Rouen. Rouen. Doctorat: 167 p.
- Callejón-Ferre, A. J., B. Velázquez-Martí, J. A. López-Maerinez and M.-A. F. (2011). "Greenhouse crop residues: energy potential and models for the prediction of their higher heating value." *Renewable and Sustainable Energy Reviews* 15: 948-955.
- Campbell, N. A., J. B. Reece and R. Mathieu, Eds. (2006). *Biologie*. Louvain-la-Neuve.
- Cavigelli, M. A. and G. P. Robertson (2001). "Role of denitrifier diversity in rates of nitrous oxide consumption in a terrestrial ecosystem." *Soil Biology and Biochemistry* 33(3): 297-310.
- Cécillon, L. and J. J. Brun (2007). Near-infrared reflectance spectroscopy (NIRS): a practical tool for the assessment of soil carbon and nitrogen budget. COST Action 639: Greenhouse-gas Budget of Soils Under Changing Climate and Land Use (BurnOut). R. Jandl and M. Olsson. Vienna, Federal Research and Training Centre for Forests, Natural Hazards and Landscape. 103-110.
- Cécillon, L., N. Cassagne, S. Czarnes, R. Gros and J.-J. Brun (2008). "Variable selection in near infrared spectra for the biological characterization of soil and earthworm casts." *Soil Biology and Biochemistry* 40(7): 1975-1979.

- Cécillon, L., N. Cassagne, S. Czarnes, R. Gros and J. J. Brun (2008). "Variable selection in near infrared spectra for the biological characterization of soil and earthworm casts." *Soil Biol. Biochem.* 40: 1975-1979.
- Chabalier, P., V. V. d. Kerchove and H. S. Macary (2006). *Guide de la fertilisation organique à La Réunion*, CIRAD Montpellier
- Chadwick, D. R., B. F. Pain and S. K. E. Brookman (2000). "Nitrous oxide and methane emissions following application of animal manures to grassland." *Journal of Environmental Quality* 29(1): 277-287.
- Chalk, P. M. and C. J. Smith (1983). *Chemodenitrification. Gaseous Loss of Nitrogen from Plant-Soil Systems. Developments in Plant and Soil Sciences.* J. R. Freney and J. R. Simpson. 9: 65-89.
- Chang, C. W., D. A. Laird, M. J. Mausbard and C. J. R. Hurburgh (2001). "Near-infrared reflectance spectroscopy - principal components regression analyses of soil properties." *Soil Sci. Soc. Am. J.* 65: 480.
- Chapuis-Lardy, L., A. Metay, M. Martinet, M. Rabenarivo, J. Toucet, J. M. Douzet, T. Razafimbelo, L. Rabeharisoa and J. Rakotoarisoa (2009). "Nitrous oxide fluxes from Malagasy agricultural soils." *Geoderma* 148: 421-427.
- Charest, M. H. and C. J. Beauchamp (2002). "Composting of de-inking paper sludge with poultry manure at three nitrogen levels using mechanical turning: behavior of physico-chemical parameters." *Bioresource Technology* 81(1): 7-17.
- Chaves Daguiar, B. (2006). *Manipulating nitrogen release from vegetable crop residues by use on- and off-farm organic wastes. Applied Biological Sciences: Land Management and Forestry Ghent University PhD*: 232.
- Chen, L., L. Xing and L. Han (2008). "Rapid evaluation of poultry manure content using artificial neural networks (ANNs) method." *Biosystems Engineering* 101(3): 341-350.
- Chen, T.-H. and A. G. Hashimoto (1996). "Effects of pH and substrate:inoculum ratio on batch methane fermentation." *Bioresour Technol* 56: 179-186.
- Chen, Y., J. J. Cheng and K. S. Creamer (2008). "Inhibition of anaerobic digestion process: a review." *Bioresour Technol* 99: 4044-4064.
- Christensen, S. r. (1985). "Denitrification in an acid soil: effects of slurry and potassium nitrate on the evolution of nitrous oxide and on nitrate-reducing bacteria." *Soil Biology and Biochemistry* 17(6): 757-764.
- Chronakova, A., V. Radl, J. Cuhel, M. Simek, D. Elhottova, M. Engel and M. Schlöter (2009). "Overwintering management on upland pasture causes shifts in an abundance of denitrifying microbial communities, their activity and N₂O-reducing ability." *Soil Biology and Biochemistry* 41(6): 1132-1138.
- CIRAD (2007). *La spectroscopie dans le proche infrarouge. Laboratoire d'alimentation animale.* CIRAD. Montpellier.
- Clapp, C. E., M. H. B. Hayes and C. Ciavatta (2007). "Organic wastes in soils: Biogeochemical and environmental aspects." *Soil Biology and Biochemistry* 39(6): 1239-1243.
- Clark, D. H., M. H. Ralphs and R. C. Lamb (1987). "Total alkaloid determinations in larkspur and lupine with near-infrared reflectance spectroscopy." *Agronomy Journal* 79: 481-485.
- Clark, D. H., M. H. Ralphs and R. C. Lamb (1987). "Total alkaloid determinations in larkspur and lupine with near infrared reflectance spectroscopy." *Agron. J.* 79: 481-485.
- Cohen, M. J., J. P. Prenger and W. F. DeBusk (2005). "Visible-Near infrared reflectance spectroscopy for rapid, non-destructive assessment of wetland soil quality." *Journal of Environmental Quality* 34: 1422-1434.
- Constantinides, M. and J. H. Fownes (1994). "Nitrogen mineralization from leaves and litter of tropical plants - Relationship to nitrogen, lignin and soluble polyphenol concentrations." *Soil Biology & Biochemistry* 26(1): 49-55.

- Corbeels, M., A. M. O'Connell, T. S. Grove, D. S. Mendham and S. J. Rance (2003). "Nitrogen release from eucalypt leaves and legume residues as influenced by their biochemical quality and degree of contact with soil." *Plant and Soil* 250: 15-28.
- Cordero, T., F. Marquez, J. Rodriguez-Mirasol and J. Rodriguez (2001). "Predicting heating values of lignocellulosics and carbonaceous materials from proximate analysis." *Fuel* 80(11): 1567-1571.
- Counil, J. (2011). Développement à court et moyen terme de la filière biomasse énergie à la Réunion. www.arer.org. St Pierre, ARER-Agence Régionale Energie Réunion: 102.
- Critto, A., S. Torresan, E. Semenzin, S. Giove, M. Mesman, A. J. Schouten, M. Rutgers and A. Marcomini (2007). "Development of a site-specific ecological risk assessment for contaminated sites: Part I. a multi-criteria based system for the selection of ecotoxicological tests and ecological observations." *Science of Total Environment* 379: 16-33.
- D'Haene, K., E. Moreels, S. De Neve, B. Chaves Daguiar, P. Boeckx, G. Hofman and O. Van Cleemput (2003). "Soil properties influencing the denitrification potential of Flemish agricultural soils." *Biology & Fertility of Soils* 38: 358-366.
- Dambreville, C. (2007). Dénitrification et emission de N₂O par des sols soumis à une fertilisation organique ou minérale-Cas des effluents porcins, Université de Bourgogne. PhD: 144.
- Dambreville, C., S. Hallet, C. Nguyen, T. Morvan, J.-C. Germon and L. Philippot (2006). "Structure and activity of the denitrifying community in a maize-cropped field fertilized with composted pig manure or ammonium nitrate." *FEMS Microbiol Ecol* 56: 119-31.
- Dambreville, C., C. Hénault, L. Philippot, F. Bizouard, R. Chaussod, T. Morvan and J. C. Germon (2004). "Effets comparés des apports de lisier de porc et d'une fertilisation minérale sur le fonctionnement de la dénitrification dans un sol. Impact sur la réduction de N₂O." *Journées Recherche Porcine* 36: 97-104.
- Darwis, S. (1993). Effet des modalités de gestion de la paille de blé sur l'évolution du carbone et de l'azote au cours de sa décomposition dans le sol. Institut National Agronomique Paris-Grignon. Doctorat: 167 p.
- De Gioannis, G., E. Massi, A. Moreno, A. Muntoni, A. Pollettini and R. Pomi (2007). Hydrogen production through anaerobic digestion of different solid and liquid waste : Batch and semi-continuous tests. 11th International Waste Management and Landfill Symposium. Sardinia.
- Demirbas, A. (2009). "Political, economic and environmental impacts of biofuels: A review." *Applied Energy* 86, Supplement 1(0): S108-S117.
- Demirbas, A. and A. H. Demirbas (2004). "Estimating the calorific values of lignocellulosic fuels." *Energy Exploration and Exploitation* 22(2): 135-143.
- Dendooven, L., E. Bonhomme, R. Merckx and K. Vlassak (1998). "Injection of pig slurry and its effects on dynamics of nitrogen and carbon in a loamy soil under laboratory conditions." *Biology and Fertility of Soils* 27(1): 5-8.
- Dendooven, L., E. Bonhomme, R. Merckx and K. Vlassak (1998). "N dynamics and sources of N₂O production following pig slurry application to a loamy soil. ." *Biology and fertility of soils* 26(3).
- Dendooven, L., P. Splatt and J. Anderson (1996). "Denitrification in permanent pasture soil as affected by different forms of C substrate." *Soil Biol Biochem* 28: 141-9.
- Derenne, S. and C. Largeau (2001). "A review of some important families of refractory macromolecules:composition, origin, and fate in soils and sediments." *Soil Science* 166(11): 833-847.
- Diaz-Barrientos, E., L. Madrid, C. Maqueda, E. Morillo, E. Ruiz-Cortes, E. Basallote and M. Carrillo (2003). "Copper and zinc retention by an organically amended soil." *Chemosphere* 50(7): 911-917.
- Dinçer, A. R. and F. Kargi (2000). "Kinetics of sequential nitrification and denitrification processes." *Enzyme and Microbial Technology* 27(1-2): 37-42.

- Direction de l'Environnement de l'Aménagement et du Logement (2012). Etude sur la caractérisation des filières de la croissance verte à La Réunion. St Denis.
- Dobbie, K. E. and K. A. Smith (2003). "Impact of different forms of N fertilizer on N₂O emissions from intensive grassland." *Nutr Cycl Agroecosyst* 67: 37-46.
- Doelsch, E., B. Deroche and V. Van de Kerchove (2006). "Impact of sewage sludge spreading on heavy metal speciation in tropical soils (Reunion Island)." *Chemosphere* 65(2): 286-293.
- Doelsch, E., A. Masion, P. Cazevielle and N. Condom (2009). "Spectroscopic characterization of organic matter of a soil and vinasse mixture during aerobic or anaerobic incubation." *Waste Management* 29(6): 1929-1935.
- Doelsch, E., A. Masion, G. Moussard, C. Chevassus-Rosset and O. Wojciechowicz (2010). "Impact of pig slurry and green waste compost application on heavy metal exchangeable fractions in tropical soils." *Geoderma* 155(3-4): 390-400.
- Doelsch, E., G. Moussard and H. Saint-Macary (2008). "Fractionation of tropical soilborne heavy metals - Comparison of two sequential extraction procedures." *Geoderma* 143(1-2): 168-179.
- Doelsch, E., N. Payet, V. Van de Kerchove and G. Moussard (2008). Composts de déchets verts urbains réunionnais: origine des concentrations élevées en Eléments Traces Métalliques (ETM). Saint-Denis, La Réunion, CIRAD & MVAD: 26.
- Doelsch, E., H. Saint Macary and V. Van de Kerchove (2006). "Sources of very high heavy metal content in soils of volcanic island (La Reunion)." *Journal of Geochemical Exploration* 88(1-3): 194-197.
- Douard, F. (2010). "Etat de la filière biogaz à la Réunion." from <http://www.bioenergie-promotion.fr/5306/etat-de-la-filiere-biogaz-a-la-reunion/>.
- Doublet, J., A. Boulanger, A. Ponthieux, C. Laroche, M. Poitrenaud and J. A. Cacho Rivero (2013). "Predicting the Biochemical Methane Potential of wide range of organic substrates by Near Infrared Spectroscopy." *Bioresource Technology* 128: 252-258.
- Ebeling, J. M. and B. M. Jenkins (1985). "Physical and chemical properties of biomass." *Transactions of the American Society of Agricultural Engineers* 28: 898-902.
- Eckard, R., C. Grainger and C. de Klein (2010). "Options for the abatement of methane and nitrous oxide from ruminant production: A review." *Livest Sci* 130: 47-56.
- Enwall, K., L. Philippot and S. Hallin (2005). "Activity and composition of the denitrifying bacterial community respond differently to long-term fertilization." *Appl. Environ. Microbiol.* 71: 8335-8343.
- Erol, M., H. Haykiri-Acma and S. Küçükbayrak (2010). "Calorific value estimation of biomass from their proximate analyses data." *Renewable Energy* 35(1): 170-173.
- Esposito, G., L. Frunzo, A. Giordana, F. Liotta, A. Panico and F. Pirozzi (2012). "Anaerobic co-digestion of organic wastes." *Rev Environ Sci Biotechnol* 11(4): 325-341.
- European Commission (2003). Commission Regulation (EC) no. 1334/2003 of 25 July 2003 amending the conditions for authorisation of a number of additives in feedingstuffs belonging to the group of trace elements. O. J. E. C. L187:11.
- Everard, C. D., K. P. McDonnell and C. C. Fagan (2012). "Prediction of biomass gross calorific values using visible and near infrared spectroscopy." *Biomass and Bioenergy* 45: 203-211.
- Falinirina, M. V. (2010). Valorisation agricole des apports organiques contenus dans les déchets urbains: qualité des matières organiques et service écosystémique. Ecole Supérieure des Sciences Agronomiques d'Antananarivo. Antananarivo, Université d'Antananarivo. Doctorat: 192.
- Firestone, M. K., R. B. Firestone and J. M. Tiedje (1980). "Nitrous oxide from soil denitrification: factors controlling its biological production." *Science* 208: 749-751.
- Flessa, H. and F. Beese (2000). "Laboratory estimates of trace gas emissions following surface application and injection of cattle slurry." *Journal of Environmental Quality* 29(1): 262-268.

- Foley, W. J., A. McIlwee, I. R. Lawler, L. Aragonés, A. Woolnough and N. Berding (1998). "Ecological applications of near-infrared spectroscopy - a tool for rapid, cost effective prediction of the composition of plant and animal tissues and aspects of animal performance." *Oecologia* 116: 293-305.
- Fontaine, S. b., A. Mariotti and L. Abbadie (2003). "The priming effect of organic matter: a question of microbial competition?" *Soil Biology and Biochemistry* 35(6): 837-843.
- Francou, C., M. Linères, S. Derenne, M. L. Villio-Poitrenaud and S. Houot (2008). "Influence of green waste, biowaste and paper-cardboard initial ratios on organic matter transformations during composting." *Bioresource Technology* 99(18): 8926-8934.
- Frankenberger, W. T. and H. M. Abdelmagid (1985). "Kinetic parameters of nitrogen mineralisation rates of leguminous crops incorporated into soil." *Plant and Soil* 87: 257-271.
- Fruit, L., S. Recous and G. Richard (1999). Plant residue decomposition : effect of soil porosity and particle size. *Effect of Mineral-Organic-Microorganism Interactions on Soil and Freshwater Environments*. J. e. a. Berthelin: 189-196.
- Galvez-Sola, L., J. Morales, A. M. Mayoral, F. C. Marhuenda-Egea, E. Martinez-Sabater, M. D. Perez-Murcia, M. A. Bustamante, C. Paredes and R. Moral (2010). "Estimation of phosphorus content and dynamics during composting: Use of near infrared spectroscopy." *Chemosphere* 78(1): 13-21.
- Geladi, P. and B. R. Kowalski (1986). "Partial least-squares regression - a tutorial." *Analytica Chimica Acta* 185: 1-17.
- Geladi, P., D. McDougall and H. Martens (1985). "Linearization and scatter correction for Near infrared reflectance spectra of meat." *Applied Spectroscopy* 39: 491-500.
- Ghysel, F., B. Godin, C. Flamin, P. Delfosse, J. Delcarte and D. Stilmant (2010). Valorisation énergétique des fourrages : Comparaison de trois filières, enjeux et opportunités. *Journées AFPP- Les usages émergents des prairies et des fourrages* 15.
- Gillon, D., C. Hernando, J.-C. Valette and R. Joffre (1997). "Fast estimation of the calorific values of forest fuels by near-infrared reflectance spectroscopy." *Canadian Journal of Forest Research* 27: 760-765.
- Gillon, D., C. Houssard and R. Joffre (1999). "Using near-infrared reflectance spectroscopy to predict carbon, nitrogen and phosphorus content in heterogeneous plant material." *Oecologia* 118: 173-182.
- Gillon, D., R. Joffre and A. Ibrahima (1999). "Can litter decomposability be predicted by near infrared reflectance spectroscopy?" *Ecology* 80(1): 175-186.
- Gobat, J.-M., M. Aragno and W. Matthey, Eds. (2003). *Le Sol vivant. Bases de pédologie, biologie des sols*. Lausanne.
- Groffman, P. M., M. A. Altabet, J. K. Böhlke, K. Butterbach-Bahl and M. B. David (2006). "Methods for measuring denitrification: Diverse approaches to a difficult problem." *Ecological Applications* 16: 2091-2122.
- Groffman, P. M., E. Holland, D. D. Myrold, G. P. Robertson and X. Zou (1999). Denitrification. *Standard soil methods for long term ecological research*. G. P. Robertson, C. S. Bledsoe, D. C. Coleman and P. Sollins. New York, Oxford University Press.
- Guerroud, N., F. Ouadjnia, F. Abdelmalek, F. Taleb and A. addou (2009). "Municipal solid waste in Mostaganem city (Western Algeria)." *Waste Management* 29(2): 896-902.
- Halgerson, J. L., C. C. Sheaffer, N. P. Martin, P. R. Peterson and S. J. Weston (2004). "Near-Infrared Reflectance Spectroscopy Prediction of Leaf and Mineral Concentrations in Alfalfa Joint contribution of the Minnesota Agric. Exp. Stn. and USDA-ARS." *Agron. J.* 96(2): 344-351.
- Hansen, T. L., J. E. Schmidt, I. Angelidaki, E. Marca, J. I. C. Jansen, H. Mosbæk and T. H. Christensen (2004). "Method for determination of methane potentials of solid organic waste." *Waste Management* 24(4): 393-400.

- Hao, X., C. Chang, G. R. Travis and F. Zhang (2003). "Soil carbon and nitrogen response to 25 annual cattle manure applications." *Journal of Plant Nutrition and Soil Science* 166: 239-245.
- Harter, R. D. and R. Naidu (1995). "Role of metal-organic complexation in metal sorption by soils." *Adv. Agron.* 55(219-263).
- Heal, O. W., J. M. Anderson and M. J. Swift (1997). Plant litter quality and decomposition: an historical overview,. Driven by nature: plant litter quality and decomposition. G. Cadisch and K. E. Giller. Wallingford, UK, CAB International: 3-30.
- Hejnfelt, A. and I. Angelidaki (2009). " Anaerobic digestion of slaughterhouse by-products." *Biomass and Bioenergy* 33(8): 1046-54.
- Henriksen, T. M. and T. A. Breland (1999). "Evaluation of criteria for describing crop residue degradability in a model of carbon and nitrogen turnover in soil." *Soil Biology and Biochemistry* 31(8): 1135-1149.
- Henriksen, T. M. and T. A. Breland (1999). "Nitrogen availability effects on carbon mineralization, fungal and bacterial growth, and enzyme activities during decomposition of wheat straw in soil." *Soil Biology and Biochemistry* 31(8): 1121-1134.
- Henriksen, T. M., A. Korsæth, T. A. Breland, B. Stenberg, L. S. Jensen, S. Bruun, J. Gudmundsson, F. Palmason, A. Pedersen and T. J. Salo (2007). "Stepwise chemical digestion, near-infrared spectroscopy or total N measurement to take account of decomposability of plant C and N in a mechanistic model." *Soil Biology and Biochemistry* 39: 3115-3126.
- Hermans, C., J. Erickson, T. Noordewier, A. Sheldon and M. Kline (2007). "Collaborative environmental planning in river management: An application of multicriteria decision analysis in the White River Watershed in Vermont." *J Environ Manag* 84: 534-546.
- Hill, A. R. and M. Cardaci (2004). "Denitrification and organic carbon availability in riparian wetland soils and subsurface sediments." *Soil Sci Soc Am J* 68: 320-325.
- Houghton, J. T., Y. Ding, D. J. Griggs, M. Noguer, P. J. Van der Linden, X. Dai, K. Maskell and C. A. Johnson (2001). *Climate change 2001: the scientific basis*, IPCC working group I.
- Houot, S., D. Clergeot, J. Michelin, C. Francou, S. Bourgeois and G. Caria (2002). *Agronomic value and environmental impacts of urban composts used in agriculture. Microbiology of Composting*. H. Insam, N. Riddech and S. Klammer. Berlin Heidelberg, Springer-Verlag: 457-472.
- Houot, S., H. Muller, C. Chenu, M. Linères, B. Nicolardot, V. Parnaudeau, D. Arrouays, J. Balesdent, B. Leclerc, J. Mellet, M. Kalassy, M. Poitrenaud and N. Pierre (2004). *Bilans environnementaux de la gestion biologique des déchets : Effet sur le sol et le stockage du carbone des apports de matières organiques issues de déchets. Rapport final provisoire du marché ADEME n° 0375C0062*, ADEME, Angers, France: 190.
- Huang, C., L. Han, Z. Yang and X. Liu (2009). "Ultimate analysis and heating value prediction of straw by near infrared spectroscopy." *Waste Management* 29 1793–1797.
- Huang, C. J., L. J. Han, X. Liu and Z. Yang (2008). "Models predicting calorific value of straw from ash content." *International Journal of Green Energy* 5: 533-539.
- Huang, G., L. Han and X. Liu (2007). "Rapid estimation of the composition of animal manure compost by near infrared reflectance spectroscopy." *Journal of Near Infrared Spectroscopy* 15: 387-394.
- Huang, G., L. Han, Z. Yang and X. Wang (2008). "Evaluation of the nutrient metal content in Chinese animal manure compost using near infrared spectroscopy (NIRS)." *Bioresource Technology* 99(17): 8164-8169.
- Image J (2012, August 14, 2012). "ImageJ.". from <http://rsbweb.nih.gov/ij/download.html>.
- ISO 11269-1 (2012). *Soil quality - Determination of the effects of pollutants on soil flora Part 1: Method for the measurement of inhibition of root growth*.
- ISO/DIS 11269-1 (2010). *Soil quality - Determination of the effects of pollutants on soil flora - Part 1: Method for the measurement of inhibition of root growth*.

- Jacobi, H. F., C. R. Moschner and E. Hartung (2011). "Use of near infrared spectroscopy in monitoring of feeding substrate quality in anaerobic digestion." *Bioresource Technol.* 102: 4688-4696.
- Jäger, N., C. F. Stange, B. Ludwig and H. Flessa (2011). "Emission rates of N₂O and CO₂ from soils with different organic matter content from three long-term fertilization experiments-a laboratory study." *Biology and Fertility of Soils* 47: 483-494.
- Jiménez, L. and F. Gonzalez (1991). "Study of the physical and chemical properties of lignocellulosic residues with a view to the production of fuels." *Fuel* 70: 947-950.
- Joubert, A., T. J. Stewart and R. Eberhard (2003). "Evaluation of water supply augmentation and water demand management options for the city of Cape Town." *J Multi-Crit Decis Anal* 12: 17-25.
- Kabata-Pendias, A., Ed. (2001). Trace elements in soils and plants,.
- Kaboré, T., M. Pansu, E. Hien, D. Brunet, B. G. Barthès, S. Houot, A. Coulibali, P. Zombré, L. Thuriès and D. Masse (2012). "Near Infrared Spectroscopy applied to model the transformation of added organic materials in soil." *Journal of Near Infrared Spectroscopy* 20: 339-351.
- Kaboré, W. T., M. Pansu, E. Hien, S. Houot, N. P. Zombré and D. Masse (2011). "Usefulness of TAO model to predict and manage the transformation in soil of carbon and nitrogen forms from West-Africa urban solid wastes." *Waste Management* 31(1): 154-167.
- Kaiser, E. A., K. Hohrs, M. Kücke, E. Schnug, O. Heinemeyer and J. C. Munch (1998). "Nitrous oxide release from arable soil: Importance of N-fertilization, crops and temporal variation." *Soil Biol. Biochem.* 30: 1553- 1563.
- Karlsson, T., P. Persson and U. Skjellberg (2006). "Complexation of Copper(II) in Organic Soils and in Dissolved Organic Matter - EXAFS Evidence for Chelate Ring Structures." *Environmental Science and Technology* 40: 2623-2628.
- Kathiravale, S., M. N. Muhd Yunus, K. Sopian, A. H. Samsuddin and R. A. Rahman (2003). "Modeling the heating value of Municipal Solid Waste." *Fuel* 82(9): 1119-1125.
- Kenyon, W. (2007). "Evaluating flood risk management options in Scotland: A participant-led multi-criteria approach." *Ecol Econ* 64: 70-81.
- Khalil, K., R. A. Rasmussen and M. J. Shearer (2002). "Atmospheric Nitrous oxide : patterns of global change during recent decades and centuries." *Chemosphere* 47: 807-821.
- Kinraide, T. B., J. F. Pedler and D. R. Parker (2004). "Relative effectiveness of calcium and magnesium in the alleviation of rhizotoxicity in wheat induced by copper, zinc, aluminum, sodium, and low pH." *Plant & Soil* 259: 201-208.
- Kirchmann, H. and A. Lundvall (1993). "Relationship between N immobilization and volatile fatty acids in soil after application of pig and cattle slurry." *Biol Fertil Soils* 15: 161-4.
- Kopittke, P. M., C. J. Asher, R. A. Kopittke and N. W. Menzies (2007). "Toxic effects of Pb²⁺ on growth of cowpea (*Vigna unguiculata*)." *Environmental Pollution* 150: 280-287.
- Kopittke, P. M. and N. W. Menzies (2006). "Effect of Cu toxicity on growth of cowpea (*Vigna unguiculata*)." *Plant and Soil* 279: 287-296.
- Köster, J. R., L. Cárdenas, M. Senbayram, R. Bol, R. Well and M. Butler (2011). "Rapid shift from denitrification to nitrification in soil after biogas residue application as indicated by nitrous oxide isotopomers." *Soil Biol Biochem* 43: 1671-7.
- Kranert, M., R. Gottschall, C. Bruns and G. Hafner (2010). "Energy or compost from green waste? - A CO₂ - Based assessment." *Waste Management* 30(4): 697-701.
- Kuzyakov, Y., J. K. Friedel and K. Stahr (2000). "Review of mechanisms and quantification of priming effects." *Soil Biology and Biochemistry* 32(11-12): 1485-1498.
- L'Herroux, L., S. Le Roux, P. Appriou and J. Martinez (1997). "Behavior of metals following intensive pig slurry applications to a natural field treatment process in Brittany (France)." *Environmental Pollution* 97: 119-130.

- Lashermes, G., S. Houot, B. Nicolardot, B. Mary, V. Parnaudeau, T. Morvan, M. Linères, R. Chaussod, L. Metzger, L. Thuriès, C. Villette, A. Tricaud and M. L. Guillotin (2007). Apport de matières organiques exogènes en agriculture: indicateur de potentialité de stockage de carbone dans les sols et définition de classes de disponibilité de l'azote. Rapport final, Convention ADEME n°0475C0078
- Lashermes, G., S. Houot, B. Nicolardot, V. Parnaudeau, B. Mary, T. Morvan, R. Chaussod, M. Linères, L. Metzger, L. Thuriès, C. Villette, A. Tricaud and M. L. Guillotin (2007). "Apport de matières organiques exogènes en agriculture: indicateur de potentialité de stockage de carbone dans les sols et définitions de classe de disponibilité d'azote." *Echo-MO* 64: 3-8.
- Lashermes, G., B. Nicolardot, V. Parnaudeau, L. Thuriès, R. Chaussod, M. L. Guillotin, M. Linères, B. Mary, L. Metzger, T. Morvan, A. Tricaud, C. Villette and S. Houot (2009). "Indicator of potential residual carbon in soils after exogenous organic matter application." *European Journal of Soil Science* 60: 297-310.
- Lashermes, G., B. Nicolardot, V. Parnaudeau, L. Thuriès, R. Chaussod, M. L. Guillotin, M. Linères, B. Mary, L. Metzger, T. Morvan, A. Tricaud, C. Villette and S. Houot (2010). "Typology of exogenous organic matters based on chemical and biochemical composition to predict potential nitrogen mineralization." *Bioresource Technology* 101(1): 157-164.
- Laudone, G. M., G. P. Matthews, N. R. A. Bird, W. R. Whalley, L. M. Cardenas and A. S. Gregory (2011). "A model to predict the effects of soil structure on denitrification and N₂O emission." *Journal of Hydrology* 409(1-2): 283-290.
- Le Gall, A.-C. (2012). "Méthodologie SIRIS." from http://www.ineris.fr/siris-pesticides/siris_pdf/SIRIS-Guide_utilisation.pdf.
- Leeson, S., E. V. Valdes and C. F. M. de Lange (2000). Near infrared reflectance spectroscopy and related technologies for the analysis of feed ingredients. Feed evaluation: principles and practice. P. J. Moughan, M. W. A. Verstegen and M. I. Visser-Reyneveld. Wageningen, The Netherlands: 93-104.
- Lehmann, J., D. Solomon, J. Kinyangi, L. Dathe, S. Wirick and C. Jacobsen (2008). "Spatial complexity of soil organic matter forms at nanometre scales." *Nat. Geosci.* 1: 238-242.
- Lensi, R., C. Lescure, A. Clays-Josserand and F. Gourbière (1991). "Spatial distribution of nitrification and denitrification in an acid forest soil." *Forest Ecol. Manag* 44: 29-40.
- Lesteur, M. (2010). Etude de l'utilisation de la spectroscopie proche infrarouge pour la prédiction du potentiel méthane de déchets solides. Ecole doctorale: Sciences des procédés - Sciences des aliments. Montpellier, Université Montpellier 2. Doctorat: 153.
- Lesteur, M., V. Bellon-Maurel, C. Gonzalez, E. Latrille, J. M. Roger, G. Junqua and J. P. Steyer (2011). "Alternative methods for determining anaerobic biodegradability: A review." *Process Biochemistry* 45(4): 431-440.
- Lesteur, M., E. Latrille, V. B. Maurel, J. M. Roger, C. Gonzalez, G. Junqua and J. P. Steyer (2011). "First step towards a fast analytical method for the determination of Biochemical Methane Potential of solid wastes by near infrared spectroscopy." *Bioresource Technology* 102(3): 2280-2288.
- Li, Z. B. and L. M. Shuman (1997). "Mobility of Zn, Cd and Pb in soils as affected by poultry litter extract - 1. Leaching in soil columns." *Environmental Pollution* 95(2): 219-226.
- Linères, M. and J. L. Djakovitch (1993). Caractérisation de la stabilité biologique des apports organiques par l'analyse biochimique. Matières organiques et agriculture, France, Actes des 4èmes journées du GEMAS et du 5ème forum du COMIFER.
- Lomborg, C. J., J. B. Holm-Nielsen, P. Oleskowicz-Popiel and K. H. Esbensen (2009). "Near infrared and acoustic chemometrics monitoring of volatile fatty acids and dry matter during co-digestion of manure and maize silage." *Bioresource Technology* 100(5): 1711-1719.

- López-Fernández, S., J. Díez, P. Hernáiz, A. Arce, L. García-Torres and A. Vallejo (2007). "Effects of fertiliser type and the presence or absence of plants on nitrous oxide emissions from irrigated soils." *Nutr Cycl Agroecosyst* 78: 279-89.
- Loveland, P. and J. Webb (2003). "Is there a critical level of organic matter in the agricultural soils of temperate regions: a review." *Soil and Tillage Research* 70(1): 1-18.
- Lovett, D. K., E. R. Deaville, D. I. Givens, M. Finlay and E. Owen (2005). "Near infrared reflectance spectroscopy (NIRS) to predict biological parameters of maize silage: effects of particle comminution, oven drying temperature and the presence of residual moisture." *Animal Feed Science and Technology* 120: 323-332.
- Lowrance, R. and D. Smittle (1988). "Nitrogen cycling in a multiple-crop vegetable production system." *Journal of Environmental Quality* 17: 158 - 162.
- Luck, S., G. Büge, H. Plettenberg and M. Hoffmann (2010). "Near-infrared spectroscopy for process control and optimization of biogas plants." *Eng. Life Sci.* 10(6): 537-543.
- Luna-delRisco, M., A. Normak and K. Orupold (2011). "Biochemical methane potential of different organic wastes and energy crops from Estonia." *Agronomy Research* 9(1-2): 331-342.
- Lynch, D., A. M. Henihan, B. Bowen, D. Lynch, K. McDonnell, W. Kwapinski and J. J. Leahy (2013). "Utilisation of poultry litter as an energy feedstock." *Biomass and Bioenergy* 49: 197-204.
- Lynch, D., A. M. Henihan, B. Bowen, D. Lynch, K. McDonnell, W. Kwapinski and J. J. Leahy (2013). "Utilisation of poultry litter as an energy feedstock." *Biomass & Bioenergy* 49: 197-204.
- Maag, M. (1990). "N₂O production rates and denitrification rates in soil amended with pig slurry." *Mitt. Dtsch. Bodenk. Ges* 65: 205-210.
- Madrid, L. and E. Diaz-Barrientos (1998). "Release of metals from homogeneous soil columns by wastewater from an agricultural industry." *Environ. Pollut.* 101: 43-48.
- Magdoff, F. (2013). "Global Resource Depletion. Is population the problem?" *Monthly Review* 64(8): <http://monthlyreview.org/2013/01/01/global-resource-depletion>.
- Malley, D. F., P. D. Martin and E. Ben-Dor (2004). Application in analysis in soil. Near-infrared Spectroscopy in Agriculture, Agronomy monograph. J. Roberts, J. J. Workman and J. B. Reeves. Madison, WI, USA, American Society of Agronomy, Inc.: 729.
- Malley, D. F., C. McClure, P. D. Martin, K. Buckley and W. P. McCaughey (2005). "Compositional Analysis of Cattle Manure During Composting Using a Field-Portable Near-Infrared Spectrometer." *Soil Science and Plant Analysis* 36(4): 455-475.
- Malley, D. F., L. Yesmin and R. G. Eilers (2002). "Rapid Analysis of Hog Manure and Manure-amended Soils Using Near-infrared Spectroscopy." *Soil Science Society American Journal* 66: 1677-1686.
- Malley, D. F., L. Yesmin, D. Wray and S. Edwards (1999). "Application of near-infrared spectroscopy in analysis of soil mineral nutrients." *Commun. Soil Sci. Plant Anal.* 30(7&8): 999-1012.
- Mark, H. L. and D. Tunnell (1985). "Qualitative near-infrared reflectance analysis." *Analytical Chemistry* 58: 379-384.
- Marmo, L., I. Feix, E. Bourmeau, F. Amlinger, C. G. Bannick, S. De Neve, E. Favoino, A. Gendebien, J. Gibert, M. Givélet, I. Leifert, R. Morris, A. Rodriguez Cruz, F. Ruck, S. Siebert and F. Tittarelli (2004). Reports of the technical working groups established under the thematic strategy for soil protection. Volume - III. Organic matter and biodiversity. Taskgroup 4 on exogenous organic matter. Luxembourg, Office for Official Publications of the European Communities.
- Marten, G. C., J. S. Shenk and F. E. Barton, Eds. (1989). Near infrared reflectance spectroscopy (NIRS): Analysis of forage quality. Agricultural Handbook. Washington, DC, USDA-ARS.

- Mc Geough, E. J., S. M. Little, H. H. Janzen, T. A. McAllister, S. M. McGinn and K. A. Beauchemin (2012). "Life-cycle assessment of greenhouse gas emissions from dairy production in Eastern Canada: A case study." *Journal of Dairy Science* 95(9): 5164-5175.
- Mc Gill, B. M., A. E. Sutton-Grier and J. P. Wright (2010). "Plant trait diversity buffers variability in denitrification potential over Changes in season and soil conditions." *Plos ONE* 5(7): 1611-1618.
- McLaughlin, M. J. (2002). Bioavailability of metals to terrestrial plants. *Bioavailability of Metals in Terrestrial Ecosystems: Importance of partitioning for Bioavailability to Invertebrates, Microbes and Plants*. A. HE. Pensacola, SETAC: 39-68.
- McLellan, T. M., J. D. Aber, M. E. Martin, J. M. Melillo and K. J. Nadelhoffer (1991). "Determination of nitrogen, lignin, and cellulose content of decomposing leaf material by near infrared reflectance spectroscopy." *Canadian Journal of Forest Research* 21(11): 1684-1688.
- Médoc, J. M. (2006). *Projet INCIVOL 974. La Réunion, Société Coopérative Agricole des Aviculteurs de la Réunion*: 24.
- Meyer, D., P. L. Price, H. A. Rossow, N. Silva-del-Rio, B. M. Karle, P. H. Robinson, E. J. DePeters and J. G. Fadel (2011). "Survey of dairy housing and manure management practices in California." *Journal of Dairy Science* 94(9): 4744-4750.
- Micò, C., H. F. Li, F. J. Zhao and S. P. McGrath (2008). "Use of Co speciation and soil properties to explain variation in Co toxicity to root growth of barley (*Hordeum vulgare* L.) in different soils." *Environmental Pollution* 156: 883-890.
- Millar, N. and E. M. Baggs (2004). "Chemical composition, or quality, of agroforestry residues influences N₂O emissions after their addition to soil." *Soil Biology & Biochemistry* 36: 935-943.
- Millmier, A., J. Lorimor, J. R. Hurburgh, C. Fulhage, J. Hattey and H. Zhang. (2000). "Near-infrared sensing of manure nutrients." *Trans. ASAE* 43: 903-908.
- Moletta, R. (2008). *La Méthanisation*.
- Molina, J.-A. and P. Smith (1998). Modeling carbon and nitrogen processes in soils. *Advances in Agronomy*. San Diego (USA), Academic Press. 62: 253-298.
- Moller, H. B., S. G. Sommer and B. K. Ahring (2004). "Biological degradation and greenhouse gas emissions during pre-storage of liquid animal manure." *Journal of Environmental Quality* 33: 27-36.
- Moller, H. B., S. G. Sommer and B. K. Ahring (2004). "Methane productivity of manure, straw and solid fractions of manure." *Biomass & Bioenergy* 26: 485-495.
- Moreno-Caselles, J., R. Moral, M. D. Perez-Murcia, A. Perez-Espinosa, C. Paredes and E. Agullo (2005). "Fe, Cu, Mn, and Zn input and availability in calcareous soils amended with the solid phase of pig slurry." *Communications in Soil Science and Plant Analysis* 36(4-6): 525-534.
- Morley, N., E. M. Baggs, P. Dörsch and L. Bakken (2008). "Production of NO, N₂O and N₂ by extracted soil bacteria; regulation by NO₂⁻ and O₂ concentrations." *FEMS Microbiol Ecol* 65: 102-112.
- Morvan, T., B. Nicolardot and L. Péan (2006). "Biochemical composition and kinetics of C and N mineralization of animal wastes: a typological approach." *Biol. Fert. Soils* 42: 513-522.
- Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger and O. Van Cleemput (1998). "Closing the global N₂O budget: nitrous oxide emissions through the agricultural nitrogen cycle." *Nutrient Cycling in Agroecosystems* 52: 225-248.
- Mougeot, L. and P. Moustier (2004). *Développement durable de l'agriculture urbaine en Afrique francophone : Enjeux, concepts et méthodes*. Dakar.
- Munch, J. C. and G. L. Velthof (2007). Denitrification and agriculture. *Biology of the Nitrogen Cycle*. H. Bothe, S. J. Ferguson and W. E. Newton. Amsterdam, The Netherlands, Elsevier: 331-341.

- Myrold, D. D. and J. M. Tiedje (1985). "Establishment of denitrification capacity in soil: effects of carbon, nitrate and moisture." *Soil Biology and Biochemistry* 17: 819 - 822.
- Nallathambi Gunaseelan, V. (1995). " Effect of inoculum/substrate ratio and pretreatments on methane yield from Parthenium." *Biomass Bioenergy* 8: 39-44.
- Nennich, T. D., J. H. Harrison, L. M. VanWieringen, D. Meyer, A. J. Heinrichs, W. P. Weiss, N. R. St-Pierre, R. L. Kincaid, D. L. Davidson and E. Block (2005). "Prediction of Manure and Nutrient Excretion from Dairy Cattle." *Journal of Dairy Science* 88(10): 3721-3733.
- Nett, L., S. Aversch, S. Ruppel, J. Rühlmann, C. Feller, E. George and M. Fink (2010). "Does long-term farmyard manure fertilization affect short-term nitrogen mineralization from farmyard manure?" *Biology and Fertility of Soils* 46(2): 159-167.
- Ngnikam, E., P. Rousseaux, E. Tanawa and R. Gourdon (2002). "Multicriteria analysis for environmental assessment of solid waste management systems in tropical african cities : case study of Yaoundé (Cameroon)." *Journal of decision systems* 11(3-4): 479 - 498.
- Nhuchhen, D. R. and P. Abdul Salam (2012). "Estimation of higher heating value of biomass from proximate analysis: A new approach." *Fuel* 99(0): 55-63.
- Nicholson, F. A., B. J. Chambers, J. R. Williams and R. J. Unwin (1999). "Heavy metal contents of livestock feeds and animal manures in England and Wales." *Bioresource Technology* 70(1): 23-31.
- Nicolardot, B., J. A. E. Molina and M. R. Allard (1994). "C and N Fluxes Between Pools of Soil Organic Matter - Model Calibration with Long-Term Incubation Data." *Soil Biology & Biochemistry* 26(2): 235-243.
- Nicolardot, B., S. Recous and B. Mary (2001). "Simulation of C and N mineralisation during crop residue decomposition: A simple dynamic model based on the C : N ratio of the residues." *Plant and Soil* 228(1): 83-103.
- Nierop, K. G. J., B. Jansen, J. A. Vrugt and J. M. Verstraten (2002). "Copper complexation by dissolved organic matter and uncertainty assessment of their stability constants." *Chemosphere* 49: 1191-1200
- Norris, K. H. (1964). "Reports on design and development of a new moisture meter." *Agricultural Engineering*: 370-372.
- Nzila, C., J. Dewulf, H. Spanjers, H. Kiriamiti and H. van Langenhove (2010). "Biowaste energy potential in Kenya." *Renewable Energy* 35(12): 2698-704.
- Obernberger, I., T. Brunner and G. Bärnthaler (2006). "Chemical properties of solid biofuels-significance and impact." *Biomass and Bioenergy* 30(11): 973-982.
- Omar, R., R. M. Harun, T. I. Mohd Ghazi, W. A. K. G. Wan Azlina, A. Idris and R. Yunus (2008). Anaerobic treatment of cattle manure for biogas production. Annual meeting of American Institute of Chemical Engineers. P. Philadelphia. Philadelphia, USA.
- Paillat, J.-M., P. Robin, M. Hassouna and P. Leterme (2005). "Predicting ammonia and carbon dioxide emissions from carbon and nitrogen biodegradability during animal waste composting." *Atmospheric Environment* 39: 6833-6842.
- Palm, C. A., C. N. Gachengo, R. J. Delve, G. Cadisch and K. E. Giller (2000). "Organic inputs for soil fertility management in tropical agroecosystems: Application of an organic residue database." *Agric. Ecosyst. Environ.* 1692: 1 - 16.
- Palmowski, L. M. and J. A. Müller (2000). "Influence of the size reduction of organic waste on their anaerobic digestion." *Water Sci Technol* 41: 155-162.
- Pansu, M., P. Bottner, L. Sarmiento and K. Metselaar (2004). "Comparison of five soil organic matter decomposition models using data from a ¹⁴C and ¹⁵N labeling field experiment." *Global Biogeochemical Cycles* 18(GB4022).
- Pansu, M., Z. Sallih and P. Bottner (1998). "Modelling of soil nitrogen forms after organic amendments under controlled conditions." *Soil Biol. Biochem.* 30(1): 19-29.

- Pansu, M., L. Sarmiento, K. Metselaar, D. Hervé and P. Bottner (2007). "Modelling the transformations and sequestration of soil organic matter in two contrasting ecosystems of the Andes." *European Journal of Soil Science* 58: 775-785.
- Pansu, M. and L. Thuriès (2003). "Kinetics of C and N mineralization, N immobilization and N volatilization of organic inputs in soil." *Soil Biology and Biochemistry* 35(1): 37-48.
- Pansu, M., L. Thuriès, M. C. Larré-Larrouy and P. Bottner (2003). "Predicting N transformations from organic inputs in soil in relation to incubation time and biochemical composition." *Soil Biology & Biochemistry* 35(3): 353-363.
- Papen, H., R. von Berg, I. Hinkel, B. Thoene and H. Rennenberg (1989). "Heterotrophic nitrification by *Alcaligenes faecalis*: NO_2^- , NO_3^- , N_2O and NO production in exponentially growing cultures." *Applied and Environmental Microbiology* 55: 2068-2072.
- Parnaudeau, V., B. Nicolardot and J. Pagès (2004). "Relevance of Organic Matter Fractions as Predictors of Wastewater Sludge Mineralization in Soil." *Journal of Environmental Quality* 33: 1885-1894.
- Pasquini, C. (2003). "Near Infrared Spectroscopy: fundamentals, practical aspects and analytical applications." *Journal of the Brazilian Chemical Society* 14(2): 198-219.
- Paul, J. W. and E. G. Beauchamp (1989). "Effect of carbon constituents in manure on denitrification in soil." *Canadian Journal of Soil Science* 69: 49-61.
- Paul, J. W., E. G. Beauchamp and X. Zhang (1993). "Nitrous and nitric oxide emissions during nitrification and denitrification from manure-amended soil in the laboratory." *Can. J. Soil Sci.* 73: 539-553
- Paustian, K., G. I. Agren and E. Bosatta (1997). "Modelling litter quality effects on decomposition and soil organic matter dynamics." in G. Cadisch and K. E. Giller, editors. *Driven by nature: plant litter quality and decomposition*. CAB International, Wallingford, UK.
- Peltre, C., L. Thuriès, B. Barthès, D. Brunet, T. Morvan, B. Nicolardot, V. Parnaudeau and S. Houot (2011). "Near infrared reflectance spectroscopy: A tool to characterize the composition of different types of exogenous organic matter and their behaviour in soil." *Soil Biology and Biochemistry* 43(1): 197-205.
- Petersen, S. O., S. G. Sommer, F. Béline, C. Burton, J. Dach, J. Y. Dourmad, A. Leip, T. Misselbrook, F. Nicholson, H. D. Poulsen, G. Provolo, P. Sørensen, B. Vinnerås, A. Weiske, M. P. Bernal, R. Böhm, C. Juhász and R. Mihelic (2007). "Recycling of livestock manure in a wholefarm perspective." *Livestock Science* 112: 180-191.
- Petit, T. (2012). *Les enjeux de la biomasse-énergie à La Réunion. Recherche, réalisations et projets. Principaux obstacles rencontrés. Les rencontres scientifiques sur les nouvelles énergies Gerri. La Réunion, www.gerri.fr.*
- Petruzzelli, G., L. Lubrano, B. M. Petronio, M. C. Gennaro, A. Vanni and A. Liberatori (1994). "Soil sorption of heavy metals as influenced by sewage sludge addition." *J. Environ. Sci. Health A* 29: 31-50.
- Philippot, L., S. Hallin, G. Börjesson and E. M. Baggs (2009). "Biochemical cycling in the rhizosphere having an impact on global change." *Plant & Soil* 321: 61-81.
- Pinay, G., V. J. Black, A. M. Planty-Tabacchi, B. Gumeiero and H. Décamps (2000). "Geomorphic control of denitrification in large river floodplain soils." *Biogeochemistry* 50: 163-182.
- Pirie, A., B. Singh and K. Islam (2005). "Ultra-violet, visible, near-infrared, and mid-infrared diffuse reflectance spectroscopic techniques to predict several soil properties." *Aust. J. Soil Res.* 43: 713-721
- Poth, M. and D. D. Focht (1985). " ^{15}N kinetics analysis of N_2O production by *Nitrosomonas europaea*: an examination of nitrifierdenitrification." *Appl. Env. Microb.* 49: 1134-1141.

- Quiroga, G., L. Castrillón, Y. Fernández-Nava and E. Maraño (2010). "Physico-chemical analysis and calorific values of poultry manure." *Waste Management* 30(5): 880-884.
- Rabenarivo, M. (2011). Potentialités d'émissions de CO₂ et de N₂O des sols de systèmes de culture en semis direct sous couverture végétale permanente (SCV) à Madagascar. Ecole Supérieure des sciences Agronomiques. Antananarivo, Université d'Antananarivo. Doctorat: 187.
- Raju, C. S., A. J. Ward, L. Nielsen and H. B. Moller (2011). "Comparison of near infrared spectroscopy, neutral detergent fibre assay and in-vitro organic matter digestibility assay for rapid determination of the biochemical methane potential of meadow grasses." *Bioresource Technol.* 102: 7835-7839.
- Raposo, F., C. J. Banks, I. Siegert, S. Heaven and R. Borja (2006). "Influence of inoculum to substrate ratio on the biochemical methane potential of maize in batch tests." *Process Biochem* 41: 1444-1450.
- Raposo, F., M. A. De la Rubia, V. Fernandez-Cegri and R. Borja (2011). "Anaerobic digestion of solid organic substrates in batch mode: An overview relating to methane yields and experimental procedures." *Renewable and Sustainable Energy Reviews* 16(1): 861-877.
- Ravishankara, A. R., J. S. Daniel and R. W. Portmann (2009). "Nitrous oxide : The dominant Ozone-Depleting substance emitted in the 21st century." *Science* 326(5949): 123-125.
- Reed, J. P., D. Devlin, S. R. R. Esteves, R. Dinsdale and A. J. Guwy (2011). "Performance parameter prediction for sewage sludge digesters using reflectance FT-NIR spectroscopy." *Wat. Res* 45: 2463-2472.
- Reeves III, J. B. (2001). "Near-infrared diffuse reflectance spectroscopy for the analysis of poultry manures." *Journal of Agricultural Food Chemistry* 49: 2193-2197.
- Reeves III, J. B., G. W. McCarty and J. J. Meisinger (2000). "Near infrared reflectance spectroscopy for the determination of biological activity in agricultural soils." *Journal of Near Infrared Spectroscopy* 8: 161-170.
- Reeves III, J. B., G. W. McCarty and T. Mimmo (2002). "The potential of diffuse reflectance spectroscopy for the determination of carbon inventories in soils." *Environmental Pollution* 116 Suppl. 1: S277-S284.
- Reeves III, J. B. and J. S. Van Kessel (2000). "Near-Infrared Spectroscopic Determination of Carbon, Total Nitrogen, and Ammonium-N in Dairy Manures." *Journal of Dairy Science* 83(8): 1829-1836.
- Reeves, J. B. and J. A. S. Van Kessel (2002). "Spectroscopic analysis of dried manures. Near- versus mid-infrared diffuse reflectance spectroscopy for the analysis of dried dairy manures." *Journal of Near Infrared Spectroscopy* 10(2): 93-101.
- Reeves, J. B. and J. S. Van Kessel (2000). "Determination of ammonium-N, moisture, total C and total N in dairy manures using a near infrared fibre-optic spectrometer." *J. Near Infrared Spectrosc.* 8: 151-160.
- Rice, W. C., P. E. Sierzega, J. M. Tjede and L. W. Jacobs (1988). "Stimulated denitrification in the microenvironment of a biodegradable organic waste injected into soil." *Soil Sci. Soc. Am. J.* 52: 102-108.
- Richardson, D., H. Felgate, N. Watmough, A. Thomson and E. M. Baggs (2009). "Mitigating release of the potent greenhouse gas N₂O from the nitrogen cycle: could enzymic regulation hold the key?" *Trends Biotechnology* 27: 388-397.
- Rieuwerts, J. S. (2007). "The mobility and bioavailability of trace metals in tropical soils: a review." *Chemical Speciation and Bioavailability* 19: 75-85.
- Rigolot, C., S. Espagnol, P. Robin, M. Hassouna, F. Béline, J.-M. Paillat and J.-Y. Dourmad (2010). "Modelling of manure production by pigs and NH₃, N₂O and CH₄ emissions. Part II: effect of animal housing, manure storage and treatment practices." *Animal* 4(8): 1413-1424.
- Robertson, G. P. and J. M. Tiedje (1987). "Nitrous oxide sources in aerobic soils; nitrification, denitrification and other biological processes." *Soil Biology & Biochemistry* 19: 187-193.

- Rodrigo, A., S. Recous, C. Neel and B. Mary (1997). "Modelling temperature and moisture effects on C-N transformations in soils : comparison of nine models." *Ecological modelling* sous presse.
- Rooney, C. P., F. J. Zhao and S. P. McGrath (2006). "Soil factors controlling the expression of copper toxicity to plants in a wide range of European soils." *Environmental Toxicology and Chemistry* 25(3): 726-732.
- Rouanne, F. (2003). "Produire du sucre et de l'électricité." *Carocanne* 2: 23-25.
- Roussis, K., K. Moustakas, S. Malamis, A. Papadopoulos and M. Loizidou (2008). "Multi-criteria analysis for the determination of the best WEEE management scenario in Cyprus." *Waste Management* 28: 1941-1954.
- Roy, B. (1985). *Méthodologie multicritère d'aide à la décision*. Economica XXII. Paris: 423.
- Rupa, T. R., C. Srinivasa Rao, A. Subba Rao and M. Singh (2003). "Effects of farmyard manure and phosphorus on zinc transformations and phyto-availability in two alfisols of India." *Bioresource Technology* 87(3): 279-288.
- Sadovnikova, L., E. Otabbong, O. Iakimenko, I. Nilson, J. Persson and D. Orlov (1996). "Dynamic transformation of sewage sludge and farmyard manure components. 2. Copper, lead and cadmium forms in incubated soils." *Agric. Ecosist. Environ.* 58: 127-132.
- Saeys, W., A. M. Mouazen and H. Ramon (2005). "Potential for Onsite and Online Analysis of Pig Manure using Visible and Near Infrared Reflectance Spectroscopy." *Biosystems Engineering* 91(4): 393-402.
- Saidur, R., E. A. Abdelaziz, A. Demirbas, M. S. Hossain and S. Mekhilef (2011). "A review on biomass as a fuel for boilers." *Renewable and Sustainable Energy Reviews* 15(5): 2262-2289.
- Sainz Rozas, H. R., H. E. Etcheverria and L. I. Picone (2001). "Denitrification in maize under no-tillage: effect of nitrogen rate and application time." *Soil Science Society of America Journal* 65: 1314-1323.
- Salminen, E. and J. Rintala (2002). "Anaerobic digestion of organic solid poultry slaughterhouse waste - a review." *Bioresource Technology* 83(1): 13-26.
- Salminen, E., J. Rintala, L. Y. Lokshina and V. A. Vavilin (2000). "Anaerobic batch degradation of solid poultry slaughterhouse waste." *Water Science and Technology* 41: 33-41.
- Sanchez-Martin, M. J., M. Garcia-Delgado, F. L. Lorenzo, M. S. Rodriguez-Cruz and M. Arienzo (2007). "Heavy metals in sewage sludge amended soils determined by sequential extractions as a function of incubation time of soils." *Geoderma* 142(3-4): 262-273.
- Sarret, G., A. Manceau, L. Spadini, J. C. Roux, J. L. Hazemann, Y. Soldo, L. Eybert-Berard and J. J. Menthonnex (1998). "Structural Determination of Zn and Pb Binding Sites in *Penicillium chrysogenum* Cell Walls by EXAFS Spectroscopy." *Environmental Science and Technology* 32: 1648-1655.
- Schaffers, A. P. (2002). "Soil, biomass, and management of semi-natural vegetation - Part I. Interrelationships." *Plant Ecology* 158(2): 229-246.
- Schimann, H., R. Joffre, J. C. Roggy, R. Lensi and A. M. Domenach (2007). "Evaluation of the recovery of microbial functions during soil restoration using near-infrared spectroscopy. ." *Appl. Soil Ecol.* 37(3): 223-232.
- Schlegel, H. G. (1993). *General Microbiology*. Cambridge, UK, Cambridge University Press.
- Schloemer, S. (1991). "Denitrifikation eines gemüsebaulich genutzten Bodens in Abhängigkeit von der Einarbeitung frischer Ernteste." *Z Pflanzenernähr Bodenk* 154: 205-209.
- Schulten, H. R. and M. Schnitzer (1998). "The chemistry of soil organic nitrogen: a review." *Biol. Fertil. Soils* 26: 1-15.
- Segatto, M., O. Bade, K. Lehmann, R. Stegmann and R. Cossu (2007). *Anaerobic digestion of Chicken manure with high ammonia content*. 11th International Waste Management and Landfill Symposium. Sardinia.

- Senbayram, M., R. Chen, A. Budai, L. Bakken and K. Dittert (2012). "N₂O emission and the N₂O/(N₂O+N₂) product ratio of denitrification as controlled by available carbon substrates and nitrate concentrations." *Agriculture, Ecosystems & Environment* 147: 4-12.
- Seregin, I. V. and V. B. Ivanov (2001). "Physiological aspects of cadmium and lead effects on higher plants." *Russian Journal of Plant Physiology* 48: 523-544.
- Sey, B. K., A. M. Manceur, J. K. Whalen, E. G. Gregorich and P. Rochette (2008). "Small-scale heterogeneity in carbon dioxide, nitrous oxide and methane production from aggregates of a cultivated sandy-loam soil." *Soil Biol. Biochem.* 40(9): 2468-2473.
- Shao, J. (1993). "Linear model selection by cross-validation." *J. Am. Stat. Ass.* 88: 486-494.
- Sheng, C. and J. L. T. Azevedo (2005). "Estimating the higher value of biomass fuels from basic analysis data." *Biomass and Bioenergy* 28: 499-507.
- Shenk, J. S. and M. O. Westerhaus (1991). "Population definition, sample selection, and calibration procedures for near infrared reflectance spectroscopy." *Crop Science* 31: 469-474.
- Shenk, J. S. and M. O. Westerhaus (1996). *Near infrared spectroscopy: the future waves. Calibration the ISI way.* A. M. C. Davies and P. H. Williams. Chichester, UK, NIR: 198-202.
- Shenk, J. S., J. J. Workman and M. O. Westerhaus (1992). *Application of NIR spectroscopy to agricultural products. Handbook of Near-Infrared Analysis* D. A. Burns and E. W. Ciurczak. M. Dekker. New York, NY: 383-431.
- Shepherd, K. D. and M. G. Walsh (2007). "Infrared spectroscopy - enabling an evidence-based diagnostic surveillance approach to agricultural and environmental management in developing countries." *J. Near Infrared Spectrosc.* 15: 1-19.
- Šimek, M. and J. Copper (2002). "The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years." *Eur J Soil Sci* 53: 345-354.
- Šimek, M., L. Jisova and D. W. Hopkins (2002). "What is the so-called optimum pH for denitrification in soil?" *Soil Biology and Biochemistry* 34(9): 1227-1234.
- Sinnaeve, G., P. Dardenne, R. Agneessens and R. Biston (1994). "The use of near infrared spectroscopy for the analysis of fresh grass silage." *J. Near Infrared Spectrosc.* 2: 79-84.
- Smith, K. A. and J. R. M. Arah (1990). *Losses of nitrogen by denitrification and emissions of nitrogen oxides from soils. The Fertiliser Society Proceedings.* London. 299.
- Smith, T. N., G. M. Pesti, R. I. Bakalli, J. Kilburn and H. M. Edwards (2001). "The use of near-infrared reflectance spectroscopy to predict the moisture, nitrogen, calcium, total phosphorus, gross energy, and phytate phosphorus contents of broiler excreta." *Poultry Science* 80: 314-319.
- Smolders, E., K. Oorts, E. Lombi, I. Schoeters, Y. Ma, S. Zrna and M. J. McLaughlin (2012). "The Availability of Copper in Soils Historically Amended with Sewage Sludge, Manure, and Compost." *Journal of Environment Quality* 41: 1-9.
- Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor and H. L. Miller (2007). *Contribution of Working Group I to the fourth Assessment Report of the Intergovernmental Panel on Climate Change. Climate Change 2007: The Physical Science Basis.* IPCC. Cambridge, UK, Cambridge University Press.
- Solomon, S., D. Qin, M. Manning, M. Marquis, K. B. Averyt, M. Tignor, H. L. Miller and Z. Chen (2007). *Contribution of Working Group I to the Fourth Assessment Report of the intergovernmental Panel on Climate Change 2007. Climate Change 2007: The Physical Science Basis.* IPCC. Cambridge, United Kingdom and New York, NY, USA, Cambridge University Press.
- Sommer, S. G., R. R. Sherlock and R. Z. Khan (1996). "Nitrous oxide and methane emissions from pig slurry amended soils. ." *Soil Biology and Biochemistry* 28: 1541-1544.
- Soon, Y. and M. Arshad (2002). "Comparison of the decomposition and N and P mineralization of canola, pea and wheat residues." *Biol Fertil Soils* 36: 10-7.

- Sorensen, L. K., P. Sorensen and T. S. Birkmose (2007). "Application of reflectance near infrared spectroscopy for animal slurry analyses." *Soil Science Society American Journal* 71: 1398–1405.
- Soriano-Disla, J. M., I. Gómez, C. Guerrero, J. Navarro-Pedreño and F. García-Orenes (2010). "The potential of NIR spectroscopy to predict stability parameters in sewage sludge and derived compost." *Geoderma* 158(1-2): 93-100.
- Stanford, G., R. A. Vander Pol and S. Dzienia (1975). "Denitrification rates in relation to total and extractable soil carbon." *Soil Sci. Soc. Amer. Proc.* 39: 284-289.
- Steffen, R., O. Szolar and R. Braun (1998). *Feedstocks for anaerobic digestion*. Vienna, Institute of Agrobiotechnology Tulin, University of Agricultural Sciences.
- Stenberg, B., L. S. Jensen, E. Nordkvist, T. A. Breland, A. Pedersen, J. Guomundsson, S. Bruun, T. Salo, F. Palmason, T. M. Henriksen and A. Korsæth (2004). "Near infrared reflectance spectroscopy for quantification of crop residue, green manure and catch crop C and N fractions governing decomposition dynamics in soil." *Journal of Near Infrared Spectroscopy* 12: 331-346.
- Stevens, R. J. and I. S. Cornforth (1974). "The effect of aeration on the gases produced by slurry during storage." *Journal of Science of Food and Agriculture* 25: 1249-1261.
- Stevenson, F. J. (1994). *Humus Chemistry: Genesis, Composition, Reactions*. New York.
- Stockl, A. and H. Oechsner (2012). "Near-Infrared spectroscopic online monitoring of process stability in biogas plants." *Engineering in Life Sciences* 12(3): 295-305.
- Suehara, K., Y. Nakano and T. Yano (2001). "Simultaneous measurement of carbon and nitrogen content of compost using near infrared spectroscopy." *Journal of Near Infrared Spectroscopy* 9(1): 35-41.
- Swift, M. J., O. W. Heal and J. M. Anderson (1979). *Decomposition in terrestrial ecosystems*. Oxford, UK.
- TCO (2010). *Exploitation de la plate-forme de compostage du Port années 2010 à 2016*. Le Port, Territoire de la Côte Ouest (TCO).
- Tejada, M. and J. Gonzalez (2005). "Beet vinasse applied to wheat under dryland conditions affected soil properties and yield." *European Journal of Agronomy* 23(4): 336-347.
- Telmo, C., J. Lousada and N. Moreira (2010). "Proximate analysis, backwards stepwise regression between gross calorific value, ultimate and chemical analysis of wood." *Bioresource Technology* 101: 3808-3815.
- Terhoeven-Urselmans, T., K. Michel, M. Helfrich, H. Flessa and B. Ludwig (2006). "Near-infrared spectroscopy can predict the composition of organic matter in soil and litter." *J. Plant Nutr. Soil Sci.* 169: 168-174.
- Terhoeven-Urselmans, T., H. Schmidt, R. G. Joergensen and B. Ludwig (2008). "Usefulness of near-infrared spectroscopy to determine biological and chemical soil properties: importance of sample pre-treatment." *Soil Biology and Biochemistry* 40: 1178-1188.
- Thakali, S., H. E. Allen, D. M. Di Toro, A. A. Ponizovsky, C. P. Rooney, F. J. Zhao, S. P. McGrath, P. Criel, H. van Eeckhout, C. R. Janssen, K. Oorts and E. Smolders (2006). "Terrestrial Biotic Ligand Model.1. Development and Application to Ni and Cu Toxicities to Barley Root Elongation in Soils." *Environ Sci Technol* 40: 7094-7100.
- Thuriès, L., D. Bastianelli, F. Davrieux, L. Bonnal and R. Oliver (2007). Prediction by NIRS of the biochemical composition of various raw materials used in the organic fertiliser industry. 12th International Conference on Near Infrared Spectroscopy. G. R. Burling-Claridge, S. E. Holroyd and R. M. W. Sumner. New Zealand NIRS Soc. Inc., AgResearch MIRINZ Publ., Hamilton: 781-785.
- Thuriès, L., D. Bastianelli, F. Davrieux, L. Bonnal, R. Olivier and M. Pansu (2005). "Prediction by NIRS of the composition of plant raw materials from the organic fertiliser industry and crop residues from tropical agrosystems." *Journal of Near Infrared Spectroscopy* 13: 187-199.

- Thuriès, L., F. Davrieux, D. Bastianelli, L. Bonnal and R. Oliver (2007). NIRS for predicting quality indexes in the organic fertiliser industry. 12th International Conference on Near Infrared Spectroscopy, New Zealand NIRS Soc. Inc., AgResearch MIRINZ.
- Thuriès, L., M. Pansu, C. Feller, P. Hermann and J.-C. Rémy (2001). "Kinetics of added organic matter decomposition in a Mediterranean sandy soil." *Soil Biology and Biochemistry* 33: 997-1010.
- Thuriès, L., M. Pansu, M. C. Larré-Larrouy and C. Feller (2002). "Biochemical composition and mineralization kinetics of organic inputs in a sandy soil." *Soil Biology and Biochemistry* 34(2): 239-250.
- Tiedje, J., S. Simkins and P. Groffman (1989). "Perspectives on measurement of denitrification in the field including recommended protocols for acetylene based methods." *Plant and Soil* 115(2): 261-284.
- Tillman, D. A., Ed. (1978). *Wood as energy resource*. New York, Academic Press.
- Triolo, J. M., S. G. Sommer, H. B. Moller, M. R. Weisbjerg and X. Y. Jiang (2011). "A new algorithm to characterize biodegradability of biomass during anaerobic digestion: Influence of lignin concentration on methane production potential." *Bioresource Technology* 102(20): 9395-9402.
- UR Risque environnemental lié au recyclage (2008). *Impact agronomique et environnemental de la gestion des matières organiques en milieu tropical*. Formation des agents du développement agricole et information publique, CIRAD.
- Vaillant, M., J. M. Jouany and J. Devillers (1995). "A multicriteria estimation of the environmental risk of chemicals with the SIRIS method." *Toxicology Modeling* 1(1): 57-72.
- Van Soest, P. J., J. B. Robertson and B. A. Lewis (1991). "Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition." *Journal of Dairy Science* 74: 3583-3597.
- Vanlauwe, B., J. Diels, N. Sanginga and R. Merckx (1997). *Residue quality and decomposition: an unsteady relationship? Driven by nature: plant litter quality and decomposition*. G. Cadisch and K. E. Giller. Wallingford, UK, CAB International: 157-166.
- Vargas-Moreno, J. M., A. J. Callejón-Ferre, J. Pérez-Alonso and B. Velasquez-Martí (2012). "A review of the mathematical models for predicting the heating value of biomass materials." *Renewable and Sustainable Energy Reviews* 16(5): 3065-3083.
- Varrault, G., Y. Fabre and A. Bermond (2001). "Kinetic fractionation of copper and cadmium from soil model compounds." *Canadian Journal of Analytical Sciences and Spectroscopy* 46: 101-107.
- Vasquez de Aldana, B. R., B. Garcia-Criado, A. Garcia-Criado and M. E. Perez-Corona (1995). "Estimation of mineral content in natural grasslands by near infrared reflectance spectroscopy." *Comm. Soil Sci. Plant Anal.* 26: 1383-1396.
- Vedrenne, F., F. Béline, P. Dabert and N. Bernet (2008). "The effect of incubation conditions on the laboratory measurement of the methane producing capacity of livestock wastes." *Bioresource Technology* 99(1): 146-155.
- Velthof, G. L., P. J. Kuikman and O. Oenema (2003). "Nitrous oxide emission from animal manures applied to soil under controlled conditions." *Biology and Fertility of Soils* 37: 221-230.
- Velthof, G. L. and J. Mosquera (2011). "The impact of slurry application technique on nitrous oxide emission from agricultural soils." *Agriculture, Ecosystems & Environment* 140(1-2): 298-308.
- Velthof, G. L., O. Oenema, R. Postma and M. L. Van Beusichem (1997). "Effects of type and amount of applied nitrogen fertilizer on nitrous oxide fluxes from intensively managed grassland." *Nutrient Cycling in Agroecosystems* 46: 257-267.
- Vergnoux, A., M. Guiliano, Y. Le Dréau, J. Kister, N. Dupuy and P. Doumenq (2009). "Monitoring of the evolution of an industrial compost and prediction of some compost properties by NIR spectroscopy." *Science of The Total Environment* 407(7): 2390-2403.



- Walker, C. and R. Shannon (2006). "Nitrate and phosphate removal effects of compost amendments in wetland mesocosms." *Trans ASABE* 49: 1773-8.
- Ward, A. J., E. Bruni, M. K. Lykkegaard, A. Feilberg, A. P. S. Adamsen, A. P. Jensen and A. K. Poulsen (2011). "Real time monitoring of a biogas digester with gas chromatography, near-infrared spectroscopy, and membrane-inlet mass spectrometry." *Bioresource Technol.* 102: 4098-4103.
- Webb, A. R. and F. R. Hawkes (1985). "The anaerobic digestion of poultry manure: Variation of gas yield with influent concentration and ammonium-nitrogen levels." *Agricultural Wastes* 14(2): 135-156.
- Weier, K., J. Doran, J. Power and D. Walters (1993). "Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate." *Soil Sci Soc Am J* 57: 66-72.
- Weitz, A., E. Linder, S. Frolking, P. Crill and M. Keller (2001). "N₂O emissions from humid tropical agricultural soils: effects of soil moisture, texture and nitrogen availability." *Soil Biol Biochem* 33: 1077-93.
- White, R. (1987). "Effect of lignin content and extractives on the higher heating value of wood." *Wood and Fiber Science* 19(4): 446-452.
- Williams, P. (2003). "Near-infrared Technology—Getting the Best Out of Light. ." PDK Grain. Nanaimo, Canada.
- Wrage, N., G. L. Velthof, M. L. van Beusichem and O. Oenema (2001). "Role of nitrifier denitrification in the production of nitrous oxide." *Soil Biology and Biochemistry* 33: 1723-1732.
- Xu, H., Z. Cai, X. Li and H. Tsuruta (2000). "Effect of antecedent soil water regime and rice straw application time on CH₄ emission from rice cultivation." *Aust J Soil Res* 38: 1-12.
- Yang, Z. L., L. J. Han and X. Fan (2006). "Rapidly estimating nutrient contents of fattening pig manure from floor scrapings by near infrared reflectance spectroscopy." *J. Near Infrared Spectrosc.* 14: 261-268.
- Yin, C. Y. (2011). "Prediction of higher heating values of biomass from proximate and ultimate analyses." *Fuel* 90(3): 1128-1132.
- Yoshinari, T., R. Hynes and R. Knowles (1977). "Acetylene inhibition of nitrous oxide reduction and measurement of denitrification and nitrogen fixation in soil." *Soil Biology and Biochemistry* 9(3): 177-183.
- Yoshinari, T. and R. Knowles (1976). "Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria." *Biochemical and Biophysical Research Communications* 69: 705 - 710.
- Zdanevitch, I., G. Masselot, S. Collet and O. Bour (2009). Etude de la composition du biogaz de méthanisation agricole et des émissions en sortie de moteur de valorisation, INERIS.
- Zhang, H., F.-J. Zhao, B. Sun, W. Davison and S. P. McGrath (2001). "A New Method to Measure Effective Soil Solution Concentration Predicts Copper Availability to Plants." *Environmental Science & Technology* 35(12): 2602-2607.
- Zhao, J., C. P. Rooney, H. Zhang and S. P. McGrath (2006). "Comparison of soil solution speciation and diffuse gradients in thin-films measurement as an indicator of copper bioavailability to plants." *Environmental Toxicology and Chemistry* 25(3): 733-742.
- Zhu, N. (2007). "Effect of low initial C/N ratio on aerobic composting of swine manure with rice straw." *Bioresource Technology* 98: 9-13.
- Zumft, W. G. (1997). "Cell biology and molecular basis of denitrification." *Microb. Mol. Biol. Rev.* 61: 533-616.

Titre

Matières Organiques Exogènes issues de l'élevage et de la ville en milieu tropical : Apport de la spectrométrie proche infrarouge pour leur orientation d'usage agronomique et/ou énergétique

Résumé

Comme dans les pays du Nord riches, il y a également une augmentation de la production de déchets organiques dans les pays du Sud moins avancés. Connues sous l'appellation de Matières Organiques Exogènes (MOEx), les déchets organiques peuvent être valorisables comme engrais ou amendement pour les sols agricoles ou bien une nouvelle source de biomasse pour la production d'énergie. L'utilisation raisonnée d'une MOEx exige toutefois une connaissance scientifique approfondie de leur nature et de leurs impacts sur l'environnement. Des analyses conventionnelles en laboratoire et des expérimentations doivent être effectuées pour maîtriser leur structure complexe liée à leurs propriétés physiques, chimiques et biochimiques. Celles-ci sont généralement longues et onéreuses.

Dans notre étude, la spectroscopie proche infrarouge (SPIR) a été choisie comme une alternative aux méthodes classiques pour la caractérisation de ces MOEx en milieu tropical humide. Les objectifs de notre travail sont (1) de montrer que la SPIR est une méthode appropriée pour la prédiction des caractéristiques de MOEx, (2) pour caractériser les MOEx en termes de leur potentiel agronomique et leur potentiel énergétique et (3) pour élaborer une typologie, construite à partir des données prédites par la SPIR, qui prend en compte quelques impacts négatifs liés à l'utilisation des MOEx.

L'ensemble des données a inclus plus de 2000 échantillons de MOEx couvrant une large gamme de MOEx fraîches ou transformées issues de l'élevage, de la ville et des agroindustries. Le spectre SPIR de chaque EOM a été acquis. En plus des caractérisations classiques de laboratoire (les dosages de carbone, azote, phosphore, potassium, etc.), d'autres expérimentations ont été conduites en vue d'évaluer (1) les potentiels « positifs » des MOEx : (i) suivi de la minéralisation du carbone et de l'azote mesurée dans des conditions contrôlées pour une valorisation agronomique, (ii) détermination du pouvoir calorifique et du potentiel méthanogène pour une valorisation énergétique ; et (2) les potentiels « négatifs » des MOEx : (i) dénitrification potentielle et (ii) phytotoxicité en présence d'éléments trace métallique. Pour élaborer la typologie, la méthode SIRIS (Système d'Ingration des Risques par Interaction des Scores) a été appliquée pour formaliser les étapes d'une procédure logique menant à une classification des MOEx selon l'objectif de l'orientation de recyclage.

La diversité des MOEx est illustrée à titre d'exemple par une large gamme des teneurs en (i) C (de 2 à 64 gC.100g⁻¹MS), (ii) N (de 0,2 à 14gN.100g⁻¹MS), (iii) P total (0,01 à 16gP.100g⁻¹MS), K total (0,04 à 30 gK.100g⁻¹MS). En prenant en compte l'ensemble des MOEx, les étalonnages des modèles SPIR sont acceptables pour la prédiction des teneurs en C, en N, en P et en K. Pour les potentiels « positifs » des MOEx (1) suivant les types de MOEx 102 à 955 kgMO.t⁻¹MOEx pourraient être stockées dans le sol pour le maintien de la fertilité, (2) les pouvoirs calorifiques des MOEx varient de 7 à 28 MJ.kg⁻¹ et les potentiels méthanogènes vont de 69 à 488 NmlCH₄.g⁻¹MO. Quant aux potentiels négatifs, que ce soit pour les émissions de N₂O ou pour la phytotoxicité des ETM, une forte interaction entre les propriétés du sol (pH, texture, ...) avec les MOEx masque souvent certains effets. La méthode SIRIS a permis de classer les MOEx selon un processus simple basé sur le classement de critères et de scores d'auto-pénalisation. Cette approche est intéressante en l'absence de données précises qui sont souvent difficiles à obtenir. L'aide des prédictions par la SPIR nous a été utile pour cette démarche d'orientation de la valorisation agronomique et/ou énergétique des MOEx. Des approches socio-économiques devraient compléter notre étude pour aboutir à l'orientation finale de valorisation des MOEx.

Mots-Clés

Déchets organiques, Typologie, Intrants agricoles, Biométhanisation, Combustion