Chemical properties of organic amendments influence nitrous oxide emissions from agricultural soils

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ABSTRACT

Prediction of organic amendment's (OA) potential to emit soil nitrous oxide (POA-N_2O) is difficult because of the variable composition of OAs and of complex interactions with soil properties and environmental conditions. The objectives of this thesis were (1) to conduct a meta-analysis of in-field N_2O emissions following OA application to agricultural soils to assess the global emission factor (EF) for all organic sources (EF_{org}) and its modulation by environmental and management-related factors; (2) to determine how experimental conditions affect the POA-N_2O and select optimal conditions for laboratory-based assessment; (3) to measure the immediate (P1), short- (P2) and medium-term (P3) POA-N_2O with the selected laboratory-based incubation method and then, relate P1, P2, and P3 to the physico-chemical characteristics of more than 131 OAs. The meta-analysis conducted on 256 EFs from 43 sites in 12 countries yielded an EF_{org} equal to 0.57 ± 0.30%, which is lower than the IPCC default EF of 1% for synthetic fertilizer (SF). Three groups of OAs with similar EFs were identified: the high-risk group including animal manures, waste waters and biosolids (1.09 ± 0.17%); the medium-risk group including composts with fertilizers and crop residues with fertilizers (0.46 ± 0.22%); and the low-risk group including composts, crop residues, paper mill sludge and pellets (0.25 ± 0.20%). The EF was modulated by the C/N ratio of the OA, soil properties and precipitation. The EFs were on average 2.8 times greater in fine-textured soils than coarse-textured soils. The comparative incubation study showed that O_2-limited conditions in headspace of a sealed-jar system increased the magnitude of N_2O fluxes by 1.1 to 2.3-fold compared to open-jar systems. Intermittent aerations of a sealed-jar system relying on repeated measurement periods was then selected to assess P1 (48h), P2 (2^{nd} wk), and P3 (3^{rd} wk). In O_2-limited conditions created in a Kamouraska clay soil, maximum P1 was reached for crop residues (CR) with C/N ratio < 15 and liquid manure. Liquid manure (LM) P1 was five-fold greater than solid manure (SM) P1, whereas P2 and P3 were higher in SM- than in LM-amended soils. Physico-chemical properties of OAs explained 23%, 27%, 27%, 56%, and 60% of the variability in P1 response for SM, LM, vegetal compost, poultry manure and CR, respectively. P1 was correlated to the concentrations of water-extractable organic C and volatile fatty acids, NO_3^-, NH_4^+, S, equivalent alkalinity and pH of OAs ($P < 0.05$). In contrast, none of those chemical characteristics were correlated to P2 and P3, suggesting that the increased N_2O emissions supported by the OA-C and N substrates occurred within 48 h of adding these OAs to soil. Further investigations are necessary to test the influence of other specific conditions, e.g., soil texture, water content, OA application techniques on POA-N_2O and their interactions with OA properties.

RÉSUMÉ

Prédire le potentiel d'émission de N_2O des amendements organiques (PAO-N_2O) au champ est difficile en raison de la composition physico-chimique variable des amendements organiques (AOs) et des interactions complexes avec le sol et les conditions environnementales. Cette thèse a pour objectifs de (1) définir le facteur d'émission (FE) par défaut des AOs (FE_{org}) à l'aide de la méta-analyse des émissions de N_2O au champ et l'influence des paramètres environnementaux et agronomiques exercée sur EF_{org}, (2) de déterminer quelle sont les conditions expérimentales qui affectent le PAO-N_2O et de sélectionner des conditions optimales pour sa mesure en incubation, (3) de mesurer dans les conditions optimales identifiées le PAO-N_2O immédiat (P1), à court (P2) et à moyen (3) terme afin de corréler P1, P2 P3 aux propriétés physico-chimiques de 131 AOs testés. La méta-analyse mondiale effectuée sur 256 FE mesurés sur 43 sites répartis à travers 12 pays a permis d'établir un EF_{org} égal à 0.57 ± 0.30% de l'azote total appliqué, ce qui est plus bas que le FE par défaut proposé actuellement par le GIEC basé sur les émissions au champ suite à l'application de fertilisants de synthèse (FS). Trois sous-groupes d'AOs se distinguent, à savoir: le groupe à risque élevé d'émissions de N_2O qui comprend les fumiers, eaux usées et biosolides (1.09 ± 0.17%); le groupe à risque moyen qui comprend les composts + FS ainsi que les résidus de culture + FS (0.46 ± 0.22%); et le groupe à faible risque qui comprend les composts, les résidus de cultures, les boues de pâtes et papier et les granules (0.25 ± 0.20%). Le rapport C/N des AO, les propriétés du sol ainsi que les précipitations sont des modérateurs significatifs de FE_{org}, avec des valeurs 2.8 fois supérieures dans les sols à texture fine comparés aux sols à texture grossière. La comparaison des méthodes d'incubation a démontré que des conditions limitées en oxygène dans les pots scellés

augmentaient jusqu'à 2.3 fois l'amplitude des flux de N_2O par rapport à des conditions standards (pots ouverts). Une méthode instaurant des périodes limitées en O_2 en intermittence avec des conditions standards a donc été sélectionnée pour mesurer P1 (48 h), P2 ($2^{ème}$ sem), and P3 (^{3ème} sem). Sous ses conditions imposées à une argile de la série Kamouraska, les valeurs maximales de P1 ont été mesurées suite à l'application de résidus de culture (RC) possédant un rapport C/N< 15, et suite à l'application de lisiers de ferme (LF). Le P1 des LF était 5 fois plus élevé que celui des fumiers solides (FS), alors que l'inverse a été observé pour les variables P2 et P3. Les propriétés physico-chimiques des AOs expliquaient 23%, 27%, 27%, 56%, and 60% de la variabilité de P1 pour les FS, les LF, le compost végétal, le fumier de poulet et les RC, respectivement. P1 a été corrélé aux contenus en carbone organique extrait à l'eau, en acides gras volatiles, NO_3^-, NH_4^+, S, à l'alcalinité équivalente et au pH des AOs ($P < 0.05$). Par contre, aucune corrélation n'a été établie entre ces propriétés et les variable P2 and P3, suggérant que l'augmentation des émissions de N_2O générée par l'apport d'AO étaiet de courte durée. D'autres recherches sont nécessaires pour tester l'influence d'autres facteurs spécifiques, tels que la texture du sol, le contenu en eau, le mode d'application des AOs, sur le PAO-N_2O et leurs interactions avec les propriétés des AOs.

DEDICATION

This thesis is dedicated to my better half, Nicolas, for his tremendous patience, love, support and wise counselling throughout this process. This is the thesis you never wanted to do, the thesis for which you worked as hard as I did, even if it had nothing to do with potatoes! You're definitely the most passionate agronomist I know, but also and especially a great dad. Je t'aime.

PREFACE AND CONTRIBUTION OF AUTHORS

This thesis is composed of a general introduction that includes the overall objectives and hypotheses, four chapters written in manuscript format according to the guidelines of the Graduate and Postdoctoral Studies Office of McGill University, followed by a general conclusion and contributions to knowledge.

The first chapter is a literature review which summarizes the previous research in the thesis research field.

The second chapter is a meta-analysis of N_2O emissions from agricultural fields receiving organic amendments. This chapter is a manuscript in preparation for submission to Global Change Biology. The third and fourth chapters are experimental results based on original laboratory experiments. Connecting paragraphs between these chapters shows the progression from one experiment to the other. The third and fourth chapters are manuscripts in preparation for submission to Soil Biology and Biochemistry. The candidate was the senior author of each manuscript and co-authors were Philippe Rochette, Joann K. Whalen, Denis A. Angers, Martin H. Chantigny and Normand Bertrand.

The candidate was fully responsible for conducting the meta-analysis in chapter 2. The candidate (1) gathered publications relevant to the objectives, (2) established inclusion criteria to meet meta-analysis objectives, (3) screened studies in a standardized manner to minimize bias as much as possible, (4) created the appropriate template for the database that contained response variables of soil nitrous oxide emissions, explanatory factors and other relevant parameters, (5) built the database with data extracted from selected studies (except some studies and data information which were done by Philippe Rochette and his team), (6) conducted exploratory analyses, statistical analysis, and interpretation, (7) wrote the manuscript.

The candidate was fully responsible for designing the experiments in chapters 3 and 4. Laboratory incubations, including pre-tests, were conducted at the Quebec Research and Development Centre of Agriculture and Agri-Food Canada.

In chapter 3, a comparative laboratory study was conducted with four different incubations to assess the influence of laboratory conditions on soil nitrous oxide emissions following the addition of organic amendments, and whether these conditions are optimal to measure the soil nitrous oxide emitting potential of a large number of organic amendments with contrasting chemical properties. The candidate therefore requested and received soil samples and crop data from the various sites. The candidate was fully responsible for the conception of the experimental design, setup, and planning with the coordination of the research team, for conducting subsequent laboratory analyses (with Normand Bertrand), statistical analyses, data interpretation and writing the manuscript.

In chapter 4, laboratory experiments were strategic and followed from the findings in chapter 3. The candidate was fully responsible for collecting organic amendments from farms, compost facilities, sewage treatment plants, research units and commercial suppliers, for their storage, and preparation for chemical analyses (that were conducted at the Institut de recherche et de développement en agroenvironnement in Quebec City), for the conception of experimental design, setup, and planning with the coordination of the research team, for conducting subsequent laboratory analyses (with Normand Bertrand), data collection (with Normand Bertrand), analysis and interpretation, and writing the manuscripts.

Funding for the thesis research project was provided by the Sustainable Agricultural Environment Systems (SAGES) program of Agriculture and Agri-Food Canada (AAFC). The candidate also received financial assistance from Centre Sève. Dr. Joann K. Whalen and Dr. Philippe Rochette provided advisory guidance and editorial assistance with all the manuscripts. Dr. Denis Angers and Dr. Martin Chantigny greatly facilitated access to training and technical assistance with chapters 2, 3 and 4. They provided advisory guidance concerning the experiments in chapters 3 and 4. Normand Bertrand provided tremendous technical assistance and expertise with chapters 2, 3 and 4.

The manuscripts are presented in the following order:

Chapter 2. Anaïs Charles, Philippe Rochette, Joann K. Whalen, Denis A. Angers, Martin H. Chantigny, Normand Bertrand. 2016. Global nitrous oxide emission factors from agricultural soils after addition of organic amendments: a meta-analysis (In preparation for Global Change Biology).

Chapter 3. Anaïs Charles, Philippe Rochette, Joann K. Whalen, Denis A. Angers, Martin H. Chantigny, Normand Bertrand. 2016. Assessing the potential of organic amendments to induce soil nitrous oxide emissions in controlled conditions: a comparative study (In preparation for Soil Biology and Biochemistry).

Chapter 4. . Anaïs Charles, Philippe Rochette, Joann K. Whalen, Denis A. Angers, Martin H. Chantigny, Normand Bertrand. 2016. Associating the potential of organic amendments for soil N_2O emissions with their physical-chemical characteristics. (In preparation for Soil Biology and Biochemistry).

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LIST OF ABBREVIATIONS

AR, alfalfa residues

BD, Bulk density

BR, biogas residues

BSD, Biosolid

BSD-CR-S, biosolid and crop residues combined with S

BSD-S, biosolid combined with IF

BSI, biological stability index

C, carbon

C_2H_2, acetylene

CMPT, compost

CMPT-S, compost combined with IF

CO_2, carbon dioxide

CR-S, crop residues combined with IF

E^- D/A, electron donors/acceptors

EA, equivalent alkalinity

EF, Emission factor of nitrous oxide

EF_{org}, the global EF for all organic sources

FertiClass, nature of organic sources ± IF

FertiRiskClass, N_2O risk classes of OAs ± IF

FertiType, the type of fertilization (organic, organic + synthetic, synthetic)

FM, farm manure

FOM, fresh organic matter

H_2O, water

IDsite, unique identifier number of sites

IDstudy, unique identifier number of studies

IF, inorganic fertilizer

L, lignin

LM, liquid manure

LM-CR, liquid manure combined with IF

LM-S, liquid manure combined with IF

MAT, mean annual temperature

MBN, microbial biomass nitrogen

MLS, organic-based meals

n, number of replicates

N, nitrogen

N_2, dinitrogen

N_2O, nitrous oxide

$N_2O_{0\text{-}72h}$, emission factor of nitrous oxide calculated for the first 72 h of the incubation

$N_2O_{ANOXMAX}$, emission factor of nitrous oxide calculated for the anoxic incubation period

$N_2O_{ANOXRATE}$, the anoxic emission rate of nitrous oxide

N_2O_c, cumulative N_2O emissions from control plots

N_2O_{cov}Weight, the N_2O coverage weight (see the Equation table)

N_2O_f, cumulative N_2O emissions from fertilized plots

N_2O_{OXIC}, the emission factor of nitrous oxide calculated for the oxic incubation period

NH_3, ammonia

NH_4^+, ammonium

NH_4NO_3, ammonium nitrate

NO_2^-, nitrite,

NO_3^-, nitrate

NO_x, nitrogen oxides

O, opened-jar methods

O_2, oxygen

OA, organic amendment

Org N, organic forms of nitrogen

O^w/S^+, it refers to the opened-jar method with the use of acetylene in the anoxic phase.

P1 is the immediate POA-N_2O (the first 48 h after application)

P2 is the short-term POA-N_2O (1 wk after the application)

P3 is the medium-term POA-N_2O (2 wks after the application)

PLTS, pellets

PM, poultry manure

PMS, paper mill sludge

PMS-CR, paper mill sludge combined with crop residues

POA-N_2O is the potential of OAs to induce soil N_2O emissions

REMB, random-effect model (Borenstein, 2009)

REML, residual maximum likelihood

RSD, relative standard deviation

S, sulphur

(method) S refers to the sealed-jar methods

(Fertitype) S refers to synthetic fertilizers

S/S^- refers to the sealed-jar method without the use of acetylene during the anoxic phase

S/S^+ refers to the sealed-jar method with the use of acetylene during the anoxic phase

SD_f is the standard deviations of cumulative N_2O emissions from the fertilized plot

SD_c is the standard deviations of cumulative N_2O emissions from the control plot

SDG, sludge

SF, synthetic fertilizer

SM, solid (animal) manure

SMC, sheep manure compost

SM-S, solid manure combined with S

SOC, soil organic carbon

SOM, soil organic matter

TAP, total annual precipitation

V_{EF}, the variance of EF

VFA, volatile fatty acids

WEOC, water extractable organic carbon

WFPS, water-filled pore space

WSR, wheat straw residues

WW, waste water

LIST OF EQUATIONS

Equation (1) **Emission factor of nitrous oxide from fertilized/manured soils** **p. 31** **p. 73**

$$EF = \frac{N_2O\text{-}N_{fertilized} - N_2O\text{-}N_{unfertilized}}{N_{input_{fertilized}} - N_{input_{unfertilized}}}$$

Equation (2) **Variance of EF** **p. 33**

$$V_{EF} = \left(100/N_{input_{fertilized}}\right)^2 \times \left({SD_f}^2/n_f + {SD_c}^2/n_c\right)$$

Equation (3) **The weighted REML function with spatiotemporal coverage of N_2O** **p. 36**

$$N_2O_{cov}Weight_i = SamplingEvent_i \times GasSurface_i$$

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$$\text{revised-Weight}_i = N_2O_{cov}Weight_{max} \times \left[1 + \left(\frac{N_2O_{cov}Weight_i}{N_2O_{cov}Weight_{max}}\right)/1000\right]$$

Equation (5) **Regression function to predict N_2O EF of crop residues** **p. 46**

EF (% of N applied) = EXP[-0.706*ln(C/N ratio + 1) + k)-1]

Equation (6) **Soil-surface gaseous fluxes** **p. 71**

$$F_{gas} = \frac{dC_{gas}}{dt} \times \frac{V}{M} \times \frac{Mm}{Mv}$$

Equation (7) **Biological stability index of an organic amendment** **p. 109**

BSI = 211.2 – (2.009 x % SOL) – (2.378 x % HEM) + (0.840 x % LIG) – (2.216 x % CF)

LIST OF APPENDICES

GENERAL INTRODUCTION

Nitrous oxide (N_2O) is the 4th most important contributory anthropogenic factor to atmospheric warming (Foster et al., 2007). Moreover, this greenhouse gas is currently the dominant ozone-depleting substance and is not regulated by the Montreal protocol (Ravishankara et al., 2009). Anthropogenic activities since the Industrial Revolution and agricultural intensification since the Green Revolution have led to greater use of fertilizer and manure, which strongly contribute to the continuing increase of atmospheric N_2O concentrations (Davidson, 2009). In Canada, agricultural soils alone represent 55% of total agricultural N_2O emissions (Helgason et al., 2005).

The ever-increasing costs of synthetic fertilizers for crop production have increased interest in recycling nutrients present in organic by-products (Larney and Pan, 2006). Organic amendments (OAs) are soil physical conditioners and a valuable source of plant-available nutrients, and include livestock manures and slurries, as well as, urban waste composts, composts from on-farm organic residues or green waste and food industries (Chaves et al., 2005). The increased use of OAs in agricultural systems is a logical way to recycle organic wastes from farms, industries and municipalities, while reducing costs related to the use of synthetic fertilizers. However, some OAs are more susceptible to nitrogen (N) loss than synthetic fertilizers and their use could enhance soil N_2O emissions. The ready metabolism of OAs by soil microorganisms is key to understanding the pattern and rate of N_2O emission from soils receiving OAs. Microbially-mediated reactions in agricultural soils are the dominant source of N_2O, mainly from nitrification and denitrification, although other microbial metabolic pathways are involved in N_2O formation or consumption (Butterbach-Bahl et al., 2013).

Generally, nitrification contributes to N_2O production under aerobic conditions and denitrification is the predominant reaction under anaerobic conditions (Wrage et al., 2001). Nitrification is the conversion of ammonium (NH_4^+) to nitrite (NO_2^-) and then nitrate (NO_3^-). Denitrification is the reduction of soil NO_3^- to the following N gases: nitric oxide (NO), N_2O and dinitrogen (N_2). Nitrous oxide produced from nitrification requires sufficient soil NH_4^+, while N_2O resulting from denitrification is a free intermediate compound controlled by the availability of carbon (C), NO_3^- and other N oxides because it is an alternative anaerobic process to aerobic respiration (Hénault and Germon, 1995).

Like fertilizers, OAs contain mineral forms of N (NH_4^+ or NO_3^-) that are immediately available for soil nitrifiers and denitrifiers after their addition. In addition, mineralization of organic N contained in OAs releases ammonium (NH_4^+), with subsequent nitrification (NO_3^-) processes leading to N_2O production. As an organic C substrate for microbial growth, OAs may also stimulate microbial N assimilation, which can increase competition for NH_4^+ between heterotrophic microorganisms and autotrophic nitrifiers (Chen et al., 2013), resulting in temporary reduction of N_2O production. Under anaerobic conditions, organic C provided by OAs enhances denitrification and N_2O production (Miller et al., 2008). Finally, OAs modulate O_2 availability in soil microsites because the labile C input enhances soil respiration; as well, animal slurries reduce gas diffusivity by saturating soil micropores in the short-term. Given the multiple ways that OAs impact the activity of microorganisms involved in N_2O production, their influence on soil N_2O emissions cannot be predicted from simple measures such as the total N application rate, which is a reasonably good estimator in the case of synthetic fertilizers (Kim et al., 2008).

For greenhouse gas inventory purposes, the Intergovernmental Panel on Climate Change (IPCC) recommends using the fertilizer-induced emission factor (EF_1) as the worldwide default value, regardless of the fertilizer source. The EF_1 is estimated to be a loss of 1% of fertilizer N and was derived from published data regarding gaseous losses from soils amended with synthetic N fertilizers (Bouwman et al., 2002). Calculating the contribution of agricultural soils to national N_2O using the Tier 1 IPCC methodology (EF_1) can result in erroneous conclusions (overestimation or underestimation of emissions) because it does not account for the additional biochemical reactions (decomposition, mineralization, and immobilization) associated with fertilizer sources. In the past two decades, numerous field studies reported emission factors of OAs that differed from EF_1 by orders of magnitude, equal to or less than 0.03% (Lemke et al., 1999; Chantigny et al., 2001; Baggs et al., 2002; Wulf et al., 2002; Ball et al., 2004; Dittert et al., 2005; Thorman et al., 2007; Bhandral et al., 2008; Chantigny et al., 2010; Dalal et al., 2010; Velthof et al., 2011; Ding et al., 2013; Abalos et al., 2012; Collins et al., 2011; Li et al., 2013a; Senbayram et al., 2014) or superior to 3% (Hansen et al., 1993; Chang et al.,1998; Tilsner et al., 2003; Ball et al., 2004; Meijide et al., 2007; Mkhabela et al., 2008; Chantigny et al., 2010; Wei et al., 2010; Velthof et al., 2011; Pelster et al., 2012; Carmo et al., 2013; Aita et al., 2014; Senbayram et al., 2014). However, at the time that EF_1 was adopted, there was insufficient information about gaseous N losses from organic materials to specify an EF for OAs. As signatory countries to the United Nations Framework Convention on Climate Change move to define region- and site-specific EF values (Tier 2 and Tier 3 methodologies) for calculating the N_2O emissions from their agricultural soils, the lack of quantitative information on how OAs contribute to N_2O emissions emerges as a research gap of global significance. One way to determine EF for OAs would be to compile and analyse a global database from field studies where OAs were applied and N_2O emissions measured from agricultural soils.

Given that an EF for OAs cannot be determined readily from field studies with diverse OA sources, climate conditions (Butterbach-Bahl et al., 2013), soil properties (Drury et al., 2004; Pelster et al., 2012) and agricultural management practices (Drury et al., 2004; Velthof and Mosquera, 2011), the mechanistic basis for OA contribution to N_2O production should be determined in controlled laboratory studies. In soils mixed with OA under controlled conditions, the N_2O emissions generally increased with increasing mineral N content, water-soluble organic C, VFA and with decreasing C/N ratio and lignin content (Paul and Beauchamp, 1989a; Lou et al., 2007; Huang et al., 2004; Chaves et al., 2005; Velthof et al., 2003; Velthof and Mosquera, 2011). Accordingly, high N_2O emissions were associated with OA containing high levels of inorganic N and easily decomposable N and C, such as pig (Velthof et al., 2003) and sheep slurries (Cardenas et al., 2007) and N-rich crop residues (Chaves et al., 2005). Generally, the addition of OAs with C/N ratio > 20 results in temporary net nutrient immobilization (Enwezor, 1976), although this is modulated by the chemical nature of the organic C compounds within the OA. Water-soluble organic C could directly stimulate denitrification because it is quickly decomposed (Hadas et al., 2004), whereas complex polymers such as lignin and ligno-cellulose are less likely to be short-term predictors of denitrification because they undergo slow decomposition (Vanlauwe et al., 1996). Mixing materials having a high C/N ratio (wheat straw residues, saw dust, composts) with manure, slurries or N-rich crop residues also reduced soil N_2O emissions (Huang et al., 2004; Chantigny et al. 2001) although contrasting results have been reported by Li et al. (2013a). Consequently, it is difficult to make generalizations; even under controlled conditions, the potential of OAs to induce soil N_2O emissions (POA-N_2O) is affected by many other factors including soil type, the duration of the experiment and O_2 availability during the incubation (Bertora et al., 2008; Cabrera et al., 1994a; Flessa and Beese, 2000; Helgason et al., 2005; Lou et al., 2007; Velthof et al., 2003). Thus, there is a need to determine how experimental conditions affect soil N_2O emissions following application of OAs and provide recommendations for a standard methodology to assess POA-N_2O.

The global objective of this study was to assess the significance and contribution of OA type and chemical properties on net N_2O emissions from agricultural soils.

The specific objectives were:

Objective 1: conduct a meta-analysis of soil N_2O experiments where OAs were applied to agricultural soils in field conditions to compare EF for OAs and OAs combined with synthetic fertilizers at the global scale, to categorize the global EF according to OA types and properties, and to determine how the global EF for OAs was influenced by environmental and management-related factors.

Hypothesis 1-i. The global EF for OAs is lower than EF_1 and that the global EF for OAs could be refined according to OA types.

Hypothesis 1-ii. Other main modulators of global EF are soil texture and climatic factors.

Objective 2: determine how experimental conditions affect soil N_2O emissions following application of OAs and select an appropriate incubation method to measure the POA-N_2O on a wide range of OAs with contrasting chemical properties.

Hypothesis 2-i. Varying soil redox potentials during the incubation provides better estimates of POA-N_2O than under a constant redox potential regime.

Hypothesis 2-ii. The sealed-jar method is the most appropriate method for routine measurement of the POA-N_2O under controlled conditions.

Objective 3: conduct a three-wk incubation to assess the immediate (P1), short- (P2) and medium-term (P3) POA-N_2O, and then, relate P1, P2, and P3 to the physico-chemical characteristics of more than 131 OAs.

Hypothesis 3-i. P1 will be correlated to available C (water-extractable organic C and volatile fatty acids), and mineral N (NO3- and NH4+) contents of OAs, while P3 will be correlated to C/N and Lignin/N ratios of OAs.

Hypothesis 3-ii. Significant differences will be detected in POA-N_2O estimates among OA categories with the lowest and the highest POA-N_2O attributed to the composts and the liquid manure, respectively.

FORWARD TO CHAPTER 1

Chapter one is a literature review discussing the influence of OA properties on net N_2O emissions following the application of OAs to agricultural soils. The review examines the multiple roles of OAs in the microbially-mediated reactions leading to N_2O production, the physico-chemical composition and diversity of OAs applied to agricultural soils, soil N_2O emission responses to OA properties in field and controlled conditions, land application of organic amendments, and the other factors that contribute to N_2O production in agricultural following OA addition.

CHAPTER 1 - LITERATURE REVIEW

1.1 Abstract

Given the multiple ways that OAs impact the activity of microorganisms involved in N_2O production, their influence on soil N_2O emissions cannot be predicted from simple factors such as the total N application rate. The effects of OA properties on soil N_2O emissions are affected by other important environmental and biological factors, such as climatic conditions (temperature, precipitation), soil properties (texture and organic C content), and management practices. Comparison of individual studies is difficult because variable amounts and nutrient concentrations of OAs were applied, different application techniques were employed, and the duration of individual experiments varied; however, liquid OAs containing high amounts of labile N and C with low C/N ratios (<15) appeared to be at equal risk or more risky than synthetic fertilizers, while more stabilized OAs containing higher lignin content or higher C/N ratio appear to be at lower risk than synthetic N sources.

1.2 Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas, with 298 times the global warming potential of carbon dioxide (CO_2) (Forster et al., 2007). Nitrous oxide is also a major source of ozone-depleting nitrogen oxides (NO and NO_2) in the stratosphere (Ravishankara et al., 2009). Agricultural sources of N_2O make a prominent contribution to the global budget with 23–31% of all global N_2O sources related to nitrogen (N) fertilizer use and manure management (4.3– 5.8 Tg N_2O–N yr^{-1}) (Syakila et al., 2011).

In Canada, animal production contributes to more than half of the agricultural greenhouse gas emissions, taking into account the 300 Mt of manure applied each year to Canadian croplands, including managed grasslands (Kebreab et al.,2006; Coote and Gregorich, 2000). Total Canadian N_2O emissions from agricultural sources averaged 58.1 Gg N_2O-N yr^{-1} between 1990 and 2005 and 68% were attributed to direct emissions, i.e., when N_2O is emitted directly to the atmosphere from cultivated soils and fertilized and/or grazed grassland systems (Rochette et al., 2008b). More specifically, organic-N sources contributed one third of the total emissions from agricultural soils (Rochette et al., 2008b), caused by difficulties in synchronizing N supply and crop N uptake (Snyder et al., 2014).

Organic amendments (OAs) include livestock manures and slurries, i.e., the decomposed mixture of dung and urine of farm animals along with litter, crop residues (green manure), composts (from on-farm organic residues, urban waste, green waste and food industries), biosolids and sludges (sewage, paper mill) (Baggs et al., 2000; Yang et al., 2002; Chaves et al., 2005; Cogger et al., 2006; Velthof et al., 2010; Gonzalez-Rosas et al., 2012; Velthof et al., 2015). Organic amendments are soil physical conditioners in agriculture and a valuable source of plant-available nutrients such as N. However, their mismanagement leads to water quality problems and air pollution while increasing *N* loss to the environment, e.g., nitrate leaching and N gas emissions (Fig.1).

For greenhouse gas inventory purposes, the Intergovernmental Panel on Climate Change (IPCC) recommends using the fertilizer-induced emission factor (EF_1) as the worldwide default value, regardless of the fertilizer source. The EF_1 is estimated to be a loss of 1% of synthetic fertilizer N and was derived from published data regarding gaseous losses from soils amended with synthetic N fertilizers (Bouwman et al., 2002). However, contradictory results that have been reported in many yield studies suggest that N_2O emissions from manured soils can be higher than, equal to, or lower than those observed from soils receiving N fertilizers (Helgason et al., 2005; Ellert and Janzen, 2008; Rochette et al., 2008c). Nitrous emission responses to manure application often correlate with manure types (liquid vs. solid; swine, dairy or beef cattle, sheep) and chemical composition (C and N content and availability, C/N ratio) (Chantigny et al., 2013; Helgason et al., 2005; Li et al., 2013a), although this is not always the case (Li et al., 2013b; Rochette et al., 2008c). Indeed, the magnitudes and patterns of soil N_2O emissions are strongly influenced by factors other than the chemical properties of OAs, such as climate, soil properties and management practices (Baggs et al., 2000; Ball et al. 2004; Rochette et al., 2008c; Bhandral et al., 2008; Pelster et al., 2012). Although considerable progress has been made in understanding the influence of OA properties on soil N_2O emissions from agricultural fields, we still cannot reliably predict N_2O emission factors from agricultural soils following OA application.

This literature review discusses the multiple roles of OAs in the microbially-mediated reactions leading to N_2O production, the physico-chemical composition and diversity of OAs applied to agricultural soils soil N dynamics, soil N_2O emission responses to OA properties in field and controlled conditions, and the influence of other factors controlling N_2O emission following land application of organic amendments.

1.3 The multiple roles of OAs in the microbially-mediated reactions leading to N_2O production

OAs have multiple roles in the microbially-mediated reactions leading to N_2O production (Fig. 2). Mineralization of organic N contained in OAs releases ammonium (NH_4^+), with subsequent ammonia oxidation and nitrification producing gaseous N losses and yielding NO_3^- that is susceptible to reactions that lead to N_2O production. As an organic C substrate for microbial growth, OAs may also stimulate microbial N assimilation, which can increase competition for NH_4^+ between heterotrophic microorganisms and autotrophic nitrifiers (Chen et al., 2013), resulting in temporary reduction of N_2O production. In soils with high N availability but low organic C, OAs may stimulate nitrifier denitrification, the oxidation of ammonia to nitrite (NO_2^-) and its subsequent reduction to NO and N_2O by autotrophic ammonia oxidizing microorganisms under low O_2 availability (Butterbach-Bahl et al., 2013). In anaerobic conditions, organic C provided by OAs enhances denitrification. The ratio of N_2O to N_2 produced during denitrification increases with increasing soil NO_3^- availability, which is influenced by the microbial consumption and production of NO_3^- due to C and N substrate availability in OA-amended soils (Terry et al., 1980; Weier et al., 1993; Miller et al., 2008). Finally, OAs modulate O_2 availability in soil microsites because the labile C input enhances soil respiration and some, such as animal slurries, reduce gas diffusivity by saturating soil micropores in the short-term. As a result, the direct impact of OAs on soil N_2O emissions is related to their mineral N content, while the indirect impact involves organic matter decomposition and mineralization in soils (Horwath, 2007).

In agricultural soil ecosystems, organic matter in decomposition also includes organic inputs from the addition of livestock manures, slurries, sludge or compost for agronomic purposes (Horwath, 2007). The degradation of these organic inputs is accompanied by the synthesis of new compounds (Sorensen, 1972). In fact, soil heterotrophic microorganisms use organic carbon as a nutrient and energy source involved in soil respiration and nitrogen mineralization (Fontaine et al., 2003). Soil organic matter (SOM) is made up of decayed organic materials (plant residues, livestock by-products, soil microorganisms, soil fauna) and the by-products of decomposition causing humification which consists of the production of humic substances resulting from oxidation and hydrolysis reactions of organic compounds leading to new chemical compounds with increased C and H and lower O content compared to the original materials (Horwath, 2007; Zech et al., 1997). Humified carbon decomposes slowly because the acquisition of energy by soil microorganisms from such substrate is slow (Fontaine et al., 2003). Fresh organic matter (FOM) is defined contrary to SOM and is composed of organic amendments added into cultivated soils, such as green manure or straw. FOM incorporation enhances SOM mineralization (Fontaine et al., 2003). Organic inputs into soil actually induce a short-term change in SOM turnover called the "priming effect" by Bingeman et al. (1953) and determined by concomitant changes in carbon dioxide (CO_2) efflux rates or N mineralization rates (Jenkinson et al., 1985; Kuzyakov, 2000). The quantity and quality of OA and microbial turnover determine the outcome of decomposition processes in soils (Horwath, 2007). For example, the addition of easily assimilated compounds into soils (glucose, fructose and mineral nutrients) have little or no effect on SOM mineralisation, contrary to the effect of ryegrass, cellulose or wheat straw (Bingeman et al., 1953; Dalenberg and Jager, 1989; Wu et al., 1993; Shen and Bartha, 1997). Indeed, Blagodatskaya and Kuzyakov (2008) mentioned that the addition of fresh available substrates to soil promotes an apparent priming effect, such as a rapid increase in soil respiration caused by a triggering effect[1] (several minutes to hours) or a pool substitution with an acceleration of microbial turnover (several days or weeks). Conversely, as reported by Jenkinson et al. (1985), FOM with a large C/N ratio induced real acceleration of SOM mineralization. Indeed, microbial responses to the addition of C-rich substrates, without N, result in decomposing SOM to acquire N with production of a real priming effect in using "the energy of most available compounds to synthesize enzymes hydrolyzing the low available compounds". Blagodatskaya and Kuzyakov (2008) reported that easy C sources in decomposition (glucose, fructose and alanine) induce a greater priming effect than less available substrates such as plant residues, manure or slurry. Moreover, availability of easy carbon and nitrogen sources influence the preferential substrate utilization of organic matter (the FOM versus the SOM) by the soil microbial community (Blagodatskaya and Kuzyakov, 2008). Indeed, if N is lacking when carbon sources are added, microorganisms supplement this shortage by increasing SOM decomposition. Conversely, most changes in N mineralization following N inputs into soil should be considered as apparent priming effects due to N displacement reactions or pool substitution. For example, in sandy soils incubated in controlled conditions, Zhu-Backer et al. (2015) noticed that 2.4 times more N_2O emitted was derived from synthetic N sources when chemical fertilizers was applied with green waste compost rather than applied alone. However, N_2O derived from soil N was suppressed by compost application.

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[1] Kuzyakov et al. (2003) define the triggering effect as "an acceleration of internal microbial metabolism with quick increase in the respiratory activity promoted by trace amounts of substrate".

1.4 The physico-chemical composition and diversity of OAs applied to agricultural soils

Composition of OAs is highly variable compared to that of synthetic N fertilizers. Carbon and N components of solid manures (SM) are influenced by animal type (Chadwick, 1999), feed (Cardenas et al., 2007; Velthof et al., 2005), and by the manure management system (Chadwick, 2005). For example, poultry manures have a lower C/N ratio than other manure types (Aulakh et al., 2000) and alteration of the legume vs. non legume proportion in the animal diet modulated sheep manure C/N ratio accordingly (Cardenas et al., 2007). Liquid and solid management systems produce manures with contrasting chemical characteristics. Liquid manures (LM) generally contain less bedding materials than solid manure (SM), resulting in lower C/N ratios (Rochette et al., 2008c). Solid-liquid separation concentrates the dry matter, C content, and fibre fractions in the solid fraction, leaving a large proportion of the simple organic compounds that are readily degraded by soil microorganisms in the liquid fraction (Bertora et al., 2008). Conversely, anaerobic digestion of LM reduces dry matter, C content, and fibre fraction but results in an incomplete decomposition and produces volatile fatty acids (VFA), a C source for soil denitrifiers (Paul and Beauchamp, 1989a; Kirchmann and Lunwall, 1993). The storage of farm manure (FM), i.e., the decomposed mixture of dung and urine of farm animals along with litter, may partially or completely compost the material, depending on how long the FM is stockpiled, to what depth the manure pile is built, and whether the pile is aerated or not (Chadwick, 2005; Guo et al., 2012). Composting is a thermophilic decomposition process that degrades raw organic materials to CO_2, resulting in an immobilization of inorganic N and in production of stable organic matter (Yang et al., 2002; Nada, 2015). Chemical and physical properties of composts applied to soil vary according to the organic matter source and composting conditions (Yang et al., 2002; Guo et al., 2012; Nada, 2015).

1.5 Soil N_2O emission responses to OA properties in field and controlled conditions

In soils mixed with OA under controlled conditions, the N_2O emissions generally increased with increasing mineral N content, water-soluble organic C, VFA and with decreasing C/N ratio and lignin content (Paul and Beauchamp, 1989a; Velthof et al., 2003; Huang et al., 2004; Chaves et al., 2005; Lou et al., 2007; Velthof, G.L., Mosquera, 2011). Accordingly, high N_2O emissions were associated with OA containing high levels of inorganic N and easily decomposable N and C, such as pig (Velthof et al., 2003) and sheep slurries (Cardenas et al., 2007) and N-rich crop residues (Chaves et al., 2005). Generally, addition of OAs with C/N ratio > 20 result in temporary net nutrient immobilization (Enwezor, 1976), although this is modulated by the chemical nature of the organic C compounds within the OA. Water-soluble organic C is quickly decomposed (Hadas et al., 2004), whereas complex polymers such as lignin and ligno-cellulose undergo slow decomposition (Vanlauwe et al., 1996). Mixing materials having a high C/N ratio (wheat straw residues, saw dust, composts) with manure, slurries or N-rich crop residues also reduced soil N_2O emissions (Chantigny et al., 2001; Huang et al., 2004). However, Li et al. (2013b) reported that the C/N ratio of plant residues was not a good predictor of OA-induced N_2O emissions even if net N mineralization was correlated to the C/N ratio of plant residues. Moreover, plant material addition affected soil N_2O emissions differently under aerobic and oxygen(O_2)-limited conditions, which confirmed POA-N_2O is not directly related to the net N mineralization potential of OAs (Li et al., 2013b). This is likely due to (1) inorganic N content of OAs directly available to soil nitrifiers and denitrifiers, and to (2) the fact that the net

N mineralization from an OA declines with time as readily-mineralizable organic N substrates are depleted, and denitrifiers would compete with other heterotrophic microorganisms for a limited amount of NO_3^- and soluble C (Marschner et al., 2015). Consequently, it is difficult to make generalizations; even under controlled conditions, the POA-N_2O is affected by many other factors including soil type, OA characteristics, the incubation duration and O_2 availability during the incubation (Cabrera et al., 1994b; Flessa and Beese, 2000; Velthof et al., 2003; Helgason et al., 2005; Lou et al., 2007; Bertora et al., 2008).

In previous field studies, emission factors for animal slurries varied from 0.009% to 7.0% of N applied (Chantigny et al., 2001; Vallejo et al., 2006; Meijide et al., 2007; Meijide et al., 2009; Chadwick et al., 2010; Chantigny et al., 2010; Sanchez-Martin et al., 2010; Tenuta et al., 2010; Velthof et al., 2011; Aita et al., 2014; Plaza-Bonilla et al., 2014; Senbayram, 2014). Combined with synthetic N sources, EF for animal slurries in field experiments underwent higher variations ranging from -0.18% to more than 11%, according to animal type and application technique (Dittert et al., 2005; Chantigny et al., 2010; Collins et al., 2011; Velthof et al., 2011; Abalos et al., 2012). EF for anaerobic digested slurries varied depending on their type and were equal to 0.9%, 0.1%, 0.05%, and -0.014% for anaerobically digested thin pig slurry fraction, pig slurry (liquid fraction), dairy effluent, and digested fiber, respectively (Meijide et al., 2009; Collins et al., 2011). The EF of composts reported in previous field experiments were generally lower than other OAs and varied from -0.85% to 1.1% of N applied (Thorman et al.,2007; Meijide et al., 2009; Dalal et al., 2010; Cai et al., 2013; Ding et al., 2013). In a 2-yr field experiment conducted on a fine-textured soil, EF of synthetic N fertilizers, raw pig slurry, paper sludges, and pig slurry-derived biosolids were equal to 4.2%, 2.5%, 0.9%, and -.04% of N applied, respectively (Chantigny et al., 2013).

OAs with large amounts of labile C and available N, such as liquid dairy cattle, liquid swine, or poultry manure, generally increased soil N_2O production rates more than mineral fertilizers (Loro et al., 1997; Petersen, 1999; Rochette et al., 2000; Velthof et al., 2003; van Groenigen et al., 2004; Dong et al., 2005; Gregorich et al., 2005) but not always (Lopez-Fernandez et al., 2007; Chantigny et al., 2010). Labile C and mineral N content of manures were positively correlated to N_2O emission rates according to Chadwick et al. (2000), Rochette et al. (2004), and Velthof and Mosquera (2011), but contrasting results have been reported by other authors (Chantigny et al., 2007; Sanchez-Martin et al., 2010). These inconsistencies may be related to other factors affecting microbial communities and C and N mineralization rates such as soil properties, climate and management practices (Baggs et al., 2000; Ball et al., 2004; Bhandral et al., 2008; Rochette et al., 2008).

1.6 Land application of organic amendments and other N_2O controlling factors

1.6-1. Impact of climatic factors

Numerous field studies reported the significant impact of rainfall on soil N_2O emissions (Ball et al., 2004; Rochette et al., 2004; Baggs et al., 2000). This impact was of major importance when rainfall occurred shortly after the application of mineral N, as noted by Ball et al. (2004) who reported the highest N_2O flux recorded (up to 4.9 kg N ha^{-1} d^{-1}) caused by heavy rainfall subsequent to NPK fertilizer application in silage grass production. The potential of pig slurry to induce soil N_2O emissions was also subject to high modulation by rainfall and climatic conditions, because it contains high amount of NH_4^+ that are rapidly nitrified and subject to denitrification in presence of easily available C from slurry (Rochette et al., 2004). Abundant rainfall may also impact N_2O emissions from soils receiving OAs on a longer term, following their mineralization and the release of NO_3^- into the soil, as noted by Velthof et al. (2003) in controlled conditions simulating dry-wet soil cycles. During winter and spring, soil freeze/thaw events create anaerobic zones in soils with high water content and the formation of ice layers, and may promote N_2O peaks which usually last for several days (Christensen and Tiedje, 1990). Despite its limited duration, the phenomenon represents a significant fraction of the total annual emissions from agricultural lands (Wagner-Riddle and Thurtell, 1998) and may exceed 50% of the annual emissions (Flessa et al., 1995). Indeed, N_2O emissions from liquid dairy manure-amended soils have been reported by Singurindy et al. (2009) at soil temperatures below 0° C and continued even after complete soil freezing. Chantigny et al. (2002) demonstrated that pig slurry and alfalfa residues stimulated more soil microbial activity during thaw events compared to maize residues and cattle manure and the differences were partly explained by the low C/N ratio of those OAs. Nitrogen transformations occurred in soils during winter and nitrification has been reported in soil below zero (Chantigny et al., 2002). Climatic factors modulate the potential of OAs immediately after their application, during the growing season, as well as during the non-growing season. Precipitations or freeze/thaw events increased the potential of OAs to emit soil N_2O because O_2 movement decreases in soil at higher moisture contents and the addition of OAs increases the O_2 demand during oxidation of readily available C. Even if upland soils rarely reach moisture conditions that exceed the optimum for N_2O emission, a decline in N_2O emissions has been reported under very wet soil conditions, possibly owing to the rapid initialization of strictly anaerobic conditions, resulting in the formation of N_2 (Butterback et al., 2013). Thus, the interactions between rainfall and OAs regarding soil N_2O emissions could be positive or negative.

Denitrification rates are also affected by rising temperature, because of temperature-sensitive enzymatic processes. Indirectly, temperature-induced increases in soil respiration promote soil anaerobiosis. However, it is difficult to draw conclusions by comparing independent studies because temperature is often confounded by other modulators in field conditions, such as irrigation practices and application methods of OAs (Vallejo et al., 2005; Meijide et al., 2007; Aïta et al., 2014).

1.6-2. Impact of soil properties

Soil organic carbon (SOC), is another soil parameter implicated in soil N_2O emissions (Giles et al., 2012). Soil N_2O emissions are often limited by soil C availability. In low-C soils, for example, N_2O emission rates were found to be correlated with soluble organic C, whereas emission rates in C-rich soils were correlated with NO_3^- availability (Pelster et al., 2012). Based on field experiments, Pelster et al. (2012) suggest that, compared with synthetic N sources, manure application only increase soil N_2O flux in soils with low C content. Several studies reported that soil texture impacted the potential of OAs to induce soil N_2O emissions. For example, compost application in sandy soils increased N_2O emitted from both heterotrophic denitrification and ammonia oxidation, but not in clay loam soil, probably due to the high capacity of fine-textured soil to buffer changes in biochemical properties such as nitrifier activity or pH (Zhu-Backer et al., 2015).

Soil pH influenced N_2O production pathways. Goodroad and Keeney (1984) and Mørkved et al. (2007) noted that the N_2O product ratios of nitrification ($N_2O/(NO_2^- + NO_3^-)$) is lower in alkaline than in acid soils. The increased soil pH due to the addition of OAs can lead to NO_2^- accumulation (Hawkins et al., 2010), which promotes N_2O production from NH_4^+ via nitrifier denitrification (Zhu et al., 2013a).

1.6-3. Impact of management practices

On both grassland and cropland, incorporation of OAs, especially pig slurry (injection) increased the average emission factor of N_2O in comparison to surface application (Chantigny et al., 2010; Velthof and Mosquera, 2011; Aïta et al., 2014). In field experiments, the potential of crop residues to induce soil N_2O emissions was also highly modulated by tillage practices and the combined application with synthetic N sources. Particular attention should be accorded to mulching of legume species (Nadeem et al., 2012), to incorporation of non-legume species as green manure when amended with farm manure simultaneously with conventional tillage (Koga N., 2013), and managed grasslands, particularly when fertilized simultaneously with ploughing (Mori and Hojito, 2007; Velthof et al., 2010). Tillage has also been proven to decrease emissions with a 2-to-3-fold reduction of N_2O emissions using full inversion tillage rather than chemical fallow for equivalent soil NO_3-N in a poorly drained soil (MacDonald et al., 2011).

1.7 Conclusions

Nitrous oxide EFs of OAs differ from EFs of synthetic fertilizers, and can be lower or higher than the EF_1 IPCC default value. Liquid OAs containing high amounts of labile N and C with low C/N ratios (<15) appear to be at equal or higher risk of N_2O emissions than synthetic fertilizers, while more stable OAs containing more lignin or having higher C/N ratios appear to be at lower risk than synthetic N sources. The variability in EF of OAs from agricultural fields is confounded by environmental and management-related factors. Key factors appear to be soil properties, climatic conditions and management practices such as tillage and application techniques. Improved emission inventories require information about the potential of OAs to induce soil N_2O emissions (POA-N_2O) and about the relationship between POA-N_2O and the chemical characteristics of OAs.

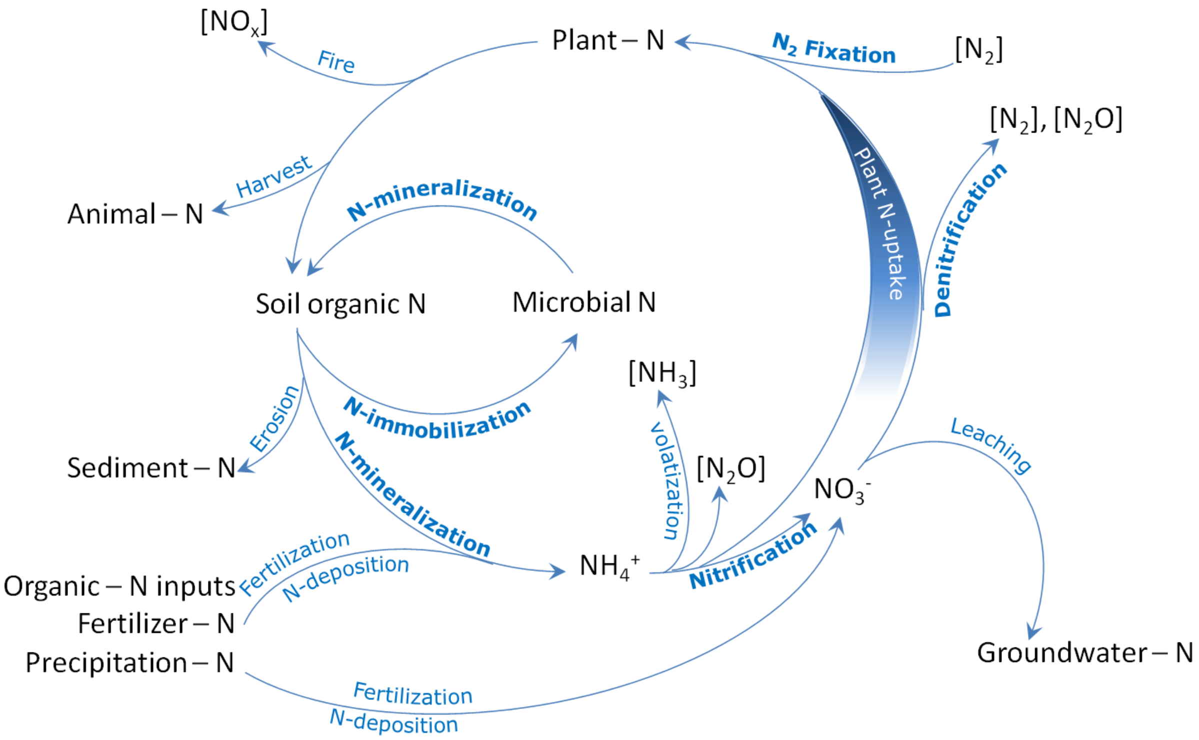

Figure 1. Schematic representation of the terrestrial nitrogen cycle.

Figure adapted from Robertson and Groffman, 2007.

Processes mediated by soil microbes appear in bold and gases appear in brackets.

NH_4^+, ammonium
NH_3, ammonia
NO_3^-, nitrate
NO_2^-, nitrite
N_2O, nitrous oxide
NO_x, nitrogen oxides
N_2, dinitrogen

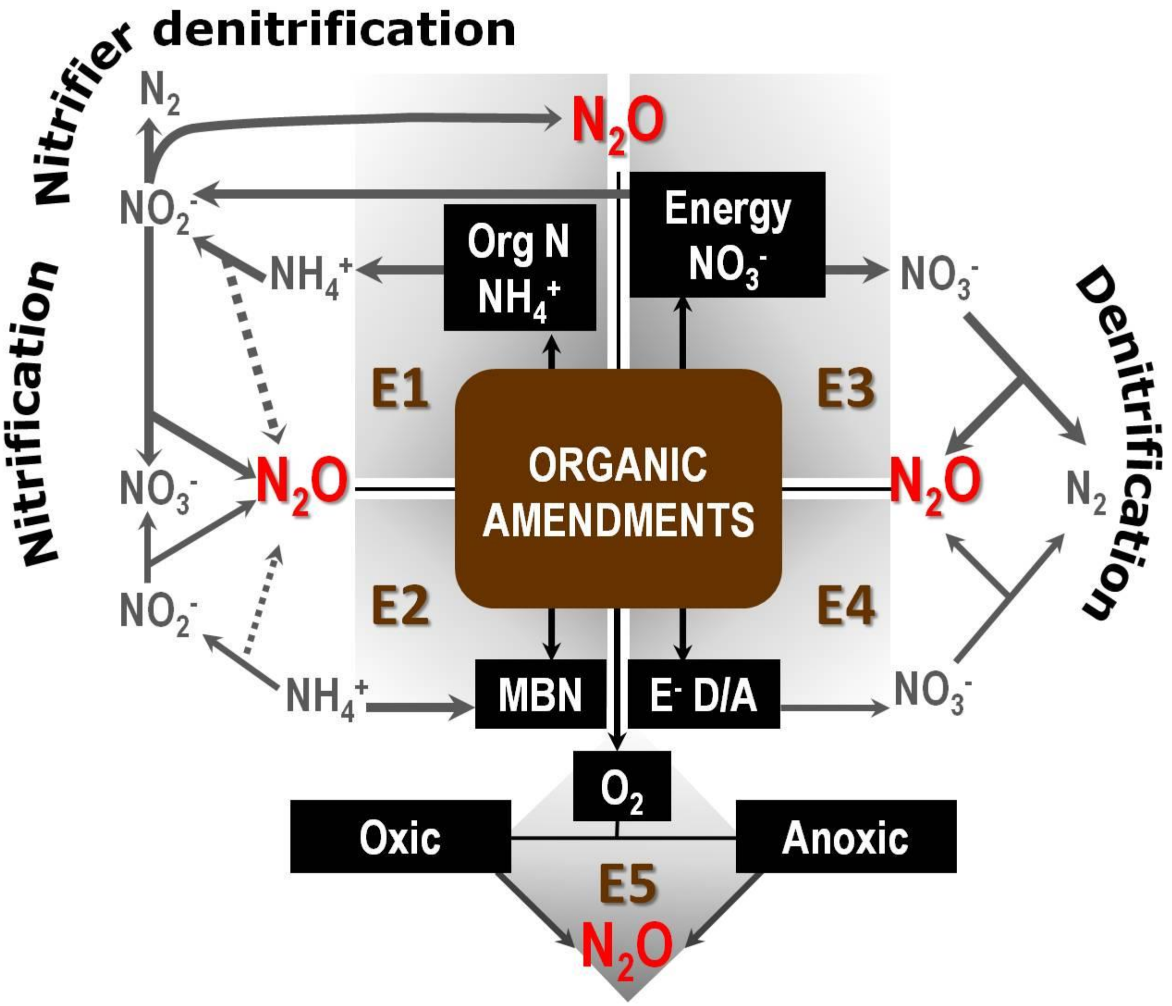

Figure 2. The multiple roles of organic amendments in the microbially-mediated reactions leading to N_2O production.

Figure adapted from Chen et al, 2013.

Org N, organic forms of nitrogen; NH_4^+, ammonium; NO_3^-, nitrate; NO_2^-, nitrite; N_2O, nitrous oxide; N_2, dinitrogen; MBN, microbial biomass nitrogen; E^- D/A, oxidation / reduction potential

Five major effects (positive or negative) of organic amendments on soil N_2O production

(E1) + Stimulate mineralization of organic N
(E1) - Stimulate microbial N assimilation
(E2) + Stimulate ammonia oxidation and nitrification
(E3) + Increase denitrification rate from organic C substrate addition
(E4) +/- Alter the denitrification ratio of N_2O to N_2 (relative abundance of organic C and nitrate)
(E5) + Modulate O_2 availability in soil microsites (increased water content and soil respiration)
(E1) (E4) (E5) + Stimulate nitrifier denitrification (under low O_2 and C but high N availability)

FORWARD TO CHAPTER 2

The literature review revealed that emission factor of N_2O (EF) of OAs differs from EF of synthetic fertilizers (SF), and can be lower or higher than the EF_1 IPCC default value. Liquid OAs containing high amounts of labile N and C with low C/N ratios (<15) appear to be at equal or higher risk of N_2O emissions than synthetic fertilizers, while more stable OAs containing more lignin or having higher C/N ratios appear to be at lower risk than synthetic N sources. The variability in EF of OAs from agricultural fields is confounded by environmental and management-related factors. Key factors appear to be soil properties, climatic conditions and management practices such as tillage and application techniques. These hypotheses can be tested using meta-analysis techniques. The objective of this work was to conduct a meta-analysis of soil N_2O experiments where OAs were applied to agricultural soils in field conditions to quantify the effect of OA type on the global N_2O EF, and to identify other main controlling environmental and management-related factors.

CHAPTER 2

Global nitrous oxide emission factors from agricultural soils after addition of organic amendments: a meta-analysis.

2.1 Abstract

Agricultural soils receiving synthetic fertilizers and organic amendments containing nitrogen (N) contribute a large part to anthropogenic nitrous oxide (N_2O) emissions. As a source of nitrate that undergoes reduction to N_2O, organic amendments also change soil C availability and redox potential, which influences the N_2O emission factor (EF) of organically-amended soils. The objective of this study was to conduct a meta-analysis of N_2O EF from agricultural soils receiving organic amendments. A global survey of peer-reviewed literature resulted in the selection of 38 studies including 422 observations at 43 sites in 12 countries. The analysis yielded a global EF for all organic sources, EF_{org}, equal to 0.57 ± 0.30%, which is lower than the IPCC default EF of 1 for synthetic fertilizer. Three groups of organic amendments with similar EFs were identified: the high-risk group including animal manures, waste waters and biosolids (1.09 ± 0.17%); the medium-risk group including composts + fertilizers, and crop residues + fertilizers (0.46 ± 0.22%); and the low-risk group including composts, crop residues, paper mill sludge and pellets (0.25 ±0.20%). The EF was higher when soils received organic amendments in combination with synthetic fertilizers, such as liquid manures + fertilizers (2.14 ± 0.53%), composts + fertilizers (0.37 ± 0.24%), and crop residues + fertilizers (0.59 ± 0.27%). The EF was modulated by amendment (C/N ratio), soil (texture, drainage, organic C and N) and climatic (precipitation) factors. For example, EFs were on average 2.8 times greater in fine-textured than coarse-

textured soils. We recommend site-specific EFs that consider organic amendment chemistry, soil characteristics, climate conditions and whether the organic amendment is applied alone or in combination with synthetic fertilizers.

Keywords: greenhouse gas inventory, farming systems, fertilization, organic by-products, modeling, weighting procedure

2.2 Introduction

Nitrous oxide (N_2O) is an important greenhouse gas, with 298 times the global warming potential of carbon dioxide (CO_2) (Foster et al., 2007). Nitrous oxide emissions are also a major source of ozone-depleting nitrogen oxides (NO and NO_2) in the stratosphere (Ravishankara et al., 2009). Agricultural sources of N_2O make a prominent contribution to the global budget. For example, Syakila et al. (2011) estimated agricultural emissions owing to N fertilizer use and manure management (4.3– 5.8 Tg N_2O–N yr^{-1}) represented 23–31% of all global N_2O sources (19 Tg N $year^{-1}$ in 2006). Human population growth and increasing global prosperity demands greater N fertilizer inputs to sustain the global food supply, and also generates more N-rich organic waste that is returned to agricultural soils as organic amendments (OAs). As a result, the N_2O emissions from agricultural soils are predicted to increase in the future, which is cause for concern.

Most N_2O emissions from agricultural soils are the result of nitrification and denitrification of mineral N following application of synthetic fertilizers and OAs. In Canada, 34% of direct soil N_2O emissions are attributed to OAs such as animal manure and crop residues (Rochette et al., 2008a). OAs have multiple roles in the microbially-mediated reactions leading to N_2O production, resulting in positive or negative effects. Mineralization of organic N contained in OAs releases ammonium (NH_4^+), with subsequent nitrification (NO_3^-) processes leading to N_2O production. As an organic C substrate for microbial growth, OAs may also stimulate microbial N assimilation, which can increase competition for NH_4^+ between heterotrophic microorganisms and autotrophic nitrifiers (Chen et al., 2013), resulting in temporary reduction of N_2O production. In soils with high N availability but low organic C, OAs may stimulate nitrifier denitrification, the oxidation of ammonia to nitrite (NO_2^-) and its subsequent reduction to NO and N_2O by autotrophic ammonia oxidizing microorganisms under low O_2 availability (Butterbach-Bahl et al., 2013). Under anaerobic conditions, organic C provided by OAs enhances denitrification and N_2O production. The ratio of N_2O to N_2 produced during denitrification increases with increasing soil NO_3^- availability, which is influenced by the microbial consumption and production of NO_3^- due to C and N substrate availability in OA-amended soils (Terry and Tate, 1980; Weier et al., 1993; Miller et al., 2008). Finally, OAs such as animal slurries modulate O_2 availability in soil microsites because the labile C input enhances soil respiration; as slurries are mostly water (up to 97% moisture content), their addition saturates soil micropores in the short-term. Given the multiple ways that OAs impact the activity of microorganisms involved in N_2O production, their influence on soil N_2O emissions cannot be predicted from simple measures such as the total N application rate, which is a reasonably good estimator of the EF from synthetic fertilizers (Kim et al., 2008).

Although simplified EF values are used in calculating the contribution of agricultural soils to national N_2O inventories following the Tier 1 methodology of the Intergovernmental Panel on Climate Change (IPCC EF_1), they can result in erroneous conclusions. There are four major weaknesses associated with simplified EF_1 values: (1) they assume a linear relationship between total N input and N_2O emissions, not considering that biological thresholds for N_2O emissions might exist (Kim et al., 2013; Shcherbak et al., 2014); (2) they are the average of EFs that vary by two orders of magnitude (from 0.03% to 3%); (3) the dataset used to generate the EF_1 is biased towards mid-latitude and temperate regions (Bouwman et al., 2002a); and (4) the simplified EF_1 values do not account for differences between N inputs from synthetic fertilizer and organic amendments on N_2O emission across soil types, agronomic systems and environmental conditions (Buckingham et al., 2014; Rochette et al., 2008a). As signatory countries to the United Nations Framework Convention on Climate Change move to define region- and site-specific EF values (Tier 2 and Tier 3 methodologies) for calculating the N_2O emissions from their agricultural soils, the lack of quantitative information on how OAs contribute to N_2O emissions emerges as a research gap of global significance.

Soil N_2O emissions from agricultural soils receiving OAs can be summarized at global and regional scales using systematic reviews (Bouwman et al., 2002a; Novoa and Tejeda, 2006; Aguilera et al., 2013; Buckingham et al., 2014) or meta-analyses techniques (Liu and Powers, 2012; Chen et al., 2013; Shan and Yan, 2013; Bouwman et al., 2002b). Manure-amended soils had a mean global N_2O EF of 0.8%, i.e. 20% lower than the default IPCC EF_1, with an uncertainty range of -40% to +70% in the N_2O emissions, using Residual Maximum Likelihood (REML)-based models and 846 N_2O cumulative emissions measurements (Bouwman et al., 2002b). In the United-Kingdom, the DNDC mechanistic model generated an EF for manure ranging from +0.01 to +1.53% with an average of 0.43% ± 0.34 (standard deviation) (Cardenas et al., 2013). A meta-analysis of N_2O emissions from OAs in soils of the Mediterranean region presented an average

EF of 0.97 ± 1.17% for solid OAs (e.g., crop residues, manure, composted municipal solid waste, composted cattle and sheep manure, and composted solid fraction of digested pig slurries), and an average EF of 1.75 ± 1.34% for liquid manure (Aguilera et al., 2013). Still, another meta-analysis suggested that the EF for pig slurry was similar to EF_1 (Liu and Powers, 2012). Decomposing crop residues generate N_2O emissions, and a global EF of 1.055% was calculated using a simple linear regression of soil N_2O emitted on residue-N applied (kg ha^{-1}) (Novoa and Tejeda, 2006). However, sensitivity analysis revealed that removing the two highest observations would decrease the EF to 0.6%, indicating the uncertainty of the estimate. A global meta-analysis by Chen et al. (2013) also concluded that crop residues produced comparable or greater N_2O emissions than synthetic fertilizer, whereas Shan and Yan (2013) reported that crop residue addition with synthetic fertilizer inhibited N_2O emissions by 11.7% compared to synthetic fertilizers alone. The variability in EF of agricultural soils receiving OAs warrants more investigation to determine how key factors, such as the OA type and its properties, soil and climate conditions, modulate the EF responsible for soil N_2O emissions.

The aim of this study was to provide a comprehensive and quantitative analysis of a dataset containing 422 EFs reported in 38 studies that measured soil N_2O emissions after OA addition in perennial and annual cropping systems. The analysis was done using three approaches: (1) a systematic review, (2) a random-effect model according to Borenstein (2009), and (3) a REML model. These analyses allowed us to compare EF for OAs and OAs combined with synthetic fertilizers, to categorize the global EF according to OA types and properties, and to determine how the global EF for OAs was influenced by environmental and management-related factors.

2.3 Material and Methods

2.3-1 Global database

The systematic literature review aimed to gather publications relevant to the objectives, while minimizing publication bias as much as possible (Buckingham et al., 2014). A detailed review of literature was carried out until June 13 2014 with Scopus (1960 to 2014) and *CAB Abstracts* (1910 to 2014) research databases using the key words listed in the Table A2-1a and A2-1b combined with Boolean Operators. It retrieved 1064 papers published in peer-reviewed journals (Fig. A2-1). The following inclusion criteria were applied to screen studies in a standardized manner, which resulted in the retention of 38 studies:

1) N_2O fluxes were measured from agricultural soils for at least 30 d (modelling outputs excluded, grazing pasture and paddy soils excluded).
2) Unamended soils that received no fertilizer/amendment addition were used as control.
3) Soils were amended with organic by-products with or without synthetic fertilizers.
4) Information on chemical properties of amendments and application rates was available to estimate the relative contribution of the applied materials (e.g., total N input) to cumulative N_2O fluxes.

We retained field experiment data only and excluded experiments done under controlled conditions such as disturbed soil and undisturbed soil column incubations. Studies without spatial replication or no replicates reported were excluded from the analysis. Using these criteria, 537 observations from the selected 38 studies were used to create the metafile with 422 observations from amended plots and 115 observations from control plots.

For each observation from amended plots, cumulative N_2O emissions were entered into the database and EF were calculated as another response variable following equation (1):

$$\boldsymbol{EF} = \frac{\boldsymbol{N_2O\text{-}N_{fertilized} - N_2O\text{-}N_{unfertilized}}}{\boldsymbol{N_{input_{fertilized}} - N_{input_{unfertilized}}}}, \text{ where} \tag{1}$$

$N_2O\text{-}N_{fertilized} - N_2O\text{-}N_{unfertilized}$ is the difference between cumulative N_2O emissions from the fertilized plot and the unfertilized control plot and $N_{input_{fertilized}}$is the total amount of N applied in the fertilized plot, and $N_{input_{unfertilized}}$ is zero.

Where cumulative N_2O emissions were not reported, the value was estimated by linear integration of the average daily fluxes over the measurement period. Graphical data (means and variation estimates) were digitized using the Datathief III software (v. 1.5). Selected explanatory variables (Table 1) were included in the database to explain the variation in N_2O emissions due to amendment additions. Studies were grouped according to their cropping system (grassland *vs.* cropland). Methodological aspects (e.g., sampling events, number and surface of closed chambers) and results from the variance analysis (e.g., number of replicates, variability estimate and degree of freedom) were used to weight studies in the meta-analysis. Those steps produced a robust dataset with minimal bias that was suitable to evaluate the response of EF to OAs and other relevant factors with a systematic review, a meta-analysis using a random-effect model and a meta-analysis with a REML model.

2.3-3 Systematic review

First, the OA effects on cumulative fluxes of N_2O and EF were studied using a general matrix containing results from the 38 selected studies (Table 2). The box plot representation was selected for raw data illustration because this non-parametric tool does not require any assumptions of the underlying statistical distribution. Box plots graphically appraised the degree of dispersion and skewness in the data, and showed outliers of cumulative N_2O flux and EF in a transparent manner, through their quartiles. Fertilizer type was grouped (Table 1) into: (i) organic (O), (ii) organic combined with synthetic (OS), and (iii) synthetic (S), hereafter referred to as "FertiType". The FertiType S does not exhaustively represent global soil N_2O emissions following synthetic fertilizer application since the observations came from studies where soil N_2O emissions were measured on sites where OAs and synthetic fertilizer effects were jointly assessed. Then, FertiType was sub-divided in categories, "FertiClass", according to the nature of amendments (Table 3).

Because OAs applied to agricultural soils depend upon national, regional and local factors (type and scale of farming systems, farm storage facilities and equipment, livestock production with manure availability, availability of non-manure-based amendments (Thangarajan et al., 2013), the database was expanded to include explanatory variables that might influence the EFs for soil N_2O such as climate, soil properties and cropping systems with their common management practices (Table 1). Soil texture classes were fine-, medium- and coarse-textured soils (Shirazi and Boersma, 1984; CRAAQ, 2010) criteria. The modulation of soil N_2O emissions by EFs at FertiType and FertiClass levels could then be evaluated while considering the variation induced by environmental and management-related factors when sufficient data were available.

2.3-4 Meta-analysis approaches

Meta-analysis was performed with two different random-effect models: the random effect model proposed by Borenstein et al. (2009) (REMB) and the Residual Maximum Likelihood method (REML) which is also appropriate for analysis of global meta-data related to soil N_2O emissions and EFs (Bouwman et al., 2002b).

2.3-4.1 Random-effect model of Borenstein (REMB)

The REMB is a classical meta-analytic approach (Borenstein, 2009) that (1) calculates a between-study variance, assigning lower weights to large studies and higher weights to small studies than the fixed-effect model, (2) attributes more weight to EFs with lower variance (weighting procedure), but (3) considers all observations being from independent studies (does not appraise the random effect of sites and types of fertilization).

Because weighted meta-analysis requires information on variance and the number of replications of N_2O observations (n), this limited the analysis to 409 observations (316 fertilized and 93 control plots). For each observation, EF was selected to compute the effect size unit as raw mean difference following Eq. 1. Standard deviations (SD) of EF were rarely provided and variance of EF (V_{EF}) was calculated from SD of cumulative N_2O fluxes and number of replicates (n) following equation (2):

$$\boldsymbol{V_{EF} = \left(100/N_{input_{fertilized}}\right)^2 \times \left(SD_f{}^2/n_f + SD_c{}^2/n_c\right)}, \text{ where} \qquad \textbf{(2)}$$

SD_f and SD_c are the standard deviations of cumulative N_2O emissions from the fertilized and the control plots, respectively, and n_f and n_c are the number of replicates of the fertilized and control plots, respectively. Observations without any reported measure of variance (25% of the datasets) were not included, nor was missing data approximated, as missing values were not at random and imputation techniques may lead to underestimation of the effect (Uijl et al., 2012).

The meta-analysis was carried out using MetaWin version 2 (Rosenberg et al., 1999). The REMB assumed that differences among studies within a class were due to both sampling error and random variation. To test the importance of the sources of variation, studies were subdivided into groups according to some of the explanatory variables (Table 1). Normality and publication bias were investigated using the normal quantile. The data had an asymmetric distribution that was skewed to the right (Fig. A2-2a). The long right tail suggested publication bias towards population of EFs differing from zero (Wang and Bushman, 1998). Power transformations using Box Cox transformation failed to normalize the data distributions, thus analyses were conducted on non-transformed data.

We compared different weighting procedures and found that weighting N_2O EF by the inverse of variance gave the best model performance (Fig. A2-3). Thus, we gave more weight to studies with little variance. However, variance tends to scale with EF (Fig. A2-2b) and variability scaled with cumulative N_2O emissions (Fig. A2-2c). Therefore, weighting based on variance could bias the analysis towards situations with low N_2O emissions.

Cumulative N_2O emissions are disproportionately influenced by a few ‘hot events’ during the growing season. Molodovskaya et al. (2012) demonstrated that up to 51% of cumulative annual N_2O emissions are caused by short-term events (rainfall) that promote high sporadic pulses of N_2O with large variance (<7% of the total observation time). Even automated measurement approaches, which provide better temporal coverage than periodic sampling, are susceptible to i) underestimate N_2O emissions because integration of point-in-time observations missed a number of transient high-flux events (Scott et al., 1999), and ii) overestimate N_2O emissions because they neglect temperature-dependent diurnal variations (Yao et al., 2009) when integrating transient high-flux events. Given the high spatiotemporal variability in soil N_2O emissions, assigning more weight to studies with low variance does not necessary favor more accurate estimates of N_2O EF. Moreover, 26% of the observations in the dataset had to be excluded from the random-effect model because they did not report the variability associated with the mean N_2O emissions, which reduces the statistical power of the model.

2.3-4.2 Residual maximum likelihood (REML)

Finally, we used the Residual Maximum Likelihood (REML) model, which is appropriate for analyzing unbalanced datasets with missing values (Bouwman et al., 2002b). This model has four main advantages: (1) it provides efficient estimates of treatment effects in unbalanced designs; (2) the interdependency of EFs obtained from the same study is taken into account; (3) all observations of the database are included in the analysis, (4) different weighting schemes can be tested. In this study we adapted the REML weighted procedure to account either for the variance of mean or the spatiotemporal coverage of N_2O emissions (number of sampling days, "SamplingEvent", and total surface of gaseous measurements, "GasSurface" as a product of the total number of chambers and the chamber surface) (Fig. A2-4, A2-5, and A2-6). We compared four weighting schemes :

- the unweighted procedure (equal weight for each observation) according to Bouwman et al., 2002b;

- the weighted procedure similar to the REMB using the inverse of N_2O EF variance;

- a new weighted procedure using the N_2O coverage weight (N_2O_{cov}Weight) for each observation *i* (Fig. A2-7a and A2-7b), according to equation (3), as follows;

$$\mathbf{N_2O_{cov}Weight_i = SamplingEvent_i \times GasSurface_i} \quad \textbf{(3)}$$

- a revised-N_2O coverage weighting procedure that tests the influence of superior weight studies defined as studies whose weight of N_2O observations was twice greater than the average weight of all N_2O observations (0.24%), according to equation (4);

$$\mathbf{revised\text{-}Weight_i = N_2O_{cov}Weight_{max} \times \left[1 + \left(N_2O_{cov}Weight_i / N_2O_{cov}Weight_{max}\right)/1000\right]} \quad \textbf{(4)}$$

where $N_2O_{cov}Weight_{max}$ is equal to 885600, the maximum weight of a non superior weight study in the dataset. All weighting schemes were automatically rescaled so that their sums equaled 1 ($\sum_i Weight_i = 1$), resulting in expressions of dispersion in the same scale as the original data (Fig. A2-7).

A linear mixed-effects model was performed using the “Proc Mixed” procedure of the SAS software, version 9.2 (SAS Institute, Cary, NC, USA). The fertilizer type variable (FertiClass) was the fixed-effect component of the model. The unique study and site identifiers (IDstudy, IDsite), as well as FertiClass or FertiType, appeared in the random-effect component to account for the dependency of several effect sizes reported in the same study (Bouwman et al., 2002b; Sauvant et al., 2008). Once model parameters were estimated, the homogeneity of variance and normality of the residuals were analyzed graphically. Normality tests (Shapiro-Wilk and Kolmogorov-Smirnov) were also performed. No power transformation improved data distribution, yet heterogeneity was corrected by controlling the covariance structure imposed upon the residuals or errors using the REPEATED statement. In particular, the GROUP= optional statement permitted different categories of fertilization effect to have different structure parameters. Statistical results were considered to be significant at the 0.05 α level. Statistical significance of selected explanatory factors was tested separately, as datasets were not complete for every explanatory factor.

2.4 Results and Discussion

2.4-1 Systematic Review

2.4-1.1 Database

The selected studies (n=38) provided N_2O measurements from 43 sites located in 12 countries (Table 2). Europe contributed 48% (n=201) of the 422 observations, North America 32% (n=137), Asia 13% (n=55), South America 6% (n=24), and Australia 1%, (n=5). In Europe, more than 70% of reported EFs came from agricultural soils receiving OA application only, hereafter referred to as FertiType O. A similar trend was observed in North America (62%) but not in Asia and South America where FertiType O measurements represented 18% and 33%, respectively, of the total EFs. In Australia, four out of five of the EFs were for FertiType O and no observations were available for EFs from agricultural soils receiving OA application combined with synthetic fertilizers, hereafter referred to as FertiType OS. Germany, Brazil and United-Kingdom provided 100% of N_2O EF for biogas residue (BR), biosolids applied with crop residues and S (BSD-CR-S), and paper mill sludge combined or not with S (PMS ± S), respectively. While more than 90% of the N_2O EF for liquid manure (LM) came from studies in Europe and North America, 92% of the N_2O EF for crop residues alone was determined in China. This is evidence of the interdependency between types of fertilization and geographical areas providing N_2O EF, which may create bias in the interpretation of results, as discussed later.

Our dataset is particularly strong in reporting EF for OAs, with 60% of the EF reported for FertiType O (n=251), 17% for FertiType OS (n=72), and 23% for FertiType S (n=99) (Table 3). This is five times more information on OAs since the last global meta-analysis conducted by Bouwman et al. (2002b) that reported 45 and 25 EFs in FertiTypes O and OS, respectively. More observations permit us to detail the EFs by "FertiClasses", listed in Table 3. The LM FertiClass represented 35% of all EFs, about five times more than solid manures (SM) or composts (CMPT) and two-fold more than the FertiClass OS. The dominant OAs were LM in 53% of studies, SM in 29% of studies and CMPT in 21% of studies. A smaller proportion of studies concerned the use of LM-S (16%) and CMP-S (13 %), BSD-S (10%), crop residues (CR) (8%) and of remaining amendments (≤ 5%). Proposing a global EF for FertiType O from the current database is biased towards EFs from the N-rich, wet LM and barely consider EFs from moderately decomposed, drier CMPT and Pellets.

Most observations (n=393) in the database came from regions with a temperate climate, so present a similar bias towards temperate climates as Bouwman et al. (2002a). While 67% (n=198) of the EFs from FertiType O were derived from studies in cool and moist conditions, the EFs from FertiType OS were studied under warm and dry conditions (n=31) with all EFs from LM addition alone occurring in a cool temperate moist climate (n=23). Therefore, the impact of FertiType is partly confounded with that of climate.

2.4-1.2 Emission Factors

Global EF averaged 0.82% for the FertiType O, 1.50% for FertiType OS and 1.34% for FertiType S (Table 3). FertiType medians were roughly two times lower than means, indicating the presence of outlier observations in a positive skew distribution of EF (Fig. 1). Global EFs ranged from -0.99 to 12.80% of N applied (Fig. 1), and both extreme values were measured following the application of ammonium nitrate (Ball et al., 2004; Dittert et al., 2005). Similarly, Bouwman et al. (2002b) reported minimum and maximum EF values of -1.71% and 14.7% following the application of synthetic N fertilizers.

FertiClasses tended to form three natural groups identified in Table 3 as follows: the high-risk group with EF around 1.0%, the medium-risk group with EF around 0.5%, and a low-risk with EF around 0.2%. Boxplot analyses suggest EF_1 should be revised according to the type (organic, synthetic, both) and the nature of fertilization. Distribution of the EF population among percentile categories at the FertiType and FertiClass levels led to visualization and identification of FertiClasses that to deviate from the central tendency with regards to N_2O EFs (Fig. 1).

In the FertiType O group, 74% of the reported EF estimates (n=251) were smaller than 1%, the IPCC EF_1 value. LM represented more than 70% of the EFs superior to the 90th percentile of the FertiType O (2.27% of N applied), but less than 30% were inferior to the 10th percentile (0.04% of N applied). Conversely, more-stabilized amendments such as CMPT, CR, and PMS ± CR did not promote any EF superior to the 90th percentile but yielded more than 58% of the EF inferior to the 10th percentile of the FertiType O.

In FertiType OS, approximately half of the observations were below $EF_{1.}$ At the FertiClass level, 80% of the observations from agricultural soils amended with CMPT and CR combined with fertilizers had global EFs lower than EF_1. In contrast, 68% of the observations from agricultural soils receiving LM-S had global EFs greater than EF_1 (data not shown).

In FertiType OS, the combined application of OA and synthetic N fertilizer increased the EF quartiles by 2.2-fold. After adjusting for the soil texture bias (since there were an unequal number of studies from fine-textured (53%) and coarse-textured (27%) soils), it was found that the combined application of OA and synthetic N fertilizers increased the EF quartiles by a factor of 1.8.

2.4-2 Meta-analyses

The REMB and REML models both confirmed the significant impact of fertilization sources (FertiType, FertiClass, FertiRiskClass) on global N_2O emissions (Table 4).

2.4-2.1 Comparison of REML with REMB procedures

At the FertiType level, EF estimates of the REMB procedure ranged between the mean and the median of raw data (Table 3) and the FertiType O (0.54%) was significantly lower than

FertiTypes S (0.72%) and OS (0.77%). Conversely, EF estimates of the unweighted REML were closed to raw means and no significant differences were detected between FertiTypes (Table 3). The REMB and the N_2O coverage weighted REML agreed, but the REML model generated higher EF estimates for the FertiType OS (1.15%) and S (1.76%), probably because (1) the REMB had to exclude observations from FertiClasses with no associated variance, (2) the REML did not compute a between-study variance. Indeed, the REML procedure using the inverse of variance in weighting procedure provided identical EF estimates to those obtained with a fixed-effect meta-analysis model (no between-study variance), which is not recommended by Borenstein (2009) for biological and environmental studies such as EF from agricultural soils receiving OAs and other fertilizers.

Interestingly, synthetic sources were attributed an estimate 1.3 times greater than the raw mean with the new N_2O coverage weighted procedure of the REML. Even if FertiType S does not exhaustively represent global N_2O EF following fertilizer application, this weighted REML procedure strongly indicated higher EF were measured after synthetic fertilizer application in studies with better spatiotemporal coverage of soil N_2O emissions.

2.4-2.2 In-depth testing of the N_2O coverage REML-weighted function

Three superior weight studies were identified in the N_2O coverage weighted REML and reported measurements from the highest surfaces reported in the selected literature (i.e., between 1 and 1.5 meter square of total monitored surface per treatment). Two studies used automated closed chamber system. Thornton et al. (1998) roughly accounted for 20.6% of the entire database (sum of all weights equal to 100%) with a reported EF of 0.73% following application of 336 kg N/ha of urea on a silty clay loam (Fig. A2-7). Ball et al. (2004) was attributed on average 4.83 times more weight than other studies, including two outliers (12.80% and -0.18% of N applied) of equal weight (around 1.7%) measured after application of 120 N kg / ha of NH_4NO_3 on a clay loam (Fig. A2-7). In Parnaudeau et al. (2009), eight chambers were installed on two replicates of each treatment allowing 2.3 times more weight than average for waste water EFs.

Sensitivity analyses were conducted to test the robustness of the weighted REML procedure and the potential gains of the N_2O coverage weighted function (Table 5). In absence of superior weight studies (31 observations deleted), the global EF estimate for OAs still fall within the range of those proposed by Bouwman et al. (2002b) with a 24.6% increase recorded that reached 0.71%. FertiType S estimate was not significantly different from the Fertitype O and fell in accordance with the IPCC EF_1 reaching 1.01% (Table 5). Additional analyses conducted separately on the three superior weight studies (data not shown) concluded (1) Thornton's study leverage was strongly negative on FertiType S estimate and set down the estimate from 3.85% to 1.76%; (2) Ball's study leverage was strongly positive on FertiType S estimate and rise the estimate from 1.01 to 1.76%; (3) Parnaudeau's study leverage was strongly negative on FertiType O and set down the estimate from 0.83% to 0.57%.

In a second sensitivity analysis, we revised the N_2O coverage factor (see section 2.3-4.2) to moderate the influence of superior weight studies whose weight of N_2O observations was twice greater than the average weight of all N_2O observations. The revised N_2O coverage weighted function pointed out the EF estimates for organic sources were quite consistent among the REMB and weighted REML procedures (0.54 to 0.64%) even if the N_2O coverage weighted REML procedure did not compute a between study variance (Table 5). We concluded differences between REMB and the N_2O coverage weighted REML procedures were mainly due to exclusion of observations with no associated variance, rather than computation of a between-study variance in the REMB procedure. The N_2O coverage weighted REML procedure appeared as better than REMB for distinguishing FertiType with regards to N_2O emissions.

2.4-2.3 New insights with the N_2O coverage weighted REML procedure

The N_2O coverage weighted REML procedure was judged more appropriate to generate EF estimates, especially for FertiClasses tested on a limited number of sites and studies such as BSD-S (Table 3). Indeed, the REMB does not take into account a substantial interdependence among the reported EFs (IDstudy and IDsite) but consider each observations of the database as study- and site-independent introducing more bias for Fertitype and FertiClasses less represented.

Interestingly, the N_2O coverage weighted REML pointed out lower EF following CMPT±SF and SM application in studies with better spatiotemporal coverage of emissions. CMPT and CMPT-S were attributed a global EF equal to 0.00 ± 0.17% and 0.37 ±0.24, respectively (Table 3). A *t* test revealed addition of CMPT±S would not affect soil N_2O emissions ($Pr > 0.05$). Sensitivity analyses pointed out the large EF estimates for LM-S were quite consistent among the weighted REML procedure (1.81 to 2.14%). Risk grouping of FertiClasses, allowed to generate new EFs for underrepresented FertiClasses (BSD-CR-S, WW, BR, SM-S, PMS-CR, PLTS, CR, LM-CR and PMS) that could not be included at first in the modeling process (Table 3).

2.4-3 Proposition of global EFs with the N_2O coverage weighted REML procedure

Our proposition for a global EF for OAs applied to agricultural soils are based on the N_2O coverage weighted REML. The global EF for OAs, hereafter referred to as "EF_{org}", was equal to 0.57 ± 0.30%. This is lower than the EF_{org} of 0.8% proposed by Bouwman et al. (2002b) probably because (1) our database contained five times more information on OAs, and because (2) the new N_2O coverage weighted function of the REML allowed considering the intrinsic spatio-temporal variability of N_2O emissions from agricultural soils receiving OAs. No global EF is proposed for organic sources combined with synthetic fertilizers because the dataset was biased toward LM-S application, which represented most of the OA plus synthetic fertilizer observations.

At the FertiClass level, the following EFs were estimated for OA combined with synthetic fertilizer: LM-S had an EF of 2.14% ± 0.53, CMPT-S had an EF of 0.37% ± 0.24 and CR-S had an EF of 0.59% ± 0.27. The CR-S estimate is consistent with Novoa and Tejeda (2006) whose meta-analysis involved unamended plots as control that were unfertilized or fertilized with synthetic N fertilizer. Considering the three risk classes of OAs led to estimates of EFs equal to 1.09% ± 0.17 for the high-risk class, 0.46% ± 0.22 for the medium-risk class, and 0.25% ± 0.20% for the low-risk class (Table 3). We are not aware of any other attempt to estimate the EFs for OAs based on risk classes, but note that the EF for the low-risk class was about half of the global EF for OAs, implying that use of the global EF for OAs would greatly over-estimate the N_2O emissions from agricultural soils that received Pellets (sewage sludge),CMPT (animal, vegetal, and municipal wastes), PMS, CR (maize or barley straw, lettuce or calabrese residues), PMS-CR, and even LM-CR.

2.4-5 Emission Factors and Controlling Factors

2.4-5.1 Physico-chemical Properties of Organic Amendments

Pig slurries that contained greater mineral N content (>10% d. w.), more water content (>95%) and low C/N ratio (< 5) had larger EFs than more viscous animal slurries (dry matter < 15%), SM (dry matter > 15%) or more stabilized products (C/N ratio > 30) (Table 3 and A2-3). These findings agree with other reports (Velthof et al., 2003; Chantigny et al., 2010; Senbayram et al., 2012). For instance, pig slurry contains high amounts of NH_4 and easily decomposable organic C that can, in concert, directly stimulate soil denitrifiers and decrease O_2 concentration; thereby further stimulating N_2O production through denitrification (Velthof et al., 2003; Chantigny et al., 2010). Senbayram et al.(2012) pointed out that application of OAs with high contents of labile C may trigger denitrification-derived N_2O emission in N-fertilized agricultural soils, coupled with a substantial increase of $N_2O/(N_2O + N_2)$ product ratio of denitrification in presence of large amount of nitrate from synthetic sources.

Chemical properties of OAs such as the mineral N content and C/N ratio were evidently important in predicting their N_2O EF. More than 20% of OAs containing less than 0.3% d.w. of mineral N yielded EFs below the range proposed for the IPCC EF_1(0.03 to 3% of N applied) (Fig. 2). Conversely, the OAs with greater mineral N content tended to have EFs above the maximum EF_1 value. For organic amendments whose mineral N content is less than 0.3% d.w, 4 of the 7 the EF estimates below 0.03% concerned surface application of cattle/co-fermented slurries, while injection of pig slurry combined with synthetic fertilizers promoted 100% of out of range EF_1 above 3% for fertilization sources containing more than 25% d.w. of mineral N (Table A2-3). Thus, mineral N alone cannot depict differences in composition between animal manures, due to litter type, and animal species and nutrition. Animal litter is a mixture of bedding material, excreta, and waste feed generated during animal production (Cabrera et al., 1994a). Manure showed contrasting N-mineralization patterns where N concentration varied among biochemical fractions (Tremblay et al., 2010). The manure-N mineralization increased in the presence of low-molecular-weight compounds such as sugar, starch, protein, uric acid N, and water-soluble organic N and decreased with lignin and polyphenol content (Morvan et al. 1997; Pansu et al. 2003). In general, the degradability of organic C and N of cattle manure is lower than that of pig and poultry manure (Chadwick et al., 2000a).

Also, the EFs decreased as the C/N ratio of OAs decreased (Fig. A2-8), which agrees with controlled laboratory studies on N_2O emissions from soils receiving OAs (Rizhiya et al., 2011). We conducted linear regressions based on log-transformed EF data to predict the N_2O EFs of crop residues from their C/N ratio according to equation (5) with 78.4% of variance in EF explained by the model (Fig. 3):

$$\mathbf{EF\ (\%\ of\ N\ applied) = EXP[-0.706*ln(C/N\ ratio + 1) + 2.121 + (0.145/2) - 1]} \qquad (5)$$

According to the above equation, CRs with C/N higher than or equal to 21.3 would not significantly increase soil N_2O emissions following their addition. According to higher N_2O observations reported in the literature (Fig. 4), OA with C/N higher than or equal to 45.9 would not significantly increase soil N_2O emissions following their addition. For OAs with C/N lower than 25, the C/N of OAs explained only a part of the variations in EF, suggesting the influence of other environmental and management-related factors (Fig. 4).

2.4-5.2 Climate

Climate type and annual mean air temperature (MAT) had no significant effect of on global EF (Table 6), probably because our database is biased toward temperate climates and under-represented tropical and arid climates. There was a significant effect ($P < 0.001$) of total annual precipitation (TAP) on global EF, where the EF estimate from FertiType O increased by a factor of 5 as TAP increased from 0-250 mm to 500-1000 mm (Table 6). This is consistent with the fact that soil moisture generating temporary anoxic conditions is a major driver of N_2O production from denitrification in microsites where a high oxygen demand from intense respiratory activity exceeds the oxygen supply (Parkin, 1987; Linn and Doran, 1984). It is notable that the EF estimates declined by a factor of 2 when TAP exceeded 1000 mm (Table 6), suggesting that N_2 was the end product of denitrification in agricultural soils receiving OAs under these conditions of higher soil moisture.

2.4-5.3 Soil properties

Texture and drainage

Soil texture modulates soil N_2O emissions in agricultural soils receiving OAs and synthetic fertilizers (Pelster et al., 2012). Similar to Bouwman et al. (2002b), our results showed that N_2O emissions were greater in fine-textured than coarse-textured soils (Table 5). In FertiType O, the EF increased by a factor of 2.8 in fine-textured than coarse-textured soils (Table 6). In FertiType OS, the EFs differed significantly between fine-textured and medium-textured soils. This may be a function of mineral N availability for microbially-mediated denitrification since the magnitude of EF response to increasing mineral N content of soil amendments is regulated by soil texture (Fig. 5), with greater EF estimates occurring in situations where mineral N content of fertilizer inputs was higher in fine-textured than in medium- and coarse-textured soils. When LM was injected with synthetic fertilizers, the EF estimates were > 3% (Chantigny et al., 2010; Wei et al. 2010; Senbayram et al., 2014), exceeding the IPCC EF_1 value.

Soil drainage that refers to the soil's natural ability to allow water to pass through it, was another significant modulator of EFs in agricultural soils receiving OAs and synthetic fertilizers (Table 6). The effect of soil drainage is related to texture because fine-textured soils hold water, while coarse-textured soils allow water to pass through quickly. The effect of soil drainage is also influenced by climate conditions and the presence of drainage structures. The attribution of a drainage class (poor, well, n/a) to reported EFs was based on explicit details provided by authors in selected studies. The EFs in poorly drained soils were two times larger than in well-drained soils in presence of OAs. For the FertiType S, the EFs were 7-fold greater in poorly drained than in well-drained soils. These differences reflect the impact of soil oxygen and moisture status on N_2O production and diffusion/emission in agricultural soils, which was also noted by Bouwman et al. (2002b).

Soil organic carbon and nitrogen

Soil organic carbon (SOC), is another soil parameter implicated in soil N_2O emissions (Giles et al., 2012) that was considered in this study (Table 1). Regardless of the FertiType applied, SOC had a significant effect on EF (Table 6) and this was more important in FertiType S ($P < 0.001$) than FertiType O and OS ($P < 0.01$), which corroborates previous findings (Pelster et al., 2012) stating that N_2O emissions are often limited by soil C availability. In synthetically fertilized soils, the SOC could be an indicator of the concentrations of C substrates accessible to nitrifying and denitrifying microorganisms that produce N_2O. The soil C/N ratio was also related to the EFs in synthetically fertilized soils (Table 6), which is consistent with findings reported by Wei et al.

(2010). In contrast, the C/N ratio or organic C content of OAs is a better representation of the C substrate availability because the labile C substrates that originate from OAs are more readily metabolised than those that originate from the native SOC, since a large proportion of the SOC is physically protected and associated with soil minerals (see Table A2-4).

2.5 Conclusion

Three analytical approaches were able to distinguish and estimate EF for soil N_2O emissions from OAs, alone and combined with synthetic fertilizers. The weighted REML model proved the most robust and could handle missing observations in the dataset and account for the intrinsic spatio-temporal variability of N_2O emissions from agricultural soils receiving OAs. In estimating the EFs for N_2O emissions from agricultural soils, we demonstrated that the IPCC EF_1 value was too high when considering the N_2O contribution from agricultural soils amended with composts, but too low to represent the EF of N_2O in agricultural soils receiving liquid manure (mostly pig slurry) combined with synthetic fertilizers. We propose a global default EF for organic sources, EF_{org}, equal to 0.57 ± 0.30% and encourage the use of FertiClasses or FertiRiskClass categories to account for the N_2O emissions from specific OA sources or groups of OAs with similar characteristics. Finally, we confirm that variations in N_2O EFs in OA-amended soils are influenced mainly by the mineral N content and the C/N ratio of OAs, rainfall (expressed as TAP), soil texture and drainage. The database assembled and the approach followed in this study could therefore be used to update the IPCC EFs for soil N_2O emissions resulting from the application of OAs to agricultural soils.

Table 1. Quantitative variables included in the meta-analysis of N_2O emission factors (EF) from organic sources of fertilizer, alone and combined with synthetic sources.

Variables	Acronyms	Units	DA* (%)
Response variables			
Cumulative N_2O emissions from control plots	N_2O_c	kg N ha^{-1}	100
Cumulative N_2O emissions from fertilized plots	N_2O_f	kg N ha^{-1}	100
Emission factor of N_2O	EF	% of total N applied	100
Explanatory variables			
Fertilization			
Type of fertilization	FertiType		100
organic	O		
organic combined with synthetic	OS		
synthetic fertilizers	S		
Total application rate of nitrogen (N)	Total N input	kg ha^{-1}	100
Application rate of organic N sources		kg ha^{-1}	100
Application rate of fertilizers N		kg ha^{-1}	100
Incorporation depth of amendments		cm	
Number of split (0 if single application)			
Type of amendments	FertiClass		100
Chemical properties of amendments			
C/N ratio			40
Ammonium content	NH_4^+	mg kg^{-1}	37
pH			34
Land-use type			100
Cropland (paddy fields excluded)			
Grassland (grazing pasture excluded)			
Crop type			100
Soil tillage			85
Soil Drainage			77
Soil Texture			91
Soil properties			
Organic C content	SOC	%	80
N content		%	72
C/N ratio			74
pH			82
Bulk density	BD	g cm^{-3}	50
Climate			
Climate type			100
Total annual precipitation	TAP	mm	92
Mean annual temperature	MAT	°C	70
Measurement techniques			
Number of N_2O sampling events			100
Length of the experiment		days	100
Number of closed chambers			100
Closed chamber surface		cm^2	100
Statistical parameters			
Number of replicated plots	*n*		100
Standard deviations of N_2O_c	sd_c	kg N ha^{-1}	75
Standard deviations of N_2O_f	sd_f	kg N ha^{-1}	75

*DA, percentage of data reported in selected studies that was available for each variable listed above.

Table 2. Studies and geographical coordinates of experimental sites included in the N_2O EF database.

IDstudy[*]	Authors	Year	Country/Province	IDsite[**]	Latitude	Longitude
1	Hansen et al.	1993	Norway	1	62.9740	8.7247
2	Lessard et al.	1996	Canada, ON	2	45.4116	-75.6982
3	Chang et al.	1998	Canada, AB	3	49.6935	-112.8418
4	Thornton et al.	1998	USA, AL	4	34.9323	-86.5719
5	Lemke et al.	1999	Canada, AB	5	53.1134	-114.4677
				6	53.4274	-113.4578
				7	53.4115	-113.1210
6	Chadwick et al.	2000a	UK, England	8	50.7396	-3.9991
7	Chantigny et al.	2001	Canada	9	46.7770	-71.1452
8	Baggs et al.	2002	UK, Scotland	10	56.3216	-3.0099
9	Wulf et al.	2002	Germany	11	50.7327	7.0963
10	Tilsner et al.	2003	Germany	12	49.9416	11.5710
11	Ball et al.	2004	UK, Scotland	13	55.8437	-3.1951
12	Dittert et al.	2005	Germany	14	53.9210	9.8822
13	Vallejo et al.	2006	Spain	15	40.4817	-3.3641
14	Chantigny et al.	2007	Canada, QC	16	46.8033	-71.2428
15	Meijide et al.	2007	Spain	17	40.3010	-3.4381
16	Thorman et al.	2007	UK, England	19	50.7695	-3.9013
				18	53.2245	-1.1124
17	Bhandral et al.	2008	Canada, BC	20	49.2401	-121.7657
18	Ellert and Janzen	2008	Canada	21	49.7020	-112.7727
19	Mkhabela et al.	2008	Canada, NS	22	45.4167	-63.5999
20	Meijide et al.	2009	Spain	23	40.5381	-3.2823
21	Parnaudeau et al.	2009	France	24	49.3794	4.1463
22	Chantigny et al.	2010	Canada	25	46.7702	-71.2049
23	Dalal et al.	2010	Australia	26	-27.5703	152.3259
24	Sanchez-Martin et al.	2010	Spain	27	40.5381	-3.2823
25	Tenuta et al.	2010	Canada, MB	28	49.5213	-96.5101
26	Wei et al.	2010	China	29	35.0653	107.6204
27	Velthof et al.	2011	The Netherlands	30	51.9668	5.6668
28	Ding et al.	2013	China	31	35.0000	114.4000
29	Cai et al.	2013				
30	Pelster et al.	2012	Canada, QC	32	46.7333	-71.5167
31	Abalos et al.	2012	Spain	33	40.5333	-3.2833
32	Collins et al.	2011	USA, WA	34	46.2561	-119.7393
33	Hu et al.	2013	China	35	36.8667	115.1667
34	Carmo et al.	2013	Brazil	36	-22.2500	-48.5667
				37	-22.6833	-47.5500
35	Li et al.	2013a	China	38	47.4333	126.6333
36	Plaza-Bonilla et al.	2014	Spain	39	41.9033	-0.5042
37	Aita et al.	2014	Brazil	40	-29.7203	-53.7053
				41	-29.7269	-53.7247
38	Senbayram	2014	Germany	42	53.9000	9.9000
				43	54.3000	10.0000

[*] IDstudy, Unique Study Identifier; [**] IDsite, Unique Site Identifier

Table 3. Global estimates of N_2O emission factors ($N_2O\ EF$) according to fertilization type.

		Fertilization	**Acronyms**	**Descriptive parameters**				**N_2O EF, % N applied**										
				Representativeness			**N rate**	**Raw Data**		**REMB[1]**			**REML[2]**					
				total #			kg N/ha						unweighted			weighted		
				Obs.	Site	Study	median	mean	median	mean	95% CI	*df*	mean	sem	*Pr* > |t|[χ]	mean	sem	*Pr* > |t|[χ]
FertiTypes		**Organic sources**	**O**	**251**	**41**	**35**	**154**	**0.82**	**0.42**	**0.54 b**	**0.48 to 0.60**	**183**	**0.84 a**	**0.22**	***<0.001***	**0.57 b**	**0.30**	***<0.001***
		Organic and synthetic sources	**OS**	**72**	**13**	**13**	**150**	**1.50**	**0.87**	**0.77 a**	**0.63 to 0.91**	**34**	**1.30 a**	**0.30**	***<0.001***	**1.15 ab**	**0.31**	***ns***
		Synthetic sources	**S**	**99**	**32**	**26**	**130**	**1.34**	**0.57**	**0.72 a**	**0.61 to 0.82**	**65**	**1.30 a**	**0.29**	***<0.001***	**1.76 a**	**0.42**	***<0.001***
FertiClasses	**High risk**	**All high-risk**						**1.18**	**0.62**	**0.70 A**	**0.63 to 0.76**	**152**	**1.09 A**	**0.17**	***<0.001***	**0.91 A**	**0.16**	***<0.001***
		Liquid manure + S	LM-S	31	5	6	130	2.44	1.72	not available[‡]			1.81 a	0.48	*<0.001*	2.14 a	0.53	*<0.001*
		Biosolid, CR + S	BSD-CR-S	6	1	1	131	1.64	1.54									
		Biosolid + S	BSD-S	6	4	4	145	1.16	0.88	1.16 a	0.75 to 1.59	5	0.39 bcd	0.55	*ns*	0.89 abcd	0.45	*<0.05*
		Waste water	WW	8	2	2	161	1.15	0.45									
		Liquid manure	LM	149	24	20	148	0.96	0.56	0.67 a	0.60 to 0.75	105	1.11 ab	0.23	*<0.001*	1.12 ab	0.18	*<0.001*
		Biogas residues	BR	10	2	1	360	0.92	0.49									
		Solid manure + S	SM-S	3	2	2	240	0.78	0.85									
		Solid manure	SM	29	13	11	170	0.97	0.24	0.56 ab	0.33 to 0.80	13	1.01 abc	0.28	*<0.001*	0.35 c	0.18	*<0.05*
	Medium risk	**All medium-risk**						**0.50**	**0.44**	**0.58 B**	**0.42 to 0.73**	**19**	**0.46 B**	**0.22**	***<0.05***	**0.43 AB**	**0.43**	***ns***
		Compost + S	CMPT-S	14	4	5	150	0.54	0.45	0.55 ab	0.34 to 0.76	12	0.52 cd	0.26	*<0.05*	0.37 cd	0.24	*ns*
		Crop residues + S	CR-S	12	3	3	210	0.46	0.33	0.64 ab	0.31 to 0.97	6	0.66 cd	0.30	*<0.05*	0.59 bc	0.27	*<0.05*
	Low risk	**All low-risk**						**0.23**	**0.14**	**0.22 C**	**0.12 to 0.32**	**45**	**0.25 B**	**0.20**	***ns***	**0.20 B**	**0.17**	***ns***
		Paper mill sludge + CR	PMS-CR	6	1	1	231	0.28	0.13									
		Compost	CMPT	29	8	8	200	0.27	0.17	0.26 b	0.12 to 0.40	25	0.43 d	0.24	*ns*	0.00 *d*	0.17	*ns*
		Pellets	PLTS	5	1	1	508	0.25	0.24									
		Crop residues	CR	8	3	3	83	0.19	0.08									
		Liquid manure + CR	LM-CR	1	1	1	178	0.07	0.07									
		Paper mill sludge	PMS	6	1	1	519	0.03	0.01									

[1] **Random effect model of Borenstein** (Borenstein, 2009), weighting procedure by the inverse of $N_2O\ EF$ variance

[‡] not available, number of observations reporting variance of N_2O EF means ≤ 2

[2] **Residual Maximum likelihood analysis**, weighting procedure with spatial and temporal N_2O coverage (Table 1)

Means sharing a small bold letter are not significantly different within FertiTypes by a LSD test (*P*<.05).

Means sharing a small letter are not significantly different within FertiClasses by a LSD test (*P*<.05).

Means sharing a capital letter are not significantly different within low-, medium-, and high-risk Ferticlasses by a LSD test (*P*<.05).

[χ] ***Pr* > |t|** refers to a ***t*** test to test the null hypothesis that the associated population quantity equals zero.

Table 4. Significance of fertilization sources on global N_2O emission factors with two statistical models.

$N_2O\ EF$, % N applied

	REMB model[1]					REML model[2]							
						unweighted				weighted			
	n	*Q*	I^2	P_{chi}^2	*df*	n	*F*	*Pr* > *F*	df	n	*F*	*Pr* > *F*	df
Fertilization													
FertiType	285	1042	73	<.0001	284	422	3.57	<0.05	376	314	14.89	<.0001	24
FertiClass	172	557	69	<.0001	171	422	2.25	<0.01	362	422	4.04	<.0001	362
FertiRiskClass	219	715	69	<.0001	218	323	8.89	<0.01	277	323	48.49	<.0001	277

[1] **Random effect model of Borenstein** (Borenstein, 2009), weight equal to the inverse of $N_2O\ EF$ variance

[2] **Residual Maximum likelihood analysis**, weight equal to N_2O coverage factor (Table 1)

FertiType, type of fertilization: organic, synthetic fertilizers, organic and synthetic fertilizers

FertiClass, nature of organic sources ± synthetic sources (Table 3)

FertiRiskClass (high, medium or low), N_2O risk classes of organic sources ± synthetic sources (Table 3)

n, total # of observations used in the analysis

df, degree of freedom

Q is the weighted sum of squares on a standardized scale

I^2 is the proportion (%) of the observed variance that reflects real differences in emission factor of N_2O

$I^2=(Q\text{-}df)/Q$

P_{chi}^2, refers to testing the assumption of homogeneity in fertilization effects on N_2O emission factor; the null hypothesis is that all studies share a common emission factor.

Table 5. Sensitivity analyses of the REML approach using spatial and temporal N_2O coverage information in weighing procedures[2].

Fertilization			Acronyms	Global estimates of N_2O emission factors , % N applied										
				Raw Data		REML[1]								
						N_2O coverage weight			revised N_2O coverage weight			weighted without superior weight studies*		
				mean	median	mean	sem	*Pr* > |t| [χ]	mean	sem	*Pr* > |t| [χ]	mean	sem	*Pr* > |t| [χ]
FertiTypes		**Organic sources**	**O**	**0.82**	**0.42**	**0.57 b**	**0.30**	***<0.001***	**0.64 a**	**0.15**	***<0.001***	**0.71 A**	**0.17**	*<0.001*
		Organic and synthetic sources	**OS**	**1.50**	**0.87**	**1.15 ab**	**0.31**	***ns***	**0.88 a**	**0.19**	***<0.001***	**1.16 A**	**0.26**	*<0.001*
		Synthetic sources	**S**	**1.34**	**0.57**	**1.76 a**	**0.42**	***<0.001***	**1.62 a**	**0.32**	***<0.001***	**1.01 A**	**0.22**	*<0.001*
FertiClasses	**High risk**	**All high-risk**				**0.91 A**	**0.16**	***<0.001***	**1.88 A**	**0.47**	***<0.001***	**1.76 A**	**0.36**	***<0.001***
		Liquid manure + S	LM-S	2.44	1.72	2.14 a	0.53	*<0.001*	1.79 a	0.31	*<0.001*	1.84 a	0.50	*<0.001*
		Biosolid, CR + S	BSD-CR-S	1.64	1.54									
		Biosolid + S	BSD-S	1.16	0.88	0.89 abcd	0.45	*<0.05*	1.00 abcd	0.56	*ns*	0.73 ab	0.44	*ns*
		Waste water	WW	1.15	0.45									
		Liquid manure	LM	0.96	0.56	1.12 ab	0.18	*<0.001*	0.95 b	0.16	*<.0001*	0.93 ab	0.18	*<.0001*
		Biogas residues	BR	0.92	0.49									
		Solid manure + S	SM-S	0.78	0.85									
		Solid manure	SM	0.97	0.24	0.35 c	0.18	*<0.05*	0.69 bc	0.29	*<0.05*	0.86 ab	0.30	*<0.01*
	Medium risk	**All medium-risk**				**0.43 AB**	**0.43**	***ns***	**0.70 AB**	**2.64**	***ns***	**1.04 A**	**0.76**	***ns***
		Compost + S	CMPT-S	0.54	0.45	0.37 cd	0.24	*ns*	0.25 cd	0.33	*ns*	0.39 b	0.39	*ns*
		Crop residues + S	CR-S	0.46	0.33	0.59 bc	0.27	*<0.05*	0.49 bcd	0.43	*ns*	0.53 b	0.39	*ns*
	Low risk	**All low-risk**				**0.20 B**	**0.17**	***ns***	**0.60 B**	**0.48**	***ns***	**0.97 A**	**0.65**	***ns***
		Paper mill sludge + CR	PMS-CR	0.28	0.13									
		Compost	CMPT	0.27	0.17	0.00 *d*	0.17	*ns*	-0.03 d	0.22	*ns*	0.31 b	0.41	*ns*
		Pellets	PLTS	0.25	0.24									
		Crop residues	CR	0.19	0.08									
		Liquid manure + CR	LM-CR	0.07	0.07									
		Paper mill sludge	PMS	0.03	0.01									

[1] **Residual Maximum likelihood analysis**, weighting procedure with spatial and temporal N_2O coverage (Table 1)
Means sharing a small bold letter are not significantly different within FertiTypes by a LSD test (*P*<.05).
Means sharing a small letter are not significantly different within FertiClasses by a LSD test (*P*<.05).
Means sharing a capital letter are not significantly different within low-, medium-, and high-risk Ferticlasses by a LSD test (*P*<.05).

[χ] ***Pr* > |t|** refers to a ***t*** test to test the null hypothesis that the associated population quantity equals zero.

* **Superior weight studies** are defined as studies whose weight of N_2O observations was twice greater than the average weight of all N_2O observations (0.24%).

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[2] **FertiType**, type of fertilization: organic, synthetic fertilizers, organic and synthetic fertilizers
FertiClass, nature of organic sources ± synthetic sources (Table 3)
FertiRiskClass (high, medium or low), N_2O risk classes of organic sources ± synthetic sources (Table 3)

Table 6. Significance of environmental and management-related factors on global N_2O emission factors with the weighted REML approach.

	FERTITYPE O					FERTITYPE O AND OS					FERTITYPE S				
	n	Raw mean	***Pr > F*** mean	**df** (sem)		n	Raw mean	***Pr > F*** mean	**df** (sem)		n	Raw mean	***Pr > F*** mean	**df** (sem)	
CLIMATE															
Climate type	**251**	**0.81**	**ns**	**197**		**323**	**0.96**	**ns**	**249**		**99**	**1.34**	**ns**	**68**	
TAP[1], mm	229	0.80	*******	**173**		**296**	**0.97**	*******	**221**		**91**	**1.37**	**ns**	**58**	
0-250	42	0.20	0.21	(0.33)	*b*	51	0.21	0.29	(0.31)	*b*	12	0.48	-	-	
250-500	26	0.94	0.59	(0.47)	*ab*	45	0.78	0.61	(0.36)	*ab*	14	1.34	-	-	
500-1000	96	0.92	1.05	(0.18)	*a*	105	0.90	1.16	(0.21)	*a*	42	1.38	-	-	
> 1000	65	0.96	0.50	(0.19)	*b*	95	1.54	0.63	(0.21)	*b*	23	1.83	-	-	
MAT[2], °C	**167**	**0.82**	**ns**	**132**		**70**	**1.40**	**ns**	**170**		**70**	**1.40**	**ns**	**48**	
CROPPING SYSTEMS															
Land-use type	**251**	**0.81**	**ns**	**196**		**323**	**0.96**	**ns**	**248**		**99**	**1.34**	**ns**	**67**	
Crop type[3]	**109**	**0.64**	**ns**	**87**		**116**	**0.65**	**ns**	**100**		**34**	**1.56**	**ns**	**67**	
SOIL MANAGEMENT															
Soil tillage	**127**	**1.02**	**ns**	**100**		**184**	**1.20**	**ns**	**142**		**57**	**1.22**	**ns**	**35**	
Incorporation[4]	**207**	**0.72**	**ns**	**63**		**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	
SOIL PROPERTIES															
Drainage	**115**	**0.81**	*******	**102**		**117**	**0.81**	*******	**104**		**34**	**1.93**	******	**24**	
Poor	49	1.10	1.02	(0.16)	*a*	49	1.11	1.02	(0.16)	*a*	15	3.70	5.34	(1.46)	*a*
Well	66	0.59	0.34	(0.03)	*b*	68	0.59	0.34	(0.03)	*b*	19	0.52	0.72	(0.13)	*b*
Texture	**221**	**0.89**	*******	**129**		**281**	**1.06**	*****	**214**		**90**	**1.41**	**ns**	**61**	
Fine	49	1.33	1.52	(0.38)	*a*	81	1.77	1.42	(0.26)	*a*	24	3.01	2.85	(1.43)	*a*
Medium	44	0.96	0.82	(0.18)	*a*	56	0.91	0.71	(0.26)	*b*	21	0.93	0.70	(1.86)	*a*
Coarse	128	0.67	0.49	(0.18)	*b*	144	0.73	0.59	(0.21)	*b*	45	0.79	0.66	(3.00)	*a*
Organic C, %	**193**	**0.80**	******	**151**		**252**	**0.96**	******	**194**		**86**	**1.03**	*******	**59**	
< 1	31	0.64	0.47	(0.22)	*b*	56	0.61	0.44	(0.21)	*b*	20	0.71	1.09	(0.73)	*b*
1-3	105	0.83	0.48	(0.18)	*b*	116	0.80	0.46	(0.18)	*b*	35	0.78	-0.71	(0.66)	*b*
3-6	35	0.77	1.47	(0.29)	*a*	53	1.74	1.46	(0.26)	*a*	23	1.68	3.83	(0.72)	*a*
> 6	22	0.84	0.72	(0.84)	*ab*	27	0.85	0.72	(0.84)	*ab*	8	1.07	1.21	(2.27)	*ab*
Nitrogen, %	**165**	**0.88**	******	**140**		**225**	**1.04**	*******	**177**		**81**	**1.04**	**ns**	**58**	
< 0.1	18	0.84	0.57	(0.35)	*b*	45	0.63	0.48	(0.22)	*b*	-	-	-	-	
0.1-0.2	117	0.72	0.50	(0.17)	*b*	124	0.72	1.69	(0.36)	*a*	-	-	-	-	
> 0.2	30	1.54	1.66	(0.31)	*a*	56	2.08	0.59	(0.16)	*b*	-	-	-	-	
Soil C/N ratio	**165**	**0.88**	**ns**	**140**		**229**	**1.04**	*******	**178**		**85**	**1.12**	******	**61**	
< 10	18	0.85	0.66	(0.27)	*a*	41	0.54	0.81	(0.31)	*a*	19	1.11	1.40	(0.57)	*ab*
10-14	117	0.72	0.80	(0.19)	*a*	90	1.51	1.16	(0.23)	*a*	26	1.79	2.55	(0.71)	*a*
> 14	30	1.54	0.55	(0.24)	*a*	98	0.83	-0.17	(0.27)	*b*	40	0.69	0.04	(0.49)	*b*
pH	**184**	**0.87**	**1.76**	**ns**	**143**	**254**	**1.04**	**ns**	**194**		**90**	**1.13**	**ns**	**60**	

FertiType, type of fertilization: organic (O), synthetic fertilizers (S), organic and synthetic fertilizers (OS)

n, total # of observations used in the analysis

***Pr* > F** refers to a F-test used for comparing the soil factors of the total deviation, **df** = degree of freedom

[1] TAP, Total annual precipitation

[2] AMAT, Annual mean air temperature

[3] Crop type, type of crops (legume, grass, legume + grass) in grassland only

[4] Incorporation, incorporation depth (cm) of organic amendments only

Significance of the effect : *Pr* < 0.001***, *Pr* < 0.01** and *Pr* < 0.05*, ns = non-significant

Means sharing a letter are not significantly different within soil factor by a LSD test (*P*<.05).

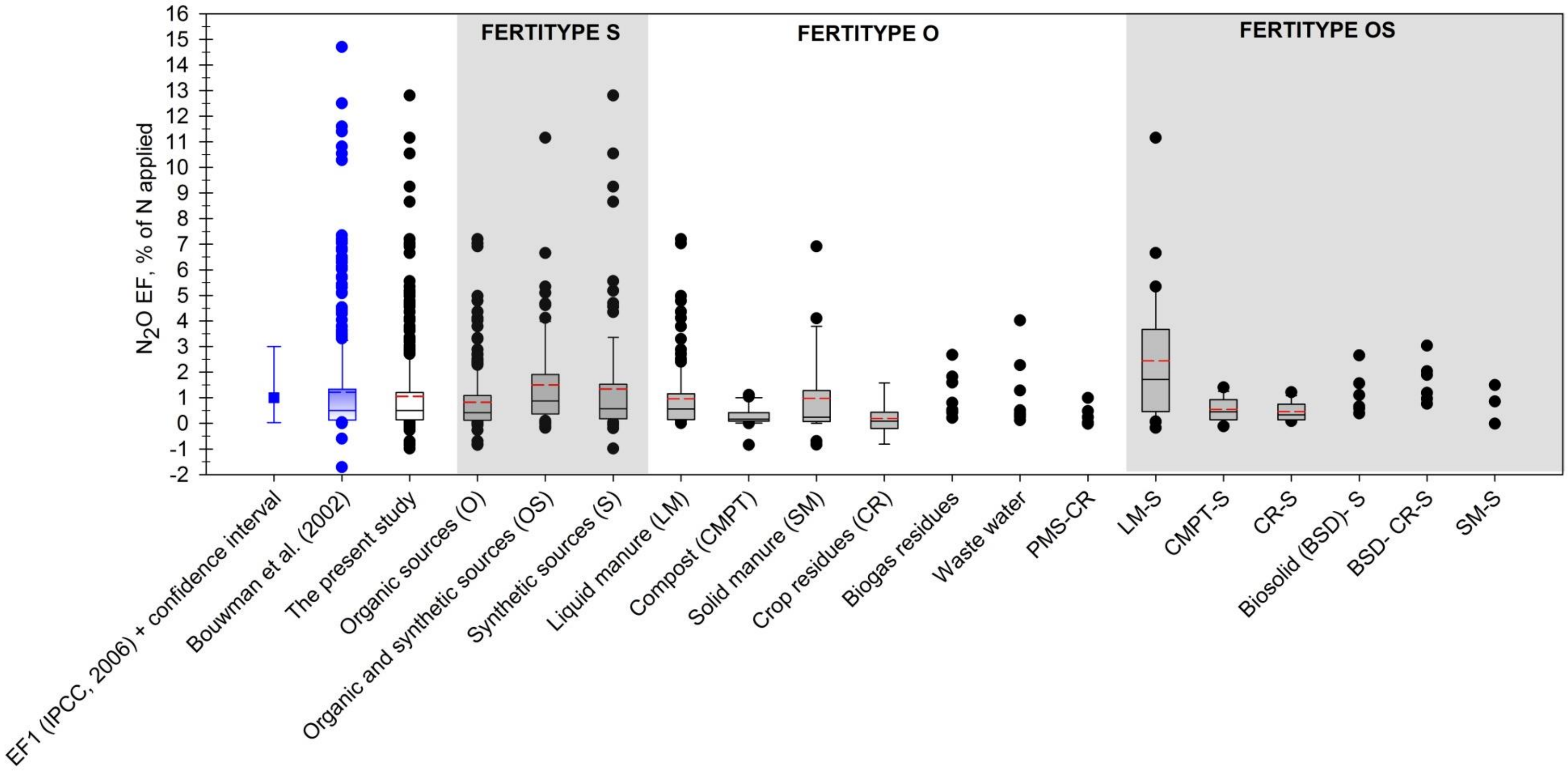


Figure 1. Global estimates of N_2O emission factors according to the type of fertilization

Vertical point plots were used for the graphical presentation of data when ten observations or less were reported in a category of fertilization. Box plots were represented when the number of observations per category of fertilization exceeded ten. The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented.

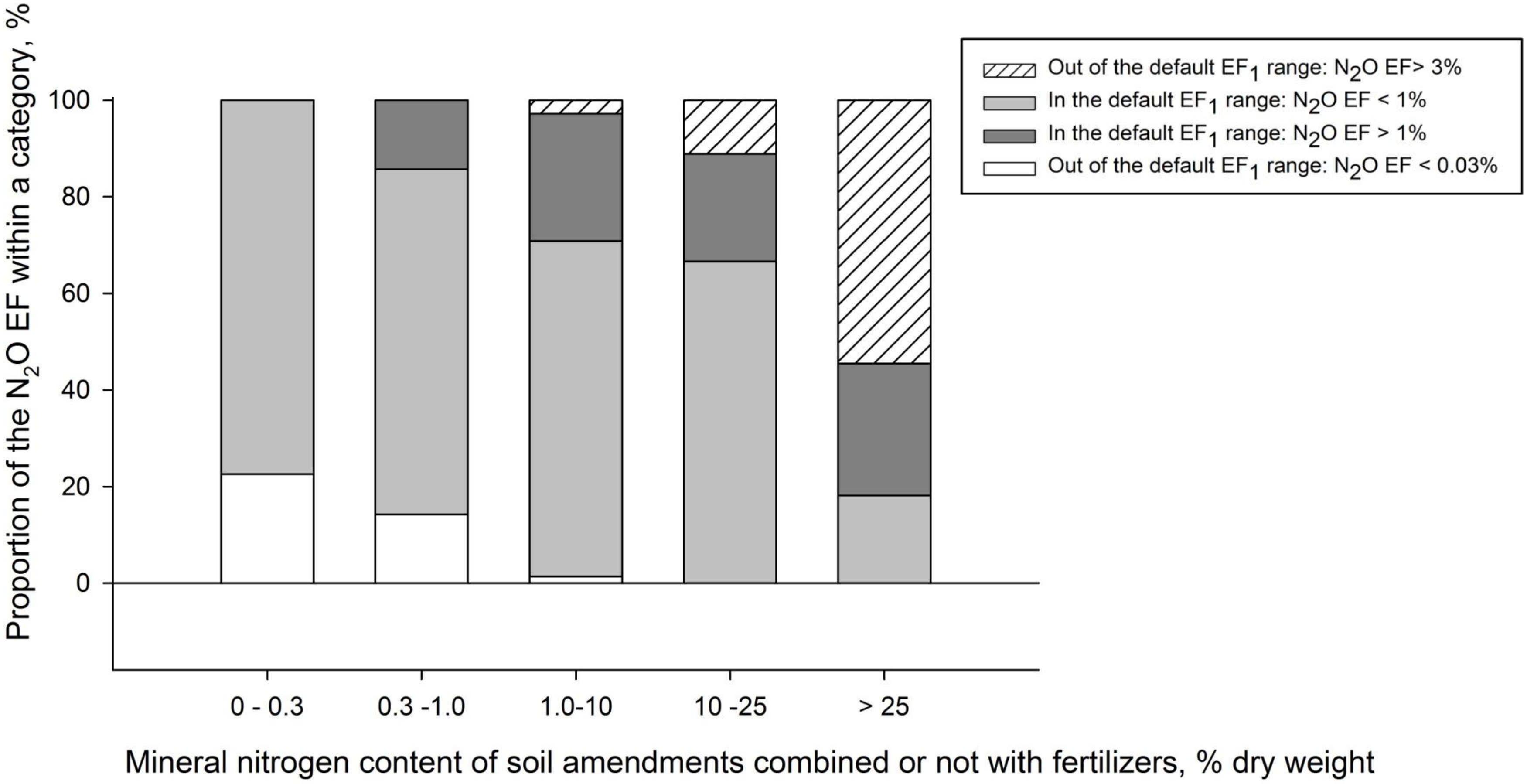


Figure 2. Global N_2O emission factors (% of N applied) according to mineral nitrogen content of inputs.

The organic sources within each mineral N class are described in Table A2-2.

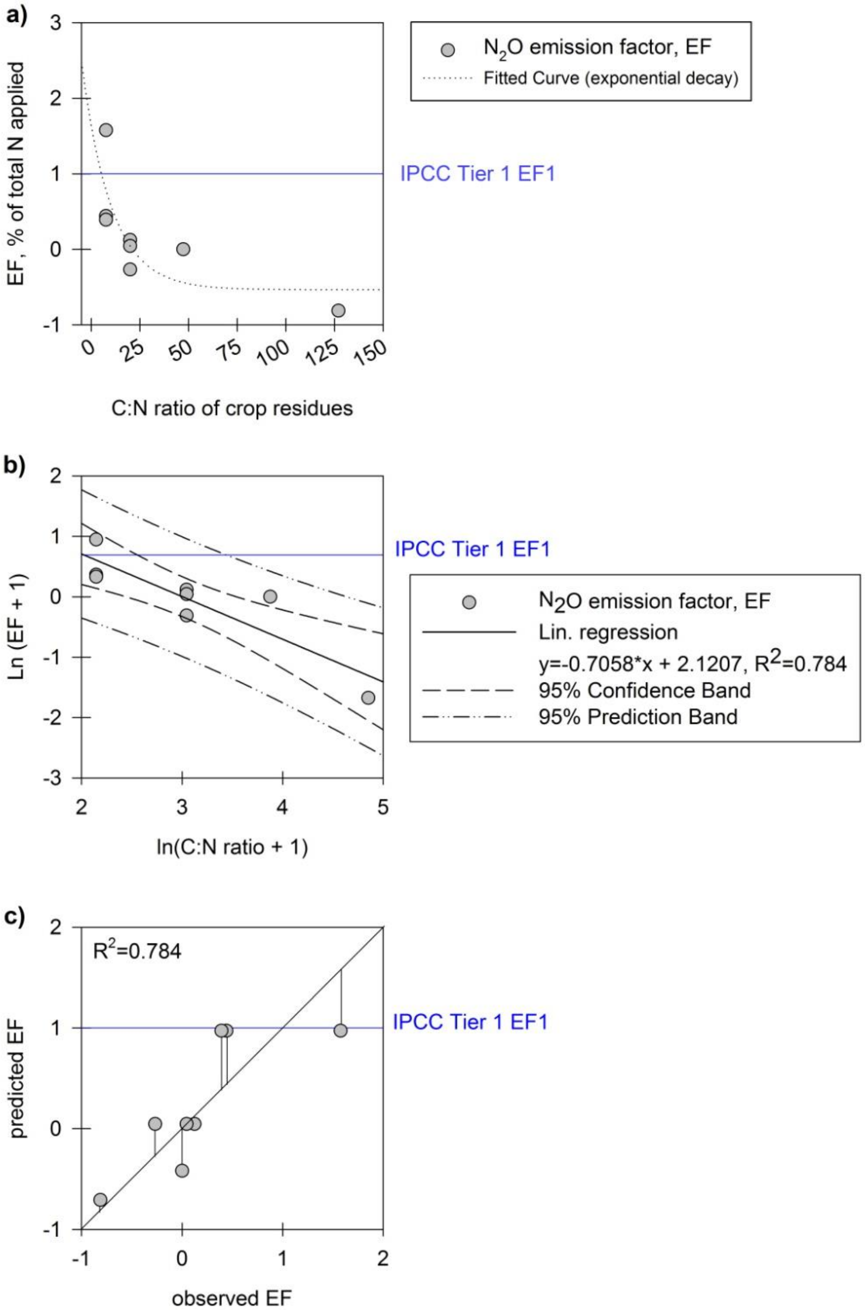


Figure 3. Nitrous oxide emission factors of crop residues as a function of C/N ratio

a) Observed N_2O emission factors as a function of crop residues C/N ratios
b) Linear regression analysis of log-transformed crop residue variables
c) Predicting N_2O emission factors of crop residues from their C/N ratio

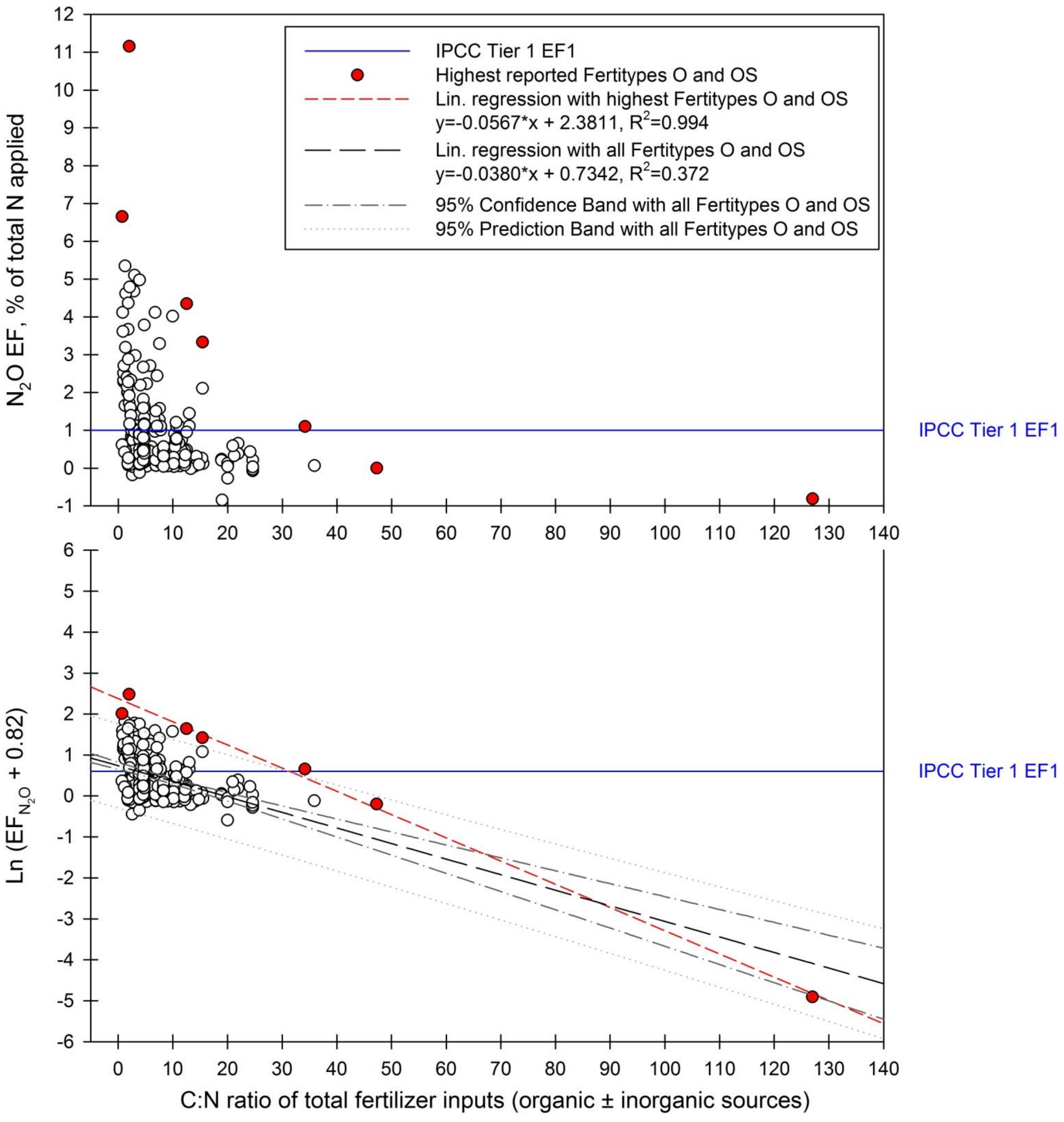


Figure 4. Global N_2O emission factors according to the C/N ratio of inputs.

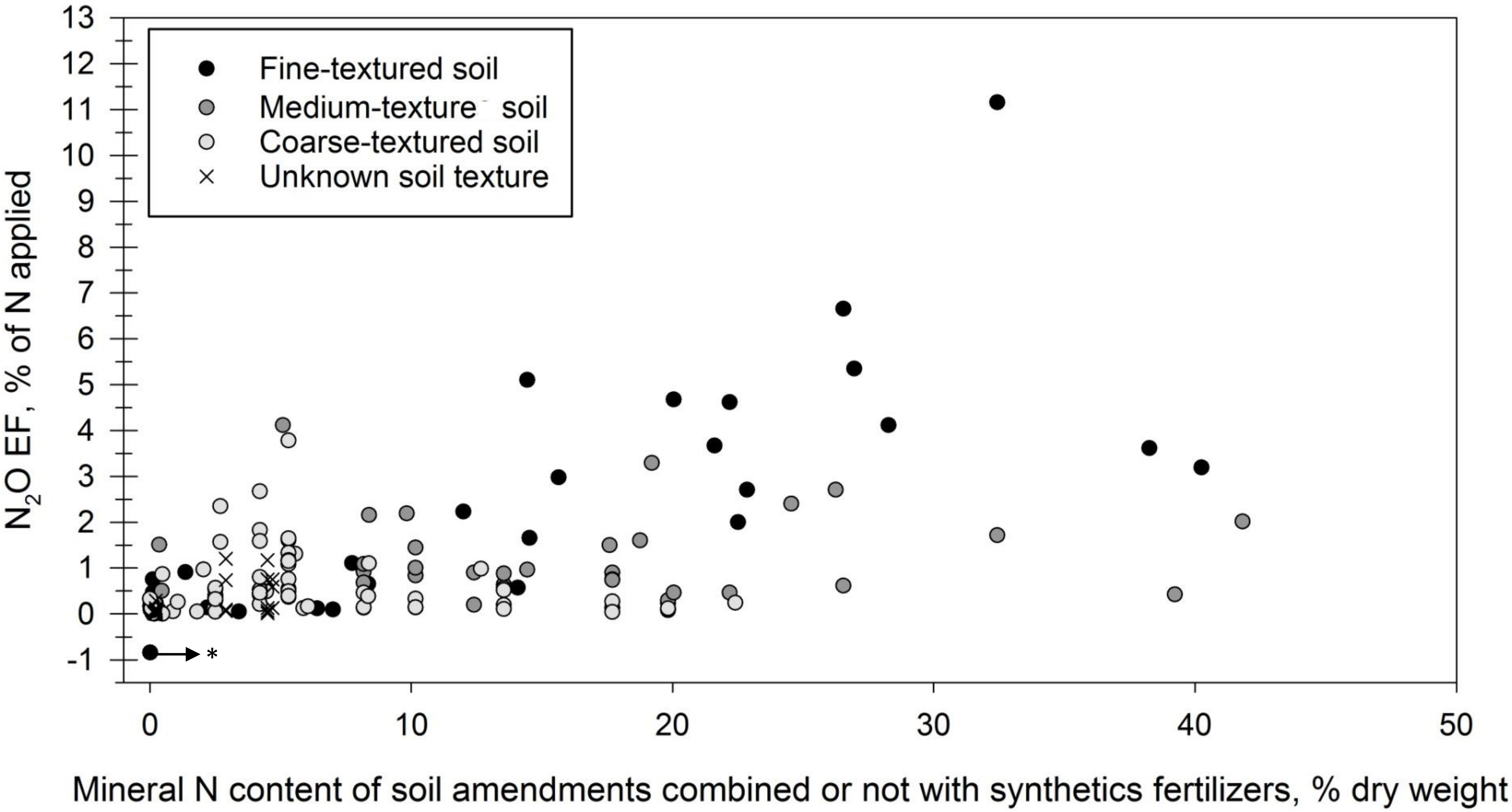


Figure 5. Modulation of global N_2O emission factors by mineral nitrogen content of inputs from organic sources, alone and combined with synthetic inputs, and soil texture.

* Emission factor reported by Dalal et al. (2010) after green waste compost application on a sorghum crop cultivated on a Vertisol (Udic Haplustert, USDA, 1975) under a subtropical climate (Australia).

FORWARD TO CHAPTER 3

The meta-analysis of on-field N_2O emissions induced by the application of OAs confirmed that variations in N_2O EFs in OA-amended soils are influenced mainly by the mineral N content and the C/N ratio of OAs, rainfall, soil texture and drainage on a global scale. Given that an EF for OAs cannot be determined readily from field studies with diverse OA sources, climate conditions, the mechanistic basis for OA contribution to N_2O production should be determined in controlled laboratory studies. However, contrasting results have been also reported in controlled conditions because the potential of OAs to induce soil N_2O emissions (POA-N_2O) is affected by many other factors including soil type, the duration of the experiment and O_2 availability during the incubation. Thus, there is a need to determine how experimental conditions affect soil N_2O emissions following application of OAs and provide recommendations for a standard methodology to assess POA-N_2O.

CHAPTER 3

Assessing the potential of organic amendments to induce soil nitrous oxide emissions in controlled conditions: a comparative study.

3.1 Abstract

Three laboratory incubation methods were evaluated to determine the potential of organic amendments (OAs) to induce N_2O emissions from a clay loam soil fertilized with either OAs or an inorganic fertilizer, or left unamended as a control. Each incubation method was done in a 1-L jar, included oxic and anoxic phases, and lasted for 92 d in the dark at 22°C. The opened/sealed-jar method with acetylene (O^w/S^+) consisted of a 43-d incubation at constant soil water content and ambient O_2, followed by an anaerobic event in an O_2-free atmosphere containing 10% $^v/_v$ of acetylene (C_2H_2). The sealed-jar methods with C_2H_2 (S/S^+) and without C_2H_2 (S/S^-) involved flushing the headspace of a closed jar with nitrogen or nitrogen containing 10% $^v/_v$ of C_2H_2 when the headspace O_2 concentration reached 5%. During the oxic phase, both S methods reflected the short-term potential of OAs to promote soil N_2O emissions 72 h after their incorporation with the $N_2O_{0\text{-}72h}$ index. The S and O methods showed different patterns of N_2O emissions, and the magnitude of N_2O fluxes was 1.1 to 2.3 times greater with the S than the O method. However, the S methods had an oxic phase limited to 72 h when testing OAs with high respiratory demand and the rapid depletion of O_2, necessitating continuous monitoring of headspace gas concentrations, is a constraint to testing numerous OAs with contrasted chemical properties. An alternative technique would involve aerating the sealed-jar system after 72 h and relying on repeated 72-h measurement periods using the $N_2O_{0\text{-}72h}$ index to assess the short-term (72-h) and long-term (multiple 72-h periods) potential of OAs to induce soil N_2O emissions. To capture the entire scope of this potential, the occurrence of an anoxic event after an oxic phase provided additional information. The duration of the oxic phase altered the magnitude of the OA effect on N_2O emissions under anoxia, as reflected in the two indices $N_2O_{ANOXMAX}$ (magnitude of N_2O emissions) and $N_2O_{ANOXRATE}$ (speed of N_2O response). The O^w/S^+ method provided the highest degree of discrimination between OAs according to $N_2O_{ANOXMAX}$ because the extended oxic period allowed for accumulation of mineral N prior to the anoxic event, as evidenced by the correlation between soil nitrate and $N_2O^{O^w/S^+}_{ANOXMAX}$ (r=0.957, $P<0.05$). $N_2O^{S/S^+}_{ANOXRATE}$ was correlated with soil CO_2 flux at the end of the S/S^+ oxic phase and, thus indicates C availability to microorganisms.

Keywords : soil incubation methodology, organic amendment, nitrous oxide, oxic/anoxic phase, acetylene, nitrification, denitrification.

Abbreviations : DM, dry matter; C, carbon; DOC, dissolved organic carbon; EF, emission factor; L, lignin; N, nitrogen; NH_4^+, ammonium; NO_3^-, nitrate; N_2O, nitrous oxide; N_2, dinitrogen; N_{min}, mineral nitrogen; N_{org}, organic nitrogen; RSD, relative standard deviation; WFPS, water-filled pore space.

3.2 Introduction

Large quantities of organic materials are added to agricultural soils in various forms including crop residues, livestock manures, sludge and composts (Chaves et al., 2005). While OAs act as physical soil conditioners and a valuable source of plant-available nutrients, they also enhance nitrification and denitrification reactions that lead to increased soil N_2O emissions, a potent greenhouse gas (Foster et al., 2007) and the dominant stratospheric ozone-depleting substance (Ravinshankara et al., 2009). In Canada, organic-N sources were estimated to contribute one third of total N_2O emissions from agricultural soils (Rochette et al., 2008b). This estimate was obtained using an emission factor derived from synthetic N fertilizers because of insufficient information about organic materials. Improved emission inventories and development of better management practices to minimize environmental impacts associated with OA application to agricultural soils will require a deeper understanding of how OA properties influence N_2O emission processes. Extreme variability in N_2O emissions from soils that received organic amendments (crop residues combined with or without inorganic fertilizers, farmyard slurries and farmyard manure) has been frequently reported in field studies with maximal relative standard deviations of N_2O cumulative fluxes ranging from 128 to 500% (Paul and Zebarth, 1997; Chantigny et al. 2001; Ellert and Janzen, 2008; Shang et al., 2011; Velthof and Mosquera, 2011; Pelster et al., 2012). Therefore, potential of OAs to induce soil N_2O emissions is often assessed in the laboratory.

Controlled studies show that N_2O emissions are related to the chemical properties of the OA, such that emissions increased with increasing mineral N content of OA and with decreasing

C/N ratio and lignin content (Lou et al., 2007; Huang et al., 2004). High N_2O emissions were associated with OA containing high levels of inorganic N and easily mineralizable N and C, such as liquid pig (Velthof et al., 2003) and sheep manure (Cardenas et al., 2007) and N-rich crop residues (Chaves et al., 2005). On the other hand, mixing manure, slurries or N-rich crop residues with materials with high C/N ratios, such as wheat straw residues (*Triticum* L.), saw dust, or composts also reduced soil N_2O emissions (Huang et al., 2004). However, it is difficult to generalize among studies due to variation in incubation conditions, which present soil temperatures ranging from -5.5 to 26° C, durations from 4 to 240 d and soil moisture either kept constant from 36 to above 90% of water-filled pore space (Cabrera et al., 1994a; De Wever et al., 2002; Chaves et al., 2005; Jezierska-Tys and Frąc, 2007; Dalal et al., 2009; Singurindy et al., 2009). Futher complexity is added when soil moisture varies to simulate dry-wet soil cycles (Cabrera et al., 1994a; Velthof et al., 2003; Bertora et al., 2008). The use of consistent experimental approaches and methodologies would help to estimate the potential of OAs to induce N_2O emissions (Flessa and Beese, 2000; Helgason et al., 2005; Lou et al., 2007). Given the diversity of incubation conditions used in the literature and the fact that there is no unique definition of potential of OAs to induce N_2O emissions, comparing several incubation approaches may help to determine how the methodology impacts the results. In this study, we opted for incubations that included the impact of two factors: the time since OA addition and the O_2 availability. Incubation duration appeared important because the mineral N (NH_4^+ or NO_3^-) in OAs is immediately available for nitrification and denitrification and can impact soil N_2O emissions in the short-term while the mineralization of organic-N substrates would be important in the long-term (Velthof et al., 2003). All incubation methods selected for this study include an oxic-anoxic cycle, which allowed build-up of NO_3^- (from nitrification) and labile C substrates (from decomposition) in the oxic phase, followed by depletion of theses substrates in the anoxic phase.

The objectives of this study were (1) to compare three incubation methods to determine how experimental conditions affect soil N_2O emissions following application of OAs and (2) provide recommendations towards a standard methodology.

3.3 Material and Methods

3.3.1 Soil properties and preparation

A Kamouraska clay (mixed, frigid, Typic Humaquept) was collected from the 0-20 cm depth (plough layer) in November 2009, about 2 wk after the field was tilled with a mouldboard plough. This poorly drained soil was collected at the Harlaka Research Farm of Agriculture and Agri-Food Canada (46°48´N, 71°23´W). This soil was selected because it showed fertilizer-induced N_2O emissions greater than the Intergovernmental Panel on Climate Change default factor (0.01 kg N_2O-N kg^{-1} N), with values ranging from 0.027 to 0.038 kg N_2O-N kg^{-1} N applied (Gagnon et al., 2011). The site was cropped with soybean (*Glycine max* L.) in 2009, so received no N fertilizer in the study year. Prior to the incubation, soil was sieved to pass a 6-mm sieve, air-dried and mixed. Selected physico-chemical properties of the Kamouraska clay are presented in Table 1. Selected physico-chemical properties of a Kamouraska clay soil (0-20 cm) used for the development of a standard method for soil N_2O emission

3.3.2 Amendment properties and preparation

Soil amendments consisted of five organic amendments: pig slurry (PS), *Medicago sativa* L. (alfalfa residues or AR), poultry manure (PM), sheep manure compost (SMC) and wheat straw residues (WSR). The inorganic fertilizer (IF) was ammonium nitrate (NH_4NO_3) (ACS reagent grade, Sigma-Aldrich, Saint Louis, MO, USA), and an unamended soil was used as control. Before application, PM and SMC were fresh and manually ground, mixed and passed through a 2 mm mesh sieve, PS was freshly mixed with a lab homogenizer (Polytron® System PT-MR 3100 D, Kinematika AG, Littau-Luzern, Switzerland) and crop residues (WSR and AR) were dried (45°C for 2 d) and manually ground, mixed and passed through a 2 mm mesh sieve. Selected characteristics of the amendments are given in Table 2. According to Palm et al. (2001) and Chivenge et al. (2011), the classification in Table 2 for amendments tested in this comparative incubation falls between that of low- and high-decomposability materials including plant residues, manures and composts. Plant residues with high decomposability (AR) refers to fresh green materials harvested before plants have senesced, whereas plant residues with low decomposability (WSR) are materials where some senescence has occurred and refers to the dead upright plant left in the field after harvest. Decomposability of manures and composts (PM, PS, SMC) are characterized by the animal that produced them (poultry, pig, sheep), the management (with or without litter) and storage of the manures (aerobic state) and whether they were composted prior to collection.

3.3.3 Soil preincubation, addition of amendments and experimental design

Pre-tests were performed on the Kamouraska clay soil to assess the impact of soil water content on structure disruption of the amendment-soil mixtures. Soil water content equal to

0.28/0.30/0.33 g H_2O g^{-1} dry soil was the minimal/optimal/maximal compromise between sample homogeneity and soil structure disruption. For the preincubation, air-dried soil (220 g oven dry basis) was moistened homogenously with distilled water to 0.28 g H_2O g^{-1} dry soil (65% of the field capacity). Wet soil was then placed in 1-L jars (one jar = one experimental unit) with gas-tight lids fitted with two 1-way male luer stopcocks. A 7-d anaerobic preincubation at 22^oC was done to remove soil NO_3-N through denitrification by sealing each jar with a lid and flushing the headspace with N_2 gas for 20 sec at 48 kPa.

After preincubation, jars were assigned randomly to four incubation methods (described below) and were either unamended (control) or received amendments (PM, PS, SMC, WSR, AR or IF) at the rates mentioned in Table 2. The amendments were applied to the soil surface, mixed homogenously by hand, and the jars were shaken horizontally to level the soil surface, leaving a headspace volume of roughly 0.87 L. Then, distilled water was added to the surface to adjust moisture of the amendment-soil mixture to 0.30 g H_2O g^{-1} dry soil (70% of the field capacity). Four replicate jars were prepared for gas analysis of each method x amendment combination (4 methods x 7 amendments x 4 replicates = 112 jars) and an additional four replicates were prepared for soil analysis at the end of the oxic phase of 3 methods x amendment combination (84 jars). The closed-jar methods were identical during the oxic phase so that the same additional replicates were attributed to both methods. Jars were placed in a constant temperature incubator (22^o C ± 0.03) in the dark for 92 d in a completely randomized design.

3.3.4 Incubation methods with oxic/anoxic phases

As summarized in Table 3, three incubation methods were evaluated: O^w/S^+, S/S^+ and S/S^-. Each method included an oxic phase with opened (O) or sealed (S) jars followed by an anoxic event with opened (/O) or sealed (/S) jars in presence ($^+$) or absence ($^-$) of acetylene: the opened/sealed-jar method with acetylene (O^w/S^+), the sealed-jar method with acetylene (S/S^+) and the sealed-jar method without acetylene (S/S^-). Duration of the oxic phase varied from 3 to 43 d, depending on the method. The anoxic event was initiated by either flushing the headspace with N_2 (S/S^- method) or flushing the headspace with N_2 enriched with 10% (v/v) of acetylene (O^w/S^+ and S/S^+ methods).

3.3.4.1 The opened/sealed-jar method (O^w/S^+)

The opened/sealed-jar method (O^w/S^+) utilized incubation in opened jars during the oxic cycle. After applying treatments, jars were capped with a lid having a central 6-mm diameter hole to provide atmospheric air exchange between successive N_2O flux measurements. Distilled water (^{w}) was added (once per wk) to maintain the initial SM moisture content at 0.3 g H_2O g^{-1} dry soil during the oxic period. After 43 days, jars were sealed with air-tight lids and the headspace air was replaced by a N_2 atmosphere enriched with 10 % (v/v) of acetylene from calcium carbide.

3.3.4.2 The sealed-jar methods (S/S^+ and S/S^-)

The sealed-jar methods refer to the S/S^+ and S/S^- methods were incubation occurred in jars continuously left closed. The S/S^+ method involved sealing jars with an air-tight lid immediately after adding amendments so O_2 in the headspace was gradually consumed by microorganisms. When the O_2 concentration in jar headspace reached 5%, the headspace was flushed with a N_2

atmosphere enriched with 10 % (v/v) of acetylene produced from calcium carbide. The O_2 threshold value of 5% was based on pre-tests and previous literature (Morley et al., 2008), which aimed at preventing high denitrification rates in localized soil microsites with reduced O_2 during the oxic phase and to synchronize replicates entering in the anoxic phase. Because soil amendments impacted O_2 consumption, the duration of the oxic phase varied from 3 to 15 d (Table 3). In contrast to the O^w/S^+ method, the transition from the oxic phase to the anoxic phase occurred steadily in the S/S^+ method. The S/S^- method followed the same method as the S/S^+ method except that the anoxic event was accomplished by flushing the headspace with N_2 that did not contain acetylene (C_2H_2).

3.3.5 Measurement of headspace gases (N_2O, CO_2 and O_2)

3.3.5.1 Frequency of gaseous measurements

During the first oxic phase under the O^w/S^+, N_2O and CO_2 concentrations in headspace gas were measured as follows: 0h, 3h and 6h after adding amendments, then 4 times during the first wk (25h, 48h, 71h and 168h), twice in the second wk (220h and 340h) and once every two wk (528h and 700h). From the moment that the anoxic event occurred, N_2O concentration was measured as follows: 5 times in the wk following the anoxic event (1032h, 1034h, 1037h, 1055h and 1080h after amendment addition), then 2 times in the next 2 wks (1103h, 1176h, 1273h and 1396h) and 4 times during the last 5 wks (1607h, 1727h, 1944h and 2207h).

During the oxic phase under the sealed-jar methods (S/S^+ and S/S^-), N_2O, O_2 and CO_2 concentrations were measured at preset frequencies until the O_2 concentration in jar headspace reached 5%, and those were: 0h, 3h and 6h after amendment addition, 6 times during the first wk (23h, 46h, 71h, 118h, 142h and 166h) and 3 times the following week (215h, 335h and 359h). After a N_2 flush with C_2H_2, headspace gas was sampled from 1 to 3 times during the first 3 d, then at least once a wk until the end of the incubation. After a N_2 flush without C_2H_2, headspace gas was sampled at least 2 times per d while N_2O emission increased, then once per d until the measured N_2O concentration was below 0.1 ppm.

3.3.5.2 Techniques for N_2O, CO_2 and O_2 measurements

For each method, soil gaseous emissions were measured using closed flux chambers and calculated by integrating of soil-surface gaseous fluxes with time. Soil-surface gaseous fluxes were expressed in µg gas kg^{-1} dry soil h^{-1} and calculated following the equation (6):

$$F_{gas} = \frac{dC_{gas}}{dt} \times \frac{V}{M} \times \frac{Mm}{Mv} \qquad \textbf{(6)}$$

where $\frac{dC_{gas}}{dt}$ (mol gas mol^{-1} h^{-1}) is the rate of change of headspace gas concentration in one h, V (m^3) is the jar headspace volume, M (kg) is the mass of dry soil contained in a jar, Mm (mg mol^{-1}) is the molecular weight of gas, Mv ($m^3 mol^{-1}$) is the air molecular volume, accounting for temperature in the room before sealing the jar (0.022 to 0.024 $m^3 mol^{-1}$). The gaseous emissions were calculated by assuming a linear change in gas concentrations within the jar with time. Hourly gaseous fluxes were then integrated over time under incubation with the O^w/S^+ method, whereas hourly gaseous concentrations were then integrated over time with incubations in sealed jars (O^w/S^+, S/S^+, S/S^-).

3.3.5.2.1 Techniques for gaseous measurements with the opened-jar method

Before closing the jar, a fan was placed vertically above the jar opening for 5 sec to mix headspace gases. Jars were closed with a gas-tight lid fitted with a two 1-way male luer stopcock. Samples of headspace gas were taken by inserting a needle fitted to a polypropylene syringe (20 mL; Becton Dickinson, Rutherford, NJ) through one stopcock equipped with a rubber septum. Before removing the 20 mL headspace gas sample, the other stopcock was opened so an equivalent volume of ambient air would enter the headspace and ensure constant pressure. Headspace gas was sampled at 0 and 60 min after closing the jar and injected into pre-evacuated vials (12-mL Exetainer, Labco, High Wycombe, UK). After gas sampling, lids were removed, jars were aerated (room atmosphere) and gas-filled vials were stored for analysis.

3.3-5.2.2 Techniques for gaseous measurements with the sealed-jar method

The closed chamber flux measured directly from sealed jars through the gas-tight lid fitted with two 1-way male luer stopcocks. One stopcock was equipped with a rubber septum for gas sampling. The other stopcock was tightly connected through a Bev-A-Line IV tube (1/8"ID x 1/4"OD) to a gas sampling bag (Kynar polyvinylidene fluoride bag, Cole-Parmer, Montreal, Canada) filled with He. Samples of headspace gas were taken by inserting a needle fitted to a polypropylene syringe (20 mL; Becton Dickinson) through one stopcock equipped with a rubber septum. Before removing the 20 mL headspace gas sample, the other stopcock was opened to replenish the headspace with He and ensure constant pressure. The dilution effect (from the gas) was accounted for in calculations. The gaseous sample was injected into pre-evacuated vials (12-mL Exetainer, Labco). After gas sampling, jars were left sealed and gas-filled vials were stored for analysis.

3.3-5.3 Gaseous measurements – Analytical procedures

Vials containing headspace gas sampled during oxic phases were analyzed for N_2O, O_2 and CO_2 concentrations within 1 wk by means of a gas chromatograph equipped with electron capture, thermal conductivity and flame ionization detectors (Model 3800, Varian Inc., Walnut Creek, CA) through a headspace autoinjector (Combi Pal, CTC Analytics, Zurich, Switzerland). Vials with gas sampled during anoxic phases were analyzed for N_2O and O_2 concentrations within 1 wk with the same gas chromatograph, except that vials containing C_2H_2 were analyzed separately within 4 to 6 wk. Because of gaseous (N_2O and C_2H_2) adsorption on rubber septa of vials derived from C_2H_2-treated jars, these septa were withdrawn from laboratory circulation to prevent cross contamination.

3.3-6 Indices of the potential of OAs to induce soil N_2O emissions

The N_2O producing potentials of various OAs added to the Kamouraska clay soil can be compared using the N_2O emission factor, EF_{N_2O}. The EF_{N_2O} expressed as the % of total N applied from a particular OA, was calculated following the equation (1):

$$EF_{N_2O} = \frac{[(N_2O\text{-}N_{treatment}) - (N_2O\text{-}N_{control})]}{N_{applied}} \times 100 \qquad \textbf{(1)}$$

where $N_2O - N_{treatment}$ is the total N_2O emissions from the soil-amendment mixture (mg N kg^{-1} dry soil) at the end of the oxic/anoxic phase and $N_2O\text{-}N_{control}$ is the total oxic/anoxic N_2O emissions from the unamended soil (mg N kg^{-1} dry soil). EF_{N_2O} was calculated for each method on the entire oxic period (N_2O_{OXIC}). Because there were short periods of time between N_2O pulses during the oxic phase, EF_{N_2O} was also calculated on a shorter period (0-72 h) in the oxic incubation ($N_2O_{0\text{-}72h}$). EF_{N_2O} was calculated for each method on the entire anoxic period ($N_2O_{ANOXMAX}$). The anoxic emission rate of N_2O ($N_2O_{ANOXRATE}$) was also calculated by linear regression and expressed in % of N applied h^{-1}, after correction for the emission rate in the unamended soil.

3.3-7 Soil analysis

Soil mineral N (NH_4-N and NO_3-N) concentration and moisture content were determined at the end of the preincubation (n=2) and at the end of the first oxic phase by destructive sampling of replicates destined for soil analysis (n=84 jars). At the end of the 92 d incubation, all jars were opened; the soil-amendment mixture was homogenized and sub-sampled for mineral N and moisture content determination. Soil mineral N was extracted by shaking 25 g of fresh soil with 125 mL of 1 M KCl for 1h, and the soil extract was analyzed with an automated continuous flow colorimeter (Model Quick-Chem 8000 FIA+, Lachat Instruments, Loveland, CO).

3.3-8 Statistical analysis

To test the fixed effect of methods on soil N_2O emissions (N_2O_{OXIC}, $N_2O_{0\text{-}72h}$, $N_2O_{ANOXMAX}$, $N_2O_{ANOXRATE}$) for each amendment, analysis of variance with heterogeneous variances was performed using the MIXED procedure of SAS (Version 9.2, SAS Institute, Cary, NC). Differences between methods or between amendments were evaluated with a Tukey-Kramer multiple comparisons test ($P < 0.05$). Precision of measurements was investigated using the relative standard deviation (RSD) (Russow et al, 1996). Relationships between N_2O_{OXIC}, $N_2O_{0\text{-}72h}$, $N_2O_{ANOXMAX}$ and $N_2O_{ANOXRATE}$, soil CO_2 emissions and chemical properties of amendments were evaluated with the CORR procedure and expressed as Spearman correlation coefficients because of a non-normal distribution of data. For all methods, least squares regressions were used to describe the functional relationship between soil NO_3-N concentration at the end of the oxic phase and soil N_2O emitted during the anoxic phase (Sigma Plot version 12.0: Systat Software Inc., San Jose, CA).

3.4 Results

3.4-1 Oxic phase

3.4-1.1 N_2O emissions and cumulative losses

The N_2O emissions showed immediate response to amendment addition with ≥ 50% of the total oxic emissions occurring during the first 72 h of incubation (Fig. 1). However, temporal patterns of emissions differed among OAs and between incubation methods. Cumulative emissions at the end of the incubation period of the S methods (3 to 15 d) were similar to those observed at the same incubation time in the O method for the CTL, SMC, WSR and IF treatments but 1.1, 2.3 and 1.4 times greater for AR, PM and PS, respectively. With the O/S^+, N_2O emission rates declined after 72 h, and OA-enhanced emissions were back to the CTL level within 7 d.

3.4-1.2 Variation in the N_2O emission factor

Compared to the O method, the N_2O_{72h} and N_2O_{OXIC} indices in the S methods were greater for the AR, PM and PS treatments but similar for the IF, WSR and SMC treatments (Table 4). The incubation method did not affect IF whereas it affected N_2O_{72h} and N_2O_{OXIC} of OAs (Table 4). Both O and S methods provide similar N_2O_{72h} and N_2O_{OXIC} for low- and very low-decomposability OAs (WSR, SMC), whereas the S method yielded significant higher N_2O_{72h} and N_2O_{OXIC} for OAs with higher decomposability (AR, PM, PS).

The $N_2O^O_{72h}$ and $N_2O^O_{OXIC}$ indices provided equivalent information: only PM addition led to a significantly higher N_2O_{72h} and N_2O_{OXIC} (Table 5). In contrast, all class I OAs led to significantly higher N_2O oxic indices using the S method but their relative classification slightly differed between 72 h and the whole oxic period due to 2.3 to 2.6 greater $N_2O^S_{OXIC}$ for the WSR and the IF treatments (Table 5). Because the first 72 hours offered the common time frame between methods that allowed comparing all OAs in oxic conditions with 50% of the total oxic cumulative N_2O emissions occurring during this time, $N_2O_{0\text{-}72h}$ was used for further comparison between and within methods. Precision of N_2O_{72h} varied between methods with relative standard deviation (RSD) from the AR- and PS-amended soils 2.4 and 1.7 greater with the O than with the S methods (Table 4). In contrast, RSD of N_2O_{72h} in the PM-amended soils decreased by a factor of 2.5 with the O compared to the S method. For all incubation methods, RSD of N_2O_{72h} in the WSR- and SMC-amended soils exceeded 67% (Table 4).

3.4-1.3 N_2O emission factor, OA properties and soil measurements

No OA properties were correlated to $N_2O_{0\text{-}72h}$ with the O method (Table 6). In contrast, the S methods yielded correlations between $N_2O_{0\text{-}72h}$ and the N_{min}/N_{org} (r = + 0.62 and r = +0.72 respectively, n = 20, $P < 0.01$ and $P < 0.001$), and between $N_2O_{0\text{-}72h}$ and the DOC:(C-DOC) ratios (r = + 0.63 and r = +0.74 respectively, n = 20, $P < 0.01$). The N_2O_{72h} index was significantly correlated with C/N and Lignin/N ratios in one of the two S methods (r = - 0.50, n = 20, $P < 0.05$). Similarly, cumulative soil N_2O and CO_2 emissions were correlated in the S methods (r = + 0.669 and r = +0.613 respectively, n = 20, $P < 0.01$), but not with the O method. At the end of the oxic phase, soil NO_3^- concentrations were greater for all treatments except WSR (Table A3-2-1).

Within methods, greater soil NO_3^- concentrations were present at the end of the oxic phase in control jars compared to all amended soils, except WSR (Table A3-2-1).

3.4-2 Anoxic phase

3.4-2.1 N_2O emissions and cumulative losses

The total amount of soil N_2O emitted (in oxic and anoxic phases) in the CTL jars after 92 d reached 16799±1436, 16207 ± 1018 and 1682 ± 410 mg N_2O-N kg^{-1} dry soil in the O^w/S^+, S/S^+ and S/S^- methods, respectively. The N_2O emissions from amended soils showed immediate response to free-O_2 flush (using N_2) with their maximum occurring within 92, 58, and 21 d of incubation in the O^w/S^+, S/S^+ and S/S^- methods, respectively (Fig. 1). In absence of C_2H_2 (S/S^-), the period required for headspace N_2O to be consumed varied between 24 h (WSR) to 23 d (IF). In presence of C_2H_2 (S/S^+), N_2O concentrations were greater than those measured with S/S^- and reached a plateau followed by a slow gradual decline for all treatments (Fig. 1).

Compared to the CTL, the O^w/S^+, S/S^+ and S/S^- methods increased N_2O emissions in the IF treatment by a factor of 5.5, 7.8 and 15.8, respectively, and decreased N_2O emissions in the WSR treatment by a factor of 14.9, 2.9 and 7.6, respectively ($P < 0.05$). In the O^w/S^+ method, cumulative emissions after 92 d increased significantly with the addition of AR, PM and PS by factors of 2.5, 4.5 and 2.9, respectively, relative to the CTL ($P < 0.05$). In contrast, the S/S^+ method did not increase N_2O emissions in jars amended with highly-decomposable OAs (AR, PM, PS) above those observed in the CTL jars. The O^w/S^+ method allows for a 3 to 14 longer oxic period than the S/S^+ method, and jars amended with highly-decomposable OAs (AR, PM, PS) emitted about 5 times more soil N_2O during the anoxic phase.

3.4-2.2 Variation in the $N_2O_{ANOXMAX}$ and $N_2O_{ANOXRATE}$ indices

Compared to the S/S^+ method, estimates of $N_2O_{ANOXMAX}$ in jars that were kept opened for 40 d during the oxic phase (O^w/S^+) were lower for WSR and IF, similar for SMC, and greater for AR, PM and PS (Table 4). However, the maximum N_2O emission was reached earlier in the S/S^+ methods. For jars that were sealed during the oxic period, the addition of C_2H_2 to the headspace (S/S^+) resulted in approximately 2-fold greater $N_2O_{ANOXMAX}$ than with C_2H_2-free air (S/S^-) and 32 to 369% greater $N_2O_{ANOXRATE}$ or similar $N_2O_{ANOXRATE}$ for the IF treatment (Table 4). Anoxic phases of all three methods highlighted the potential of WSR, but not the other OAs, in reducing N_2O emissions compared to CTL jars.

The O/S^+ method was better at controlling $N_2O_{ANOXMAX}$ precision in amended jars with up to 10-fold lower RSD value than the S/S^+ method for the PS treatment. The S/S^+ method was the best at controlling $N_2O_{ANOXRATE}$ precision with up to a 42-fold lower RSD value than the O^w/S^+ method for the AR treatment. Regardless of the method, the $N_2O_{ANOXMAX}$ of the SMC treatment and the $N_2O_{ANOXRATE}$ of the WSR treatment were highly variable, with RSD averaging 168±148 and 96 ± 54% respectively (Table 4).

3.4-2.3 $N_2O_{ANOXMAX}$, $N_2O_{ANOXRATE}$, OA properties and soil measurements

Estimates of anoxic indices correlated to several OA characteristics. Values of $N_2O_{ANOXMAX}$ from all methods correlated to the C/N, Lignin/N, N_{min}/N_{org} and DOC/(C-DOC) ratios (Table 6). Among the three methods, the S/S^- method yielded highest correlations between both anoxic indices and the Lignin/N, N_{min}/N_{org} and DOC/(C-DOC) ratios whereas in the S/S^+

method, $N_2O_{ANOXRATE}$ was only correlated to the N_{min}/N_{org} and DOC/(C-DOC) ratios. No correlation was established with the O/S^+ method between $N_2O_{ANOXRATE}$ and OA properties.

Values of $N_2O_{ANOXMAX}$ were related to the soil NO_3 concentration generated from OA decomposition during the oxic phase with the best linear fit obtained with from the O/S+ method (Fig. 2). In the S/S^+ method, $N_2O_{ANOXRATE}$ values were positively correlated to the soil CO_2 flux at the onset of the anoxic event (Spearman correlation, r = 0.79478, $P < 0.001$) with the best linear fit obtained with from the S/S^+ method (Fig. 3). The most striking difference in $N_2O_{ANOXRATE}$ values were observed with the S methods for the WSR treatment that reached 5454 ± 2269 or -2028±3043 mg N kg^{-1} N applied h^{-1} in presence or absence of C_2H_2, respectively (Table 4).

3.5 Discussion

The three methods tested in this study included an oxic and an anoxic phase, in line with the strong impact of redox potential on N_2O-producing reactions in soils. The impact of protocol differences on creating oxic and anoxic conditions are discussed and involved whether jars were sealed or kept open during the oxic phase, the duration of each phase, and the use of C_2H_2 during the anoxic phase.

3.5-1 Sealed vs. opened jars during the oxic phase

Compared to the open-jar system, sealing jars provided greater N_2O_{72h} estimates for most OAs, a better discrimination between OAs and higher correlations between N_2O_{72h} with OA properties. Possible explanations for the greater expression of this potential in S methods include: a better temporal integration of emissions with the S method; a decreased redox potential at the active microsites. Emissions of N_2O are notoriously episodic and short peaks of emissions may have been missed with the intermittent monitoring of the open-jar system (See Fig. A3-2). Occurrence of these peaks may have been greater when highly decomposable organic materials were added, resulting in greater underestimation using the periodic sampling of the O method. Greater CO_2 emissions (72 h) observed in the sealed than open chambers for the soils amended with class I OAs ($P<0.05$), (data not shown) provide additional support for an incomplete temporal integration of gas emissions by the open method. The redox potential at the active microsites is mostly determined by the rate at which O_2 is consumed and that at which it is replenished. The replacement of consumed O_2 at the active microsites depends on the concentration gradient and the resistance to O_2 diffusion. Soil properties that determine gas diffusivity (bulk density and water content) were identical in both methods and differences in gas resistance are unlikely. In contrast, sealing jars resulted in a gradual decrease in O_2 concentration that likely resulted in lower O_2 concentration at the outer boundary of the soil aggregates in sealed compared to open-jars, and associated slower O_2 diffusion towards the active microsites. The combination of slower O_2 diffusion and greater or equal respiration rates (see above) in sealed than in open jars suggest that lower redox potential occurred at the soil active microsites in the sealed than in the open jars. Our results therefore support that higher N_2O_{72h} in sealed than in open jars resulted from a decreased redox potential at the active microsites that promoted greater N_2O yield of nitrification and greater denitrification rates, especially where OAs with greater decomposability (class I) were added. The progressive decline of O_2 below ambient level in the headspace of the sealed-jar system permits greater measurements of the potential of class I OAs in enhancing soil N_2O on a short period of time using the $N_2O^S_{72h}$index, which is not possible with the O method.

Concentration in O_2 and redox potential decreased with time following the sealing of jars and it is legitimate to ask how these changes affected net N_2O production. Accumulation of N_2O in sealed-jar headspace increased linearly with decreasing O_2 concentration for all treatments, except PM for which N_2O concentrations increased non-linearly (Fig. A3-1). This indicates that for most situations, the net N_2O production did not differ drastically along the range of redox potential resulting of O_2 depletion from 21 to 5%. The rate of O_2 consumption in PM-amended soils wasn't the fastest among class 1 OAs, thus, such nonlinear N_2O response could not be entirely explained by lower redox potentials in PM-amended soils compared to other class 1 OAs with the S methods, as O_2 uptake was faster in AR and PS (72 h) than in PM (120 h) treatments (Fig. 1). We hypothesize that the non-linear response of N_2O emission to O_2 levels in PM is the result of a release of NH_4-N from the mineralization of uric acid and urea that occurred following incorporation into soil. Therefore, the different response of PM would be related to variations in mineral N supply to N_2O producing processes rather than by factors related to C dynamics or redox potential. High N_2O emissions from the PM-amended soil, observed in the S methods but not in the O method, are in agreement with especially increased emissions in field situations where PM applications were often found to increase soil N_2O production rates more than mineral fertilizers (Thornton et al., 1998; Akiyama et al., 2003; Dong et al., 2005; Jones et al., 2007; Pelster et al., 2012).

In controlled conditions, N_2O emissions were positively correlated to inorganic N and easily mineralizable N and C contents in linquid pig (Velthof et al., 2003) and sheep manure (Cardenas et al., 2007), and in N-rich crop residues (Chaves et al., 2005). By contrast, N_2O emissions were positively correlated to C/N ratios (wheat straw residues, saw dust, composts) of manure, slurries or N-rich crop residues (Huang et al., 2004). Thus, that the N_2O_{72h} estimated using the S method (but not those obtained with the O method) correlated with several OAs characteristics suggests that the S method provides conditions that better favor the expression of OAs potential for N_2O emission. Finally, sealing the jar with the S method presented the following advantages (Table 7a):

- the method was sensitive to short-lived pulses of class I OA-induced N_2O emissions with a good integration of soil N_2O emissions;

- the method did not require soil water monitoring, minimizing possible perturbations (Mikha et al., 2005);

- the method provided a better discrimination between N_2O_{72h} indices of OAs, probably due to transient conditions from oxic to anoxic (Liang et al., 1996);

- the method is fast and economical for N_2O monitoring.

3.5-2 Duration of the oxic phase

For each method, we investigated whether the first 72 h of incubation provided enough information for ranking OAs related to their potential to enhance soil N_2O emissions, or if measurements during the whole oxic period were necessary. The oxic phase for the S method did not exceed 14 d and the OA rankings based on N_2O_{oxic} and N_2O_{72h} were similar, except for the IF and SMC treatments whose variability of N_2O_{oxic} was greater than that of N_2O_{72h} with a mean 2.2 and 1.3 fold increase in RSD values, respectively. For the O method, the OA-induced N_2O emissions were not sustained beyond 7 d following OA addition (Fig. A3-2) and N_2O_{72h} captured most of the OA N_2O potential with similar OA rankings based on N_2O_{oxic} and N_2O_{72h}. Moreover, the variability of N_2O_{oxic} was greater than that of N_2O_{72h} with a mean 2.2 fold increase in RDS values of all treatments. Therefore, extending the oxic period beyond 72 h did not bring additional information about the oxic potential of tested OAs to enhance soil N_2O emissions for both methods.

The O^w/S^+ method maintained oxic conditions during 29 d that favored OA decomposition, mineralization, nitrification and build-up of soil NO_3^- for an extended period of time, before an anoxic event occurred that could trigger soil N_2O emissions. Whereas a short oxic phase (72-h) was efficient for capturing the oxic N_2O potential, extending the duration of the oxic phase had major impacts on the anoxic N_2O potential. We investigated whether the impact of oxic phase duration reflected in $N_2O_{ANOXMAX}$ and $N_2O_{ANOXRATE}$ indices could be explained by changes induced by OA addition on soil mineral N and C availability. The $N_2O_{ANOXMAX}$ index was related to soil NO_3^--N concentrations at the end of the oxic phase and expressed in % of N applied (Fig. 2), and the $N_2O^{O^w/S^+}_{ANOXMAX}$ was generally greater than the $N_2O^{S/S^+}_{ANOXMAX}$ as the longer oxic phase in the O method allowed for greater mineralization and accumulation of NO_3^- than in the S method. A better discrimination of OA using $N_2O_{ANOXMAX}$ was also obtained in the O than in the S method, in part because of the greater mineralization but also because of a larger NO_3 immobilization in WSR-amended jars than the S method prior to the anoxic cycle (Table A3-2-1). When C_2H_2 efficiently inhibits the N_2O reductase, the amount of N_2O-N emitted in anoxic conditions should correspond to the amount of soil NO_3^--N present at the onset of the anoxic phase (Yoshinari et al., 1977). The slope (0.95 N_2O-N/soil NO_3^-N) of the linear relationship for the O/S^+ method (Fig. 2a) is in agreement with these expected results. In contrast, the S/S^+ method yielded $N_2O_{ANOXMAX}$ values 1.9±0.6 times greater than the soil NO_3^--N accumulated at the onset of the anoxic phase. Similar observations have also been reported occasionally in sealed-bottle incubations of silty loam soil mixed with wheat straw or alfalfa residues and fertilized with KNO_3 (deCatanzaro et al., 1987). Total gaseous products of denitrification were also shown to exceed the amounts of initial NO_3^--N substrates in a soil amended with $Ca(NO_3)^2$ (Yeomans and Beauchamp, 1981). It is unclear why this unbalance between soil NO_3^- and soil N_2O emitted in the anoxic phase was observed following IF addition in the S/S^+ but not in the O/S^+ method. The soil NH_4^+ concentration increased in both S/S^+ and O^w/S^+ methods during the anoxic phase, indicating that N transformations other than denitrification occurred. Possible explanations for a N_2O-N/NO_3-N ratio >1 include: (1) Short-lived ammonification/nitrification occurred if residual O_2 was present in soil early after flush of jars with N_2, and greater amounts of easily decomposable C could have been available following the shorter oxic phase in the S/S^+ method, (2) greater co-denitrification in IF-amended soils with the S/S^+ than with the O/S^+ method, possibly fueled by N substrates originating from the soil organic matter resulting in 2 mol of N_2O produced per 2 mol NO_3^- (Spott et al., 2011).

Whereas $N_2O_{ANOXMAX}$ is determined by the size of the soil NO_3^- pool, $N_2O_{ANOXRATE}$ is expected to reflect the impact of the amount of easily decomposable organic C on the denitrification rate. Accordingly, $N_2O_{ANOXRATE}$ was greater for the S/S^+ than for the O/S^+ method because the 3 to 14 times longer oxic phase of the O/S^+ method allowed for the oxidation of a greater part of the OAs' degradable organic substrates. This is in line with the close correlation between $N_2O_{ANOXRATE}$ and the CO_2 flux at the onset of the anoxic phase with the S/S^+ but not with the O^w/S^+ method (Fig. 3). Therefore, we expect $N_2O_{ANOXRATE}$ would increase with increasing amounts of decomposable C in OAs and would decrease as the duration of the oxic phase increases (with time since OA application).

3.5-3 The use of C_2H_2

Without the use of acetylene (S/S^-), $N_2O_{ANOXMAX}$ was approximately 3.8 times smaller than the soil NO_3^- present prior to the anoxic phase (Fig. 2c). This finding is in line with the reduction of some of the N_2O produced as the NO_3^- became more scarce (Senbayram et al., 2012). The relationship between $N_2O_{ANOXMAX}$ and the soil NO_3^--N was not linear mostly because of increased $N_2O_{ANOXMAX}$ values for the IF treatment (Fig. 2c). Relationship between $N_2O_{ANOXMAX}$ and OA-induced NO_3^- was similar between the S/S^- and the S/S^+ method but presented a lower slope without C_2H_2 (Fig. 2b et 2c).

3.6 Conclusion

Three methods of assessing the potential N_2O emissions from soils with OAs were evaluated and comparative evaluations of oxic and anoxic phases were summarized in Tables 7a and 7b, respectively. In oxic conditions that do not exceed 14 d, the two S methods reflected the short-term potential of OAs to promote soil N_2O emissions 72 h after their incorporation, presumably due to the rapid depletion of O_2 in sealed jars. In contrast, the O method maintained oxic conditions during 29 d that favored OA decomposition, mineralization, nitrification and build-up of soil NO_3^- for an extended period of time, before an anoxic event occurred that could trigger soil N_2O emissions. In the oxic phase, the S and O methods showed different patterns of N_2O emissions, and the magnitude of N_2O fluxes was 1.1 to 2.3 times greater with the S methods than the O method. From 0 to 72h of incubation, the sealed-jar system was judged more sensitive than the open-jar system to short-lived pulses of N_2O emissions caused by the addition of OAs with high decomposability. The progressive decline of O_2 below ambient level in the headspace of the sealed-jar system permits evaluation of OAs role in enhancing soil N_2O in a O_2-limited environment (oxic phase ceased at 5% O_2 concentration), which is not possible with the O method. However, the S methods had a limited oxic phase (about 72 h) when testing OAs with high respiratory demand and the rapid depletion of headspace O_2 necessitated continuous monitoring of headspace gas concentrations. This is a constraint to testing OAs with a broad range of chemical properties using the S method. An alternative technique would involve aerating the sealed-jar system after 72 h and relying on repeated 72-h measurement periods with the S method to assess the short-term (72-h) and medium-term (multiple 72-h periods) potential of OAs to induce soil N_2O emissions with the $N_2O_{0\text{-}72h}$ index.

We considered that both oxic and anoxic conditions were necessary to adequately assess the potential of OAs to enhance soil N_2O emissions because oxic conditions favor the accumulation of substrates for N_2O production in soil, while anoxic conditions (e.g., after a rainfall event) trigger substrate consumption through denitrifier activity (Sextone et al., 1985; Baggs et al., 2000). The duration of the oxic phase altered the magnitude of the OA effect on N_2O emissions under anoxia, as reflected in the two indices $N_2O_{ANOXMAX}$ (magnitude of N_2O emissions) and $N_2O_{ANOXRATE}$ (speed of N_2O response). The O^w/S^+ method provided the highest degree of discrimination between OAs according to $N_2O_{ANOXMAX}$ because the extended oxic period (up to 43 days) allowed for accumulation of mineral N prior to the anoxic cycle, as evidenced by the correlation between mineral N and $N_2O_{ANOXMAX}^{O^w/S^+}$ (r=0.957, $P<0.05$). With the S methods, anoxic conditions were induced by heterotrophic respiration in the sealed-jar system and were related to the amount of C from OAs that was oxidized during a short oxic phase (72 to 336 h). The $N_2O_{ANOXRATE}^{S/S^+}$ index was correlated with the soil CO_2 flux at the end of the oxic phase and thus, was an indicator of C availability to microorganisms.

Table 1. Selected physico-chemical properties of a Kamouraska clay soil (0-20 cm) used for the development of a standard method for soil N_2O emission

Parameter		**Mean**	**(SD)**
Texture			
Clay	g kg^{-1} DM	559.6	
Silt	g kg^{-1} DM	373.3	
Sand	g kg^{-1} DM	67.1	
Before pre-incubation			
C	g kg^{-1} DM	36.3	(0.0)
N	g kg^{-1} DM	2.7	(0.0)
DOC	mg kg^{-1} DM	29.6	(2.1)
NO_3-N	mg kg^{-1} DM	19.2	(0.6)
NH_4-N	mg kg^{-1} DM	0.7	(0.4)
After the 1-wk pre-incubation			
NO_3-N	mg kg^{-1} DM	3.8	(2.8)
NH_4-N	mg kg^{-1} DM	2.7	(0.2)

C, total C content measured by dry combustion (Model TruSpec CN, Leco Corp., St-Joseph, MI)
N, total N content measured by dry combustion except for the N in pig slurry determined by acid digestion (Isaac and Johnson, 1976)
DOC, dissolved organic carbon (distilled water) measured with a Formacs TOC/TN analyzer (Skalar, Breda, The Netherlands)
NO_3-N and **NH_4-N**, nitrate and ammonium concentrations (KCl 1M) measured with an automated continuous flow colorimeter (Model Quick-Chem 8000 FIA+, Lachat Instruments, Loveland, CO).

Table 2. Chemical composition and application rate of soil amendments used for the development of a standard method for soil N_2O emission

(in parenthesis are standard deviation values, n=3)

Amendment	**Abbr**	**Chemical properties**								**Application rates** [b]		**Quality class** [c]	
			g kg^{-1} DM						g gk^{-1}	mg-N kg^{-1} dry soil	kg-N ha^{-1}	Category [c]	Decomposition rate [c]
		C:N	**C**	**N**	**DOC**	**NO_3-N**	**NH_4-N**	**L**	**DM**				
NH_4NO_3	**IF**		nd	343	nd	77.10 [a]	266.80 [a]	nd	996 (0.0)	73	120		
Pig slurry	**PS**	6	439 (1)	75.64 (0)	106.2 (18.7)	0.03 (0.01)	46.79 (4.48)	2 (0)	53 (0.2)	101	165	I	High
Alfalfa residues	**AR**	9	437 (0)	49 (0)	nd	35.84 (0.69)	4.17 (0.06)	8 (0)	144 (0.1)	73	120	I	High
Poultry manure	**PM**	10	414 (8)	41 (2)	89.2 (4.3)	0.00 (0.00)	11.74 (0.08)	44 (2)	565 (0.2)	73	120	I	High
Sheep manure compost	**SMC**	30	278 (5)	9 (0)	1.0 (0.0)	0.02 (0.00)	0.00 (0.00)	188 (1)	394 (0.4)	73	120	IV	Very Low
Wheat straw residues	**WSR**	140	491 (1)	4 (0)	15.5 (0.5)	0.02 (0.01)	0.02 (0.02)	120 (12)	961 (0.2)	11	18	III	Low

DM, dry matter

C, total C content measured by dry combustion (Model TruSpec CN, Leco Corp., St-Joseph, MI)

N, total N content measured by dry combustion except for the N in pig slurry determined by acid digestion (Isaac and Johnson, 1976)

DOC, dissolved organic carbon (distilled water) measured with a Formacs TOC/TN analyzer (Skalar, Breda, The Netherlands)

NO_3-N and **NH_4-N**, nitrate and ammonium concentrations (1M KCl) measured with an automated continuous flow colorimeter (Model Quick-Chem 8000 FIA+, Lachat Instruments, Loveland, CO).

L, lignin fraction calculated as L= ADF-C

nd, not determined

[a] Estimation based on the chemical properties given by the manufacturer (Sigma-Aldrich).

[b] Application rates were N-based and representative of agronomic rates (CRAAQ, 2003).

[c] Organic resource quality classification according to Palm et al. (2001) and Chivenge et al. (2011).

Table 3. Incubation parameters of four laboratory methods proposed to evaluate the N_2O producing potential from soils receiving organic amendments.

	The opened-jar methods (O)	**The sealed-jar methods (S)**	
Method *(Abbreviation)*	**opened/sealed jar** ***(O^w/S^+)***	**sealed jar without C_2H_2** ***(S/S^-)***	**sealed jar with C_2H_2** ***(S/S^+)***
Oxic phase	43 days Opened jar Constant soil moisture 70% of field capacity [‡]	3 to 15 days Sealed jar Constant soil moisture 70 % of field capacity [‡] headspace O_2 concentration: 21 →5 vol% O_2	
Anoxic event	49 days Sealed jar Constant soil moisture 70% of field capacity [‡] N_2 Flush at 10 vol% C_2H_2	77 to 89 days Sealed jar Constant soil moisture 70 % of field capacity [‡] N_2 Flush at 10 vol% C_2H_2	N_2 Flush

[‡] The field capacity of the incubated soil correspond to a gravimetric soil moisture content of 0.43 g H_2O g^{-1} dry soil.

[†] The O^d/O^{w-} method has been adapted from the dry-wet soil cycle method of Velthof et al. (2003).

Table 4. Emissions factors of N_2O during the first 72h, the whole oxic phase and the whole anoxic period, for the Harlaka soil incubation methods.

		Oxic phase				Anoxic phase			
Amendment✷	Method✦	$N_2O_{0\text{-}72h}$		N_2O_{OXIC}		$N_2O_{ANOXRATE}$		$N_2O_{ANOXMAX}$	
		mg N kg^{-1} N applied				mg N kg^{-1} N applied h^{-1}		% of N applied	
IF	O^w/S^+	459 a	(76)	1149 a	(885)	267 b	(282)	72.9 b	(7.6)
	S/S^+	529 a	(96)	1059 a	(510)	1241 a	(395)	102.5 a	(18.4)
	S/S^-	602 a	(265)	1924 a	(1497)	1398 ab	(725)	37.2 c	(5.9)
AR	O^w/S^+	340 b	(125)	922 a	(519)	284 c	(302)	34.7 a	(6.1)
	S/S^+	1199 a	(245)	1435 a	(316)	6268 a	(159)	8.0 b	(1.2)
	S/S^-	1242 a	(137)	1499 a	(167)	4740 b	(838)	6.5 b	(1.9)
PM	O^w/S^+	927 b	(92)	1328 b	(273)	607 c	(231)	63.8 a	(6.2)
	S/S^+	1555 a	(301)	4042 a	(713)	5268 a	(472)	7.6 b	(3.5)
	S/S^-	1551 ab	(518)	3783 a	(1098)	3260 b	(326)	2.2 c	(1.2)
PS	O^w/S^+	272 b	(83)	337 b	(216)	374 c	(124)	20.7 a	(1.6)
	S/S^+	907 a	(140)	1018 a	(162)	4862 a	(279)	2.7 b	(2.1)
	S/S^-	791 a	(152)	777 a	(154)	3654 b	(749)	5.5 b	(0.5)
SMC	O^w/S^+	172 a	(125)	242 a	(300)	359 b	(234)	-3.4 b	(1.5)
	S/S^+	30 a	(36)	39 a	(89)	977 a	(230)	-1.7 ab	(2.3)
	S/S^-	134 a	(213)	578 a	(748)	521 b	(125)	0.4 a	(1.3)
WSR	O^w/S^+	452 a	(453)	1219 a	(1502)	-3414 b	(3313)	-151.8 c	(19.5)
	S/S^+	536 a	(504)	937 a	(515)	5454 a	(2269)	-93.9 b	(13.5)
	S/S^-	512 a	(174)	1256 a	(227)	-2028 b	(3043)	-14.0 a	(2.5)

Means sharing a letter are not significantly different within amendment type by a Tukey-Kramer test (α=0.05).

In parenthesis are standard deviation values (n=4).

✷ See table 2 for an explanation of the abbreviations used in this table.

✦ See table 3 for an explanation of the abbreviations used in this table.

Table 5. Comparative classification of organic amendments within methods using N_2O_{72h} or N_2O_{OXIC}

		Oxic phase	
Method✦	**Amendment✷**	N_2O_{72h}	N_2O_{OXIC}
		mg N kg^{-1} N applied	
O	PM	927 a (92)	1328 a (273)
	IF	459 b (76)	1149 ab (885)
	WSR	452 b (453)	1219 ab (1502)
	AR	340 b (125)	922 ab (519)
	PS	272 b (83)	337 b (216)
	SMC	172 b (125)	242 b (300)
S	PM	1553 a (139)	3913 a (307)
	AR	1221 a (66)	1467 b (84)
	PS	849 b (53)	897 cd (69)
	IF	565 c (67)	1492 bcd (401)
	WSR	523 bc (124)	1200 bc (115)
	SMC	81 d (54)	308 d (202)

Means sharing a letter are not significantly different within amendment type by a Tukey-Kramer test (α=0.05).

In parenthesis are standard errors (n=4).

✷ See table 2 for an explanation of the abbreviations used in this table.

✦ See table 3 for an explanation of the abbreviations used in this table.

Table 6. Correlations between emission factors of N_2O and organic amendments properties (n = 20, Spearman correlation)

		Chemical indices of organic amendments								
		Lignin/N			N_{min}/N_{org}			DOC/(C-DOC)		
	Methods	O^w/S^+	S/S^+	S/S^-	O^w/S^+	S/S^+	S/S^-	O^w/S^+	S/S^+	S/S^-
N_2O indices	$N_2O_{0\text{-}72h}$	ns	ns	-0.50*	ns	0.62**	0.72***	ns	0.63**	0.74**
	$N_2O_{ANOXMAX}$	-0.63**	-0.67**	-0.91***	0.63**	0.71***	0.85***	0.58*	0.71***	0.78***
	$N_2O_{ANOXRATE}$	ns	ns	-0.80***	ns	0.54*	0.85***	ns	0.54*	0.77***

$N_2O_{0\text{-}72h}$ and $N_2O_{ANOXMAX}$ were expressed in % of N applied and were corrected for the emissions of the CTL treatment.

$N_2O_{ANOXRATE}$ was expressed in % of N applied h^{-1} and was corrected for the emissions of the CTL treatment.

N_{min} referred to mineral nitrogen content of OAs.

N_{org} referred to organic nitrogen content of OAs.

* Significant at probability level $P < 0.05$

** Significant at probability level $P < 0.01$

*** Significant at probability level $P < 0.001$

ns = non-significant

Table 7a. Comparative evaluation of the oxic phases conducted in the tested incubation methods.

		(1)	Optimum incubation conditions	(2)	Precision[§] and absence of bias	(3)	Easy to run
OXIC PHASE	The opened-jar method (O)	-	Less sensitive to short-lived pulses of class I OA-induced N_2O emissions	-	Increased risk of missing N_2O peaks	-	Soil water content monitoring
		-	Poor discrimination between OAs related to the N_2O_{0-72h} index: PM[✱] > other OAs **($P < 0.05$)**	-	Precision decreased by a factor of 2 after addition of OAs with high NH_4^+ content	-	Labor intensive for N_2O measurements: twice as many vials and gas analyses required for measurements of 1-h N_2O fluxes.
		-	No correlation between the N_2O_{0-72h} index and OA properties	+	Precision increased by a factor of 2.5 after addition of PM[✱]	+	Duration of the oxic phase ≈ 7 d (Time required for enhanced N_2O emissions back to control level)
	The sealed-jar methods (S)	+	Sensitive to short-lived pulses of class I OA-induced N_2O emissions	+	No risk of missing N_2O peaks Good integration of soil N_2O emissions	+	No soil water monitoring
		+	Good discrimination between OAs within method using the N_2O_{0-72h} index: PM, AR > PS ≥ WSR > SMC[✱] **($P < 0.05$)**			+	Fast and economical for N_2O monitoring
		+	N_2O_{0-72h} index of poultry manure relevant to field situations: PM[✱] > IF **($P < 0.05$)**			-	Require daily O_2 monitoring to decide upon the anoxic event
		+	N_2O_{0-72h} index correlated with OA properties			-	Duration of oxic phase limited to 72 h for OAs with high respiratory demand: enhanced N_2O emissions won't back to control level.

Criterion 1: creating conditions that favor OA-induced emissions of N_2O while establishing relationships with OAs' properties

Criterion 2: precision and absence of bias in measurements of N_2O indices while maximizing discrimination of OAs within methods

Criterion 3: minimizing labor requirements

[§] Precision reflects how close a number of replicated measurements are to each other. It was investigated with the relative standard deviation (Russow et al, 1996)

[✱] See table 2 for an explanation of the abbreviations used in this table for organic amendments.

See the Material and Methods sections for definition and conceptual framework of the N_2O_{0-72h} index.

Table 7b. Comparative evaluation of the anoxic phases conducted in the tested incubation method.

Method		**(1)**	**Optimum incubation conditions**	**(2)**	**Precision[§] and absence of bias**	**(3)**	**Easy to run**
ANOXIC PHASE	**O^w/S^+**	+	Highest degree of discrimination between OAs using to the $N_2O_{ANOXMAX}$ index: (***P*** **< 0.05)** IF, PM > AR > PS > SMC > WSR✱	+	Good integration of soil N_2O emissions	+	Do NOT require daily N_2O monitoring to capture the entire scope of anoxic N_2O indices
		+	The $N_2O_{ANOXMAX}$ index allowed predicting the N mineralization potential of OAs.	+	Best precision in $N_2O_{ANOXMAX}$ measures		
				-	Few impact in case of an interference with C_2H_2	-	Required the longest oxic (43 d) and anoxic (49 d) duration
	S/S^+	+	The $N_2O_{ANOXRATE}$ index as an indicator of soil C availability at the end of the oxic cycle.	+	Best precision in $N_2O_{ANOXRATE}$ measures	+	Do NOT required daily N_2O monitoring to capture the entire scope of anoxic N_2O indices
				+	Good integration of soil N_2O emissions		
				- -	How much impact in case of an interference with C_2H_2?	-	Absence of synchronization between treatments (oxic phase ending at 5% O_2 concentration in the jar headspace)
	S/S^-	+	The $N_2O_{ANOXMAX}$ index was best correlated to L:N, N_{min}/N_{org} and DOC:(C-DOC) ratios of OAs (*P*<0.001)	+	No interference with C_2H_2	-	Required daily N_2O monitoring to capture the entire scope of anoxic N_2O indices
		+	The $N_2O_{ANOXRATE}$ index was best correlated to L:N, N_{min}/N_{org} and DOC:(C-DOC) ratios of OAs (*P*<0.001)	-	Risk of missing N_2O peaks	-	Absence of synchronization between treatments (oxic phase ending at 5% O_2 concentration in the jar headspace)

Criterion 1: creating conditions that favor OA-induced emissions of N_2O while establishing relationships with OAs' properties

Criterion 2: precision and absence of bias in measurements of N_2O indices while maximizing discrimination of OAs within methods

Criterion 3: minimizing labor requirements

[§] Precision reflects how close a number of replicated measurements are to each other and **was investigated with the relative standard deviation (Russow et al, 1996)**

✱ See table 2 for an explanation of the abbreviations used in this table for organic amendments.

See the Material and Methods sections for definition and conceptual framework of the $N_2O_{ANOXMAX}$ and $N_2O_{ANOXRATE}$ indices.

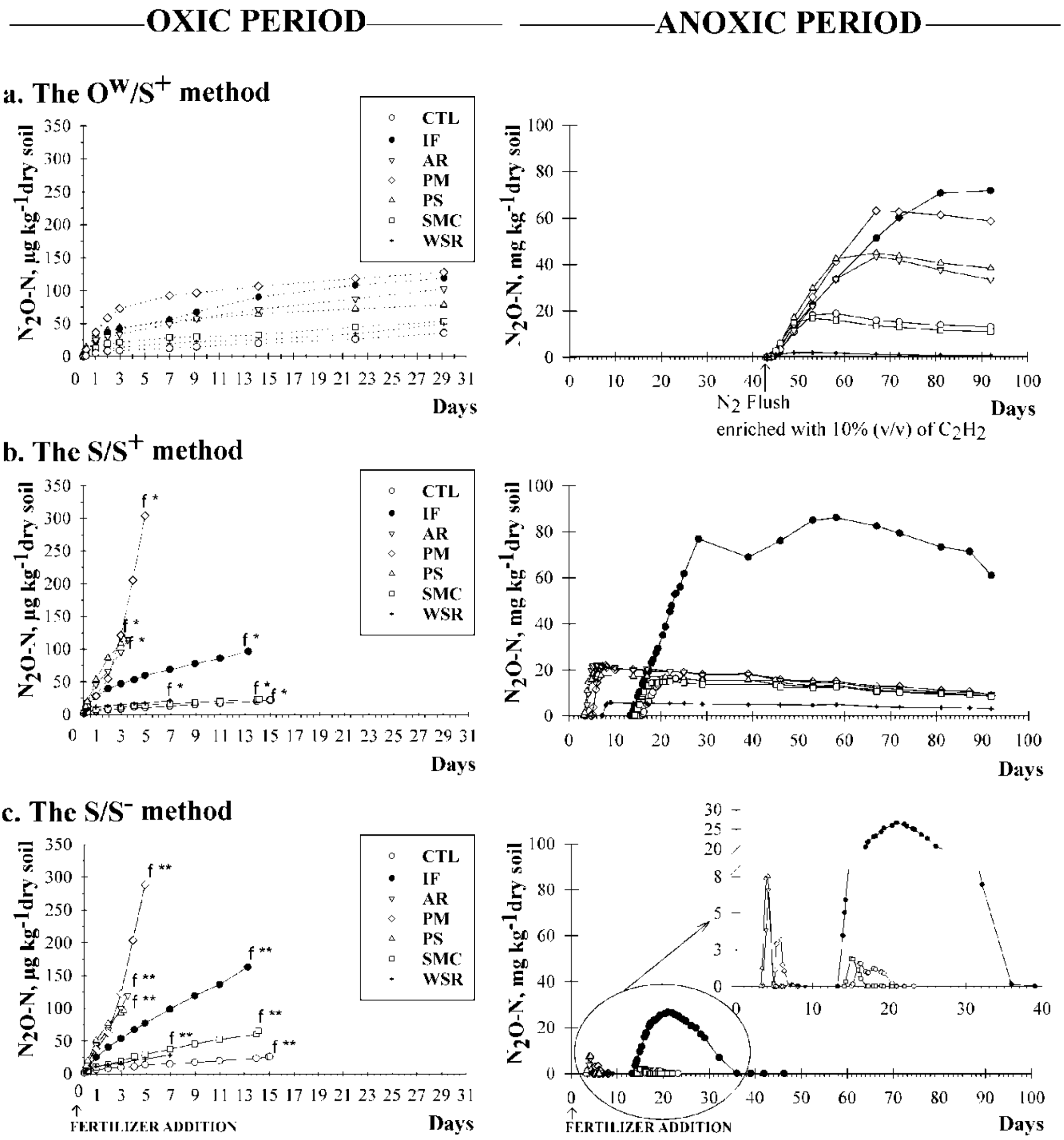
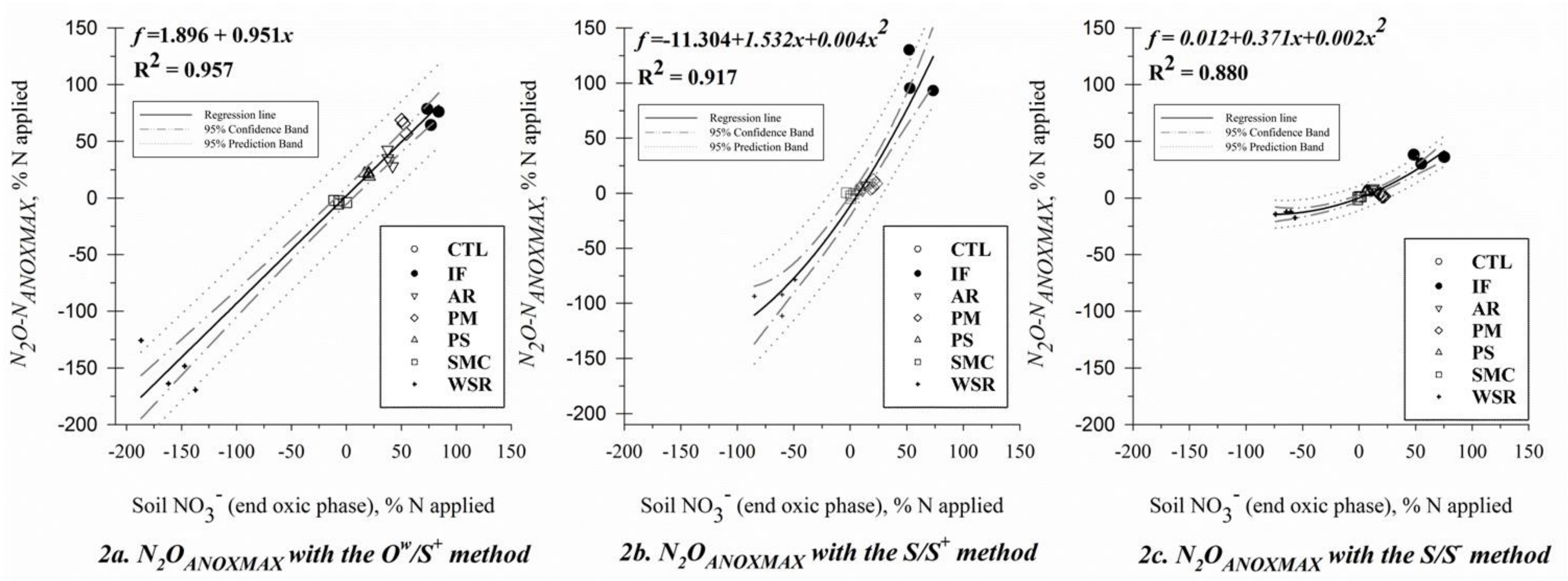


Figure 1. Emissions of N_2O from fertilized soils as influenced by incubation methods (n=4).

In the S/S$^+$ method, the end of the oxic cycle occurred at a different time for each amendment with a N_2 flush at 10% ($^V/_V$) of C_2H_2 when $[O_2]_{headspace}$ reached 5% (f*). In the S/S$^-$ method, the end of the oxic cycle occurred at a different time for each amendment with a N_2 flush when $[O_2]_{headspace}$ reached 5% (f**).

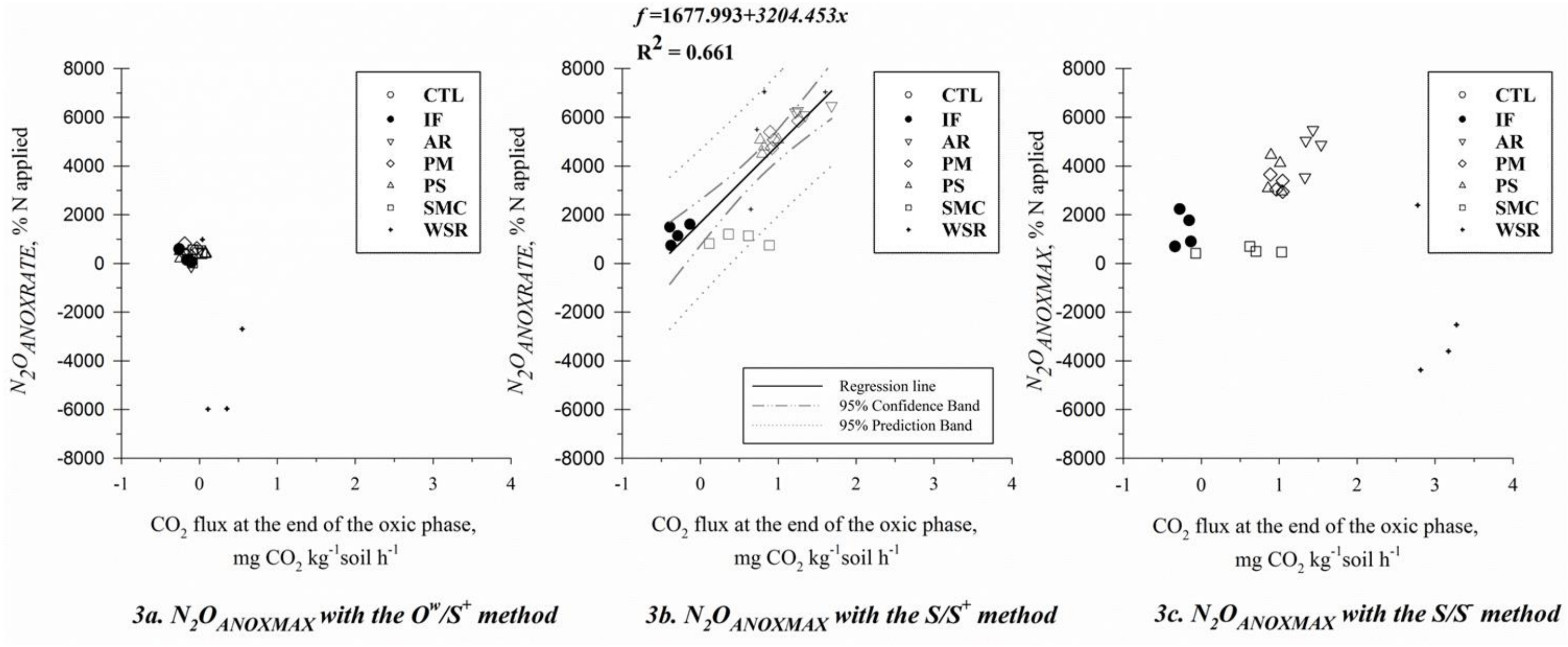


2a. $N_2O_{ANOXMAX}$ with the O^w/S^+ method

2b. $N_2O_{ANOXMAX}$ with the S/S^+ method

2c. $N_2O_{ANOXMAX}$ with the S/S^- method

Figure 2. Relationships between the $N_2O_{ANOXMAX}$ index and soil nitrate build-up during the oxic phase.



3a. $N_2O_{ANOXMAX}$ with the O^w/S^+ method

3b. $N_2O_{ANOXMAX}$ with the S/S^+ method

3c. $N_2O_{ANOXMAX}$ with the S/S^- method

Figure 3. Relationships between the $N_2O_{ANOXRATE}$ index and soil CO_2 fluxes at the end of the oxic phase.

FORWARD TO CHAPTER 4

The comparative incubation study of Chapter 3 helped identifying optimal laboratory conditions for the expression and the measurements of the POA-N_2O. The selected method involved intermittent aerations of a sealed-jar system relying on repeated 72-h measurement periods in headspace O_2-limited conditions to assess the short-term (72-h) and medium-term (multiple 72-h periods) potential of OAs to induce soil N_2O emissions. In Chapter 4, this incubation method was used to relate short-term (72-h) and medium-term POA-N_2O to the physical state (liquid, solid, powered, pelletized) and the chemical characteristics (e.g., mineral N concentration, C/N ratio, lignin content) of more than 131 OAs with a wide range of physico-chemical properties.

CHAPTER 4

Associating the potential of organic amendments for soil N_2O emissions with their physico-chemical characteristics.

4.1 Abstract

Predicting nitrous oxide (N_2O) emissions after applying organic amendments (OAs) to soil is difficult because the physico-chemical composition of OAs leads to complex interactions between OAs, soil properties and environmental conditions. In this laboratory study, we determined the immediate (P1), the short- (P2) and the medium-term (P3) potentials of OAs to induce soil N_2O emissions of 149 products, including 131 OAs, 12 inorganic fertilizers, and 16 organic-based products (meals (ML), pellets (PLT), and others). The OAs included 65 liquid or solid farm manures (FM), 31 crop residues (CR), 30 composts (CMPT), and five sludges. A three-wk incubation involved intermittent aeration of a sealed-jar system to assess P1 48 h after OA addition, and P2 and P3 during the second and the third wk, respectively. The objective of this study was to relate P1, P2, and P3 to the physical state (liquid, solid, powdered, pelletized) and the chemical characteristics of OAs. In a C-limited environment, CR promoted the highest P1 ($P < 0.05$) of all OA categories tested, with up to 0.25% of the total N applied being lost as N_2O. CR C/N ratio explained 60% of the variability in $P1^{CR}$. Farm manure addition resulted in 0.055% of the total N applied being lost as N_2O. Liquid manure P1 was five-fold greater than solid manure P1. Compost (CMPT) addition resulted in 0.006% of the total N applied being lost as N_2O but only immature composts (piles under construction, age < 3 months) significantly increased soil N_2O emissions compared to control soils. P1 was correlated to available forms of C (water-extractable organic C and volatile fatty acids) in interaction with nitrate, to ammonium and sometimes to sulphur (S) contents, equivalent alkalinity and pH of OAs ($P < 0.05$). Multiple robust regressions suggest $P1^{PLT\text{-}ML}$ was mainly due to denitrification, $P1^{LM}$ and $P1^{SM}$ was due to both nitrification and denitrification, and $P1^{CMPT}$ was mainly due to nitrification. Properties of OAs explained 18% to 56% of variability in P1 response with better performance for poultry manure. None of the chemical characteristics were correlated to P2 and P3, indicating the enhanced N_2O emissions supported by the OA-C and N substrates were short-lived. However, significantly higher P2 and P3 were observed with OAs of lower particle size (powdered MLS) and higher pH (horse manure).

4.2 Introduction

Large quantities of organic amendments (OAs) are added to agricultural soils in various forms including livestock manures, crop residues, sludge and composts (Chaves et al., 2005). While OAs act as physical soil conditioners and a valuable source of plant-available nutrients, they also promote nitrification, nitrifier denitrification and denitrification reactions that lead to increased soil N_2O emissions, a potent greenhouse gas (Foster et al., 2007; Butterbach-Bahl et al., 2013) and the dominant stratospheric ozone-depleting substance (Ravinshankara et al., 2009). For greenhouse gas inventory purposes, the Intergovernmental Panel on Climate Change (IPCC) recommends using the fertilizer-induced emission factor (EF_1) as the worldwide default value, regardless of the fertilizer source. The EF_1 is estimated to be a loss of 1% of fertilizer N and was derived from published data regarding gaseous losses from soils amended with synthetic N fertilizers (Bouwman et al., 2002). It is unlikely that adding N in organic forms results in increases in N_2O emissions that are similar to those following addition of synthetic N fertilizers.

However, at the time that EF_1 was adopted, there was insufficient information about gaseous N losses from organic materials to specify an emission factor for OAs.

OAs have multiple roles in the microbially-mediated reactions leading to N_2O production. Mineralization of organic N contained in OAs releases ammonium (NH_4^+), with subsequent ammonia oxidation and nitrification producing gaseous N losses and yielding NO_3^- that is susceptible to reactions that lead to N_2O production. As an organic C substrate for microbial growth, OAs may also stimulate microbial N assimilation, which can increase competition for NH_4^+ between heterotrophic microorganisms and autotrophic nitrifiers (Chen et al., 2013), resulting in temporary reduction of N_2O production. In soils with high N availability but low organic C, OAs may stimulate nitrifier denitrification, the oxidation of ammonia to nitrite (NO_2^-) and its subsequent reduction to NO and N_2O by autotrophic ammonia oxidizing microorganisms under low O_2 availability (Butterbach-Bahl et al., 2013). In anaerobic conditions, organic C provided by OAs enhances denitrification. The ratio of N_2O to N_2 produced during denitrification increases with increasing soil NO_3^- availability, which is influenced by the microbial consumption and production of NO_3^- due to C and N substrate availability in OA-amended soils (Terry et al.,1980; Weier et al., 1993; Miller et al., 2008). Finally, OAs modulate O_2 availability in soil microsites because the labile C input enhances soil respiration and some; such as animal slurries, reduce gas diffusivity by saturating soil micropores in the short-term. Given the multiple ways that OAs impact the activity of microorganisms involved in N_2O production, their influence on soil N_2O emissions cannot be predicted from simple factors such as the total N application rate, which is a reasonably good estimator of the EF_1 from synthetic fertilizers (Kim et al., 2008). Improved emission inventories require information about the potential of OAs to induce soil N_2O emissions (POA-N_2O) and about the relationship between POA-N_2O and the chemical characteristics of OAs.

Composition of OAs is highly variable compared to that of synthetic N fertilizers. Carbon and N components of solid manures (SM) are influenced by animal type (Chadwick, 1999), feed (Cardenas et al., 2007; Velthof et al., 2005), and by the manure management system (Chadwick, 2005). For example, poultry manures have a lower C/N ratio than other manure types (Aulakh et al., 2000) and alteration of the legume vs. non legume proportion in the animal diet modulated sheep manure C/N ratio accordingly (Cardenas et al., 2007). Liquid and solid management systems produce manures with contrasting chemical characteristics. Liquid manures (LM) generally contain less bedding materials than solid manure (SM), resulting in lower C/N ratios (Rochette et al., 2008c). Solid-liquid separation concentrates the dry matter, C content, and fibre fractions in the solid fraction, leaving a large proportion of the simple organic compounds that are readily degraded by soil microorganisms in the liquid fraction (Bertora et al., 2008). Conversely, anaerobic digestion of LM reduces dry matter, C content, and fibre fraction but results in an incomplete decomposition and produces volatile fatty acids (VFA), a C source for soil denitrifiers (Paul and Beauchamp, 1989a; Kirchmann and Lunwall, 1993). The storage of farm manure (FM), i.e., the decomposed mixture of dung and urine of farm animals along with litter, may partially or completely compost the material, depending on how long the FM is stockpiled, to what depth the manure pile is built, and whether the pile is aerated or not (Chadwick, 2005; Guo et al., 2012). Composting is a thermophilic decomposition process that degrades raw organic materials to CO_2, resulting in an immobilization of inorganic N and in production of stable organic matter (Yang et al., 2002; Nada, 2015). Chemical and physical properties of composts applied to soil vary according to the organic matter source and composting conditions (Yang et al., 2002; Guo et al., 2012; Nada, 2015).

In low-C soils, for example, N_2O emission rates were found to be correlated with soluble organic C, whereas emission rates in C-rich soils were correlated with NO_3^- availability. In soils mixed with OA under controlled conditions, the N_2O emissions generally increased with increasing mineral N content, water-soluble organic C, VFA and with decreasing C/N ratio and lignin content (Paul and Beauchamp, 1989a; Lou et al., 2007; Huang et al., 2004; Chaves et al., 2005; Velthof et al., 2003; Velthof, G.L., Mosquera, 2011). Accordingly, high N_2O emissions were associated with OA containing high levels of inorganic N and easily decomposable N and C, such as pig (Velthof et al., 2003) and sheep slurries (Cardenas et al., 2007) and N-rich crop residues (Chaves et al., 2005). Generally, addition of OAs with C/N ratio > 20 result in temporary net nutrient immobilization (Enwezor, 1976), although this is modulated by the chemical nature of the organic C compounds within the OA. Water-soluble organic C is quickly decomposed (Hadas et al., 2004), whereas complex polymers such as lignin and ligno-cellulose undergo slow decomposition (Vanlauwe et al., 1996). Mixing materials having a high C/N ratio (wheat straw residues, saw dust, composts) with manure, slurries or N-rich crop residues also reduced soil N_2O emissions (Huang et al., 2004; Chantigny et al. 2001). However, Li et al. (2013b) reported that the C/N ratio of plant residues was not a good predictor of OA-induced N_2O emissions even if net N mineralization was correlated to the C/N ratio of plant residues. Moreover, plant material addition affected soil N_2O emissions differently under aerobic and oxygen(O_2)-limited conditions, which confirmed POA-N_2O is not directly related to the net N mineralization potential of OAs (Li et al., 2013b). This is likely due to (1) inorganic N content of

OAs directly available to soil nitrifiers and denitrifiers, and to (2) the fact that the net N mineralization from an OA declines with time as readily-mineralizable organic N substrates are depleted, and denitrifiers would compete with other heterotrophic microorganisms for a limited amount of NO_3^- and soluble C (Marschner et al., 2015). Consequently, it is difficult to make generalizations; even under controlled conditions, the POA-N_2O is affected by many other factors including soil type, OA characteristics, the incubation duration and O_2 availability during the incubation (Bertora et al., 2008; Cabrera et al., 1994b; Flessa and Beese, 2000; Helgason et al., 2005; Lou et al., 2007; Velthof et al., 2003).

Incubation in O_2-limited conditions favoured expression of POA-N_2O when O_2 headspace concentration did not fall below 6% (Chantigny et al., 2002), with large N_2O production due to the addition of OAs that increased soil microbial activity and O_2 consumption. In the 29 d following OA addition in O_2-limited environment, denitrification rate increased as O_2 concentration decreased in soils, nitrification stopped whereas N mineralization allowing NH_4^+ accumulation and NO_3^- depletion (Chantigny et al., 2002). Potential of OAs to induce soil N_2O emissions evaluated immediately after OA addition differed from POA-N_2O evaluated 40 d after OAs (Velthof et al., 2003).

In this study, we conducted a three-wk incubation involving intermittent aeration of a sealed-jar system to assess immediate (P1), short- (P2) and medium-term (P3) POA-N_2O. The objective of this study was to relate P1, P2, and P3 to the physical state (liquid, solid, powered, pelletized) and the chemical characteristics (e.g., mineral N concentration, C/N ratio, lignin content) of more than 131 OA with a wide range of physico-chemical properties.

4.3 Material and Methods

4.3-1 Soil sampling and preparation

A poorly drained Kamouraska clay (mixed, frigid, Typic Humaquept) soil was collected at the Harlaka Research Farm of Agriculture and Agri-Food Canada (46°48´N, 71°23´W) from the 0-20-cm depth (plough layer) in November 2009, about 2 wk after the field was tilled with a mouldboard plough. This soil was selected because it showed fertilizer-induced N_2O emissions greater than the Intergovernmental Panel on Climate Change default factor (0.01 kg N_2O-N kg^{-1} N), with values ranging from 0.027 to 0.038 kg N_2O-N kg^{-1} N applied (Gagnon et al., 2011). The site did not receive N fertilizer in the study year because it was under soybean production. The soil was sieved to pass through a 6-mm sieve, air-dried and mixed to thoroughly homogenize it. Selected physico-chemical properties of the Kamouraska clay are presented in Table 1.

4.3-2 Experimental design

A total number of 588 experimental units consisting of 1-L glass jars were set out in a randomized complete block design with four replicates. Starting of each block was delayed by one week for logistical reasons. Within each block, the experimental design included 4 unamended controls, and 149 treatments of 131 OAs, 12 inorganic fertilizers, and 16 organic-based products. The OAs included 65 animal manures (liquid and solid), 31 crop residues, 30 composts of varying ages and origins, and five sludges (Fig. 1). The organic-based products included three organic-based meals (bone ash crabmeal, fishmeal), eight pellets, and five other organic by-products (liquid seaweed, shrimp waste, shrimp shells, cow refuse, mouldy silage). Application rates and nature of amendments and fertilizers are mentioned in Table 2.

4.3-3 Amendment sampling, storage, preparation and analyses

Amendments and fertilizers were collected from farms, compost facilities, sewage treatment plants, research units and commercial suppliers located within 30 km of Quebec City (Quebec, Canada) in summer 2011. Organic by-products such as peat, woodchip, sunflower straw residues and phragmites are not routinely used as amendment sources, but were included in the experiment to provide a wide range of chemical properties (Fig. 1).

Crop residues were dried at 30° C, ground and sieved through 2 mm and stored at ambient temperature. Liquid manures were stored at -12° C and solid manures at +4° C until preparation. Each 4-L sample of manure was blended with dry ice using a vertical cutter-mixer (R10-U, Robot Coupe Inc., MS, U.S.A.) and sieved (< 2 mm). Liquid manures were filtered through a plastic colander to collect solid particles that were first blended with dry ice before mixing the entire sample during 2 min using a Polytron (Model PT 3100, Kinematica AG, Littau-Lucerne, Switzerland). After preparation, solid manures samples were distributed in freezer bags, stored at -12° C and, then weighed 3 d before starting each block. Liquid manures were transferred into Nalgene bottles and stored at -12° C until 24 h before starting each block.

All OAs were analyzed for total C and total N. Farm manures, composts, sludges, plant residues, meals, pellets, other products and selected crop residues (32%) were analyzed for dry matter (DM), ash, organic matter (OM), water-extractable organic C (WEOC), N-NH_4, N-NO_3, and fiber contents, pH, equivalent alkalinity, and metals and major elements. DM was obtained by oven-drying fresh OAs at 105° C for 24 h or to a constant weight. Ash and OM were determined by loss on ignition of dry residue at 500°C during 2 h for vegetal residues and 4 h or more for other amendments. Total C of liquid manures (DM < 15%) was determined by directly injecting the homogenized material into a TOC analyzer (Model Shimadzu ,5000A, Kyoto, Japan), whereas total C of solid manures and other amendments was measured by dry combustion (Leco Corp., St. Joseph, MI) on subsamples that had been dried at 55°C. Water-extractable organic C (WEOC) was determined on amendments by shaking fresh OAs with deionized water (1:10 fresh amendment: water ratio) for 30 min at 160 rpm. Extracts were centrifuged for 15 min (15,000 × g) and analyzed for total (TC) and inorganic dissolved C (TIC) using the Combustion / NDIR method of the Shimadzu TOC analyzer. WEOC was the difference between total and inorganic dissolved C.

The total N content of farm manures, composts and sludges was determined by the Kjeldahl method (TKN). The total N content of crop residues was determined by dry combustion (Leco CNS-1000, Leco Inc.). Mineral N content in farm manures, composts, or sludges, was determined by shaking 2.5-5 g of amendment with 50 mL of 2 M KCl solution for 60 min. Mineral N content in vegetal residues was determined by shaking 0.25 g of vegetal residues with 25 mL of distilled water for 30 min. The NH_4^+, NO_3^-, and NO_2^- concentrations were measured in the extracts with an automated colorimeter (Technicon Industrial Systems, Tarrytown, NY).

Soluble (SOL), hemicellulose- (HEM), cellulose- (CEL), and lignin-like (LIG) were determined using a fiber analyzer (Ankom A2000, Ankom Technology, Macedon, NY). Biochemical fractions were expressed as g kg^{-1} total OM. The fractions were defined according to their solubility in detergents as initially used to determine forage digestibility (Van Soest et al., 1991). Biological stability index (BSI) was calculated according to Robin (1997), following the equation (7):

$$\mathbf{BSI = 211.2 - (2.009 \times \%\ SOL) - (2.378 \times \%\ HEM) + (0.840 \times \%\ LIG) - (2.216 \times \%\ CF)} \qquad \mathbf{(7)}$$

Amendment pH was either directly measured in liquid slurries or measured in slurries suspended in water (water, 1:1). For solid manures, composts and sludges, pH was measured in a pulp suspension brought to saturation. Equivalent alkalinity of OAs, defined as the neutralizing capacity of hydrogen ion, was determined by titrating samples against diluted acid (HCl 0.02N) until pH reached 4.5 and the equivalent alkalinity expressed in mg/L of $CaCO_3$.

Metals and major elements were determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) following digestion with acid and hydrogen peroxide. Liquid manure was also analyzed for volatile fatty acids (VFAs) according to APHA (1992).

4.3-4 Incubation protocol

The protocol included a 14-d pre-incubation and a 21-d incubation involving 3 captures of POA-N_2O (P1, P2, and P3) with intermittent aerations of a sealed-jar system, in a constant temperature incubator (22^{o} C ± 0.03) in the dark. Soil preincubation began by moistening air-dried soil (220 g oven dry basis) homogenously with distilled water to 0.28 g H_2O g^{-1} dry soil (65% of the field capacity). Wet soil was then placed in 1-L Mason jars (one jar = one experimental unit) with gas-tight lids fitted with two 1-way male luer stopcocks. After sealing each jar with a lid, the headspace was flushed with N_2 gas for 20 sec at 48 kPa and the preincubation continued for 14 d, to remove the soil NO_3-N through denitrification. After preincubation, jars were aerated (room atmosphere) for 24 h. Then, distilled water was added to the surface to adjust soil moisture according to water content of assigned treatment. The targeted soil + amendment/fertilizer mixture was 0.30 g H_2O g^{-1} dry soil (70% of the field capacity).

The incubation started 24h after soil rewetting. Each treatment (amendment or fertilizer) was applied to the soil surface, mixed homogenously by hand, and jars were shaken horizontally to level the soil surface, leaving a headspace volume of roughly 0.87 L. Then, jars were weighed and water added to reach the target soil moisture content. The first sealed-jar period started immediately after applying treatments and lasted for 72h, whereas the second (222 to 270h) and third (388h to 436h) sealed-jar periods lasted 48h. Sealed-jar periods involved sealing jars with air-tight lids immediately followed by air sampled at 0, 3, 6, 24, 48 and 72h for the first period and at the beginning and at the end of the second and third periods. Between sealed-jar periods, lids were removed, jars were aerated (room atmosphere) for 24 h and then, capped with a lid having a central 6-mm diameter hole to provide atmospheric air exchange. Distilled water was added at regular intervals (e.g., every 2 days) to maintain the initial SM moisture content at 0.3 g H_2O g^{-1} dry soil.

4.3-5 Headspace gas sampling technique

During the first sealed-jar period, the headspace air was sampled through the gas-tight lid fitted with two 1-way male luer stopcocks. Stopcock 1 was equipped with a rubber septum for gas sampling. Stopcock 2 was tightly connected through a Bev-A-Line IV tube (1/8"ID x 1/4"OD) to a gas sampling bag (Kynar polyvinylidene fluoride bag, Cole-Parmer, Montreal, Canada) filled with He. Samples of headspace gas were taken by inserting a needle fitted to a polypropylene syringe (20 mL; Becton Dickinson, Rutherford, NJ) through one stopcock equipped with a rubber septum. Before removing the 20 mL headspace gas sample, the other stopcock was opened to replenish the headspace with He and ensure constant pressure. Dilution effect (from the gas sampling) was accounted for in calculations. The gas sample was injected immediately into a pre-evacuated vial (12-mL Exetainer, Labco, High Wycombe, UK) that were stored at ambient temperature until analysis (< 14 d). Following the first week of the incubation, all subsequent headspace gas samples were done similarly except that stopcock 2 was not connected to a He bag. Once the stopcock opened, an equivalent volume of ambient air would enter the headspace and ensure constant pressure.

Vials containing headspace gas sampled were analyzed for N_2O, O_2 and CO_2 concentrations within 1 wk by means of a gas chromatograph equipped with electron capture, thermal conductivity and flame ionization detectors (Model 3800, Varian Inc., Walnut Creek, CA) through a headspace autoinjector (Combi Pal, CTC Analytics, Zurich, Switzerland).

4.3-6 Gaseous flux calculations

Fluxes of soil N_2O and CO_2 were expressed in µg gas kg^{-1} dry soil h^{-1} and calculated following equation 6:

$$F_{gas} = \frac{dC_{gas}}{dt} \times \frac{V}{M} \times \frac{Mm}{Mv} \text{, where} \qquad \textbf{(6)}$$

$\frac{dC_{gas}}{dt}$ (mol gas mol^{-1} h^{-1}) is the rate of change of headspace gas concentration in one h, V (m^3) is the jar headspace volume, M (kg) is the mass of dry soil contained in a jar, Mm (mg mol^{-1}) is the molecular weight of gas, Mv (m^3 mol^{-1}) is the air molecular volume, accounting for temperature in the room before sealing the jar (0.022 to 0.024 m^3 mol^{-1}).

4.3-7 Immediate, short- and medium-term POA-N_2O

The immediate POA-N_2O (P1) was defined as the cumulative OA-induced N_2O emissions 48 h after the treatments were added and also expressed as the % of total N applied from a particular treatment, calculated following equation 7:

$$\mathrm{P}t = \frac{\left\lfloor F_{N_2O\text{-}N_{treatment}}(t) - F_{N_2O\text{-}N_{control}}(t) \right\rfloor}{N_{applied}} \times 100, \text{ where} \qquad \textbf{(7)}$$

$F_{N_2O\text{-}N_{treatment}}(t)$ and $F_{N_2O\text{-}N_{control}}(t)$ are the cumulative emissions of N_2O (µg N kg^{-1} dry soil) from the soil-amendment or soil-fertilizer mixture and the unamended (control) soil, respectively, at the time t = 48 h of the incubation period to ensure O_2 concentration in the jar-headspace was above 5%, to minimize total denitrification (Morley et al., 2008). Indeed, high P1 variability within amendment category was observed 72 h after OA addition (Fig. A4-2) probably due to total denitrification for some OA-soil mixtures (Fig. A4-3). The short-(P2) and medium-term (P3) POA-N_2O respectively refer to OA-induced emission rates of N_2O in the 2nd (t = 222-270 h) and 3rd (t = 388-436 h) sealed-jar periods of 48 h.

4.3-8 Statistical analyses

Statistical analyses were conducted with SAS (Version 9.2, SAS Institute, Cary, NC). To test the fixed effect of OA type on POA-N_2O components (P1, P2, and P3), analysis of variance with heterogeneous variances was performed using the MIXED procedure. Differences between OA types were evaluated with a LSD test ($P < 0.05$). Relationships between P1, P2, P3 and soil CO_2

emissions were evaluated with the CORR procedure and expressed as Spearman correlation coefficients because of a non-normal distribution of data. For crop residues, least squares regressions were used to describe the functional relationship between C/N ratio and POA-N_2O components using log-transformed values. Robust multiple linear regression analyses were performed for farm manures (liquid and solid) and composts to model the relationship between selected chemical properties of OAs and the immediate, short-term and medium-term POA-N_2O. Robust regression techniques allowed the detection of outliers and helped providing resistant (stable) results in the presence of outliers using the MM estimation, introduced by Yohai (1987). Outliers were defined as observations with large residual or difference (above 50%) between the predicted value (based on the regression equation) and the observed value, as illustrated in red in Fig. 2 and Fig. 3. To avoid multicollinearity in the regression analysis, selection of chemical properties of OAs was checked against three key criteria, as follows:

1) When computing the matrix of Pearson's Bivariate Correlation among all independent variables, the correlation coefficients need to be smaller than .08;

2) The Variance Inflation Factor (VIF) of the linear regression needs to be smaller than 10. The VIF is defined as VIF = 1/T, where T is the tolerance, a measure of the influence of one independent variable on all other independent variables calculated with an initial linear regression analysis;

3) The condition index calculated using a factor analysis on the independent variables needs to be smaller than 30.

In cases where the check of the OA chemical parameters against the three criteria failed, a factor analysis (Principal Component Analysis, PCA) was conducted before the regression analysis with the PROC FACTOR to develop artificial variables (PCs) that accounted for much of the variance contained in the N_2O variables.

4.4 Results and discussion

4.4-1 Emissions of N_2O from control and synthetic N treatments

The N_2O emissions from control jars (no amendment, no fertilizer) reached 20.7 ± 7.3 (n = 16) µg N_2O-N kg^{-1} dry soil after the first 72 h of the incubation. Cumulative emissions were 1.5-fold greater in soils fertilized with N synthetic sources than in control soils with 30.62 ± 7.36 (n = 48) µg N_2O-N kg^{-1} dry soil emitted during the first 72 h. However, fertilizer-induced N_2O emissions did not respond to increasing rates of ammonium nitrate equivalent to 30, 60, 90, and 120 kg of N ha^{-1} (data not shown), indicating that N_2O production is limited by factors other than N availability (Breitenbeck et al., 1980; Koops et al, 1997; Rochette et al., 2010; Kim et al., 2013). Soil CO_2 emissions in control and synthetic N treatments were not significantly different and respectively reached 3.02 (± 0.46) and 2.96 (± 0.46) g C kg^{-1} dry soil after the first 72 h of the incubation ($P < 0.05$). It is possible that C availability was low in the incubated soil (Rochette et al., 2000). Jarecki et al. (2008) reported high cation exchange capacity of clay soils may also reduce N availability for soil microorganisms through NH_4^+ adsorption in the clay, although the sorbed organo-NH_4^+ complexes remained more susceptible to microbial decomposition, resulting in significant increase in soil N_2O emissions following the addition of 220 kg N ha^{-1} of manure to an incubated clay soil but not following the addition of the equivalent amount of urea-ammonium nitrate. In the present study, the soil environment was suitable for detecting the POA-N_2O from both C and N substrates that were provided in mixtures of soil and by OAs (Table 2).

4.4-2 The immediate potential of OAs to induce soil N_2O emissions, P1

Soil receiving crop residues (CR), farm manure (FM), and sludges (SDG) induced soil N_2O emissions that were significantly (t test, $Pr > 0.05$) greater than the N_2O emissions of soil mixed with pellets (PLTS), composts (CMPT) and synthetic fertilizers (Fig.4). Large differences in N_2O emissions were observed between organic-based meals (MLS), PLTS, and CMPT categories due to the wide range of physico-chemical characteristics of OAs in these classes (Table 2).

4.4-2.1 Crop residues

Crop residues had the highest P1 ($P < 0.05$) of all OA categories tested, with up to 0.25% of the total N applied being lost as N_2O after 48 h of incubation, hereafter referred to as $P1^{CR}$ (Table 2). The CR class included legume, non legume and legume mixed with non legume crops, and more than 70% of these had C/N <30 (Fig. 1). The magnitude of $P1^{CR}$ was significantly affected by the C/N ratio of CR, and those with C/N< 15 had a $P1^{CR}$ that was 2.1-fold greater than mean $P1^{CR}$ of all CR (Fig. 2). It is also notable that CR with C/N > 30 had a $P1^{CR}$ which was not significantly different from zero by a *t* test ($Pr > |t|$), meaning that those CR did not induce N_2O emissions (Table 2). The trend was a linear decline in the $P1^{CR}$ with increasing C/N ratio and the minimum (i.e., zero N_2O emissions) was reached around C/N= 76 for the CR category (Fig. 2a) and around C/N = 120 when other vegetal residues (such as peat, woodchip, sunflower straw residues, pruning residues and phragmites) were taken into account (Fig. 2b). Toma and

Hatano (2007) reported cumulative N_2O increased as the C/N ratio decreased, but not significantly. Proportion of the total N applied being lost as N_2O has been negatively correlated to plant C/N ratio by Huang et al. (2004). Crop residues with C/N ratio < 7.5 seemed to promote N_2O compared to crop residues with C/N ratio > 16 (Baggs et al., 2000; Jarecki et al. 2009)

Simple linear regression models relating $P1^{CR}$ to C/N ratio explained 60% of the variability in $P1^{CR}$ based on the C/N ratio of CRs (Fig. 2c-d). However, the regression equations underestimated the $P1^{CR}$ of specific CR, e.g., N-rich grassland mixtures of non legume and legume crops, and N-rich legume crops (*Lotus corniculatus*, *Trifolium repens*) (Fig. 2e-f). Those CR also contained the highest WEOC content of their category, e. g., above 10% dry weight (Fig. A4-3). In accordance with Miller et al., (2008), CR addition may also trigger denitrification in localized soil microsites with reduced O_2, as illustrated in Fig. A4-3e with net N_2O consumption measured 48 h after *Lotus corniculatus* addition. The outliers in the dataset indicate that prediction of $P1^{CR}$ from the C/N ratio alone would miss the peak N_2O production from plant residues high-emitting plant residues. A robust multiple regression model examining the C/N ratio along with other residue chemical properties (i.e., NH_4^+, NO_3^-, BSI, WEOC and S concentrations) was performed but did not improve $P1^{CR}$ prediction (Fig. 3a).

Accordingly, C/N ratio appeared as an interesting predictor to be considered in N_2O inventory report, separating CRs into three major classes: high risk (C/N< 15), medium risky (C/N between 15 and 30) and low risk (C/N> 70). In field experiments, $P1^{CR}$ was highly modulated by tillage practices and fertilization regime. Particular attention should be accorded to mulching of legume species (Nadeem et al., 2012), to incorporation of non legume species as green manure when amended with farm manure simultaneously with conventional tillage (Koga N., 2013), and managed grasslands, particularly when fertilized simultaneously with ploughing (Mori and Hojito, 2007; Velthof et al., 2010). Tillage has also been proven to decrease emissions with a 2-to-3-fold reduction of $P1^{CR}$ using full inversion tillage rather than chemical fallow for equivalent soil NO_3-N in a poorly drained soil (MacDonald et al., 2011).

4.4-2.2 Farm manures and sludges

Farm manure P1 ($P1^{FM}$) was 0.55%, a value similar to sludge P1 ($P1^{SDG}$) (Table 2). Liquid manure (LM) from all sources was grouped together based on the report of similar impact of pig and cattle LMs on N_2O production under laboratory (Velthoft et al.,2013) and field (Chadwick et al., 2000b) conditions. Liquid manure ($P1^{LM}$) was five-fold greater than solid manure ($P1^{SM}$), which is consistent with the 6 times greater N_2O emissions from liquid dairy-cattle than solid beef-cattle manure reported under controlled conditions (Paul et al., 1993). Similar N_2O emissions between LM and SM have been also reported by Rochette et al. (2008c). The solid manures could themselves be differentiated according to the animal source. Compared to the average $P1^{SM}$, the P1 estimates of sheep and alpaca manure was 2 to 3 times lower, and those of poultry and pig manures were 3.3 and 1.75 times greater (Table 2). This is consistent with previous reports of greater N_2O emission with poultry than pig solid manure (Pelster et al., 2012), and from pig than cattle solid manure Chantigny et al. (2002). Thus, relationships between P1 and manure chemical properties were assessed separately with multiple linear regression models for liquid ($P1^{LM}$) and solid ($P1^{SM}$) manure (Table 3).

4.4-2.2.1 Liquid manure

For liquid manure, the predictive model ($P < 0.001$) indicated that $P1^{LM}$ was related to the manure NH_4^+, WEOC and S concentrations, which were significant at $P < 0.01$, $P < 0.001$, and $P < 0.01$, respectively (Table 3). The positive slope associated with NH_4^+, NO_3^- X VFA and WEOC concentration may indicate nitrification- and denitrification-derived N_2O emissions. Liquid manure (excepted cow feces and urine) contained 48% of its total N as NH_4^+ (Fig. A4-5), which can be rapidly nitrified (Morvan et al., 1997; Rochette et al., 2000b; Chantigny et al., 2001). Goodroad and Keeney (1984) and Mørkved et al. (2007) noted that the N_2O product ratios of nitrification ($N_2O/(NO_2^- + NO_3^-)$) is lower in alkaline than in acid soils. This is consistent with the negative slope associated with NH_4^+ X pH. Denitrification was stimulated by the converted NH_4^+ into NO_3^- in presence of available C forms from liquid manure as noted by Paul and Beauchamp (1989a), Loro et al. (1997), and Cardenas et al. (2007). Although S-containing compounds are not metabolites for heterotrophic denitrifiers, Tam and Knowles (1979) noted that sulphide inhibited N_2O reduction in the denitrification process, which can favour N_2O production rather than complete reduction to N_2. This is consistent with the positive slope associated with S concentration and $P1^{LM}$ (Table 3). Significant interaction between S and WEOC indicated that the effect of S depends on the amount of WEOC added. The negative slope associated with S X WEOC may indicate that the possible inhibiting effect of S on N_2O reduction decreased with increased WEOC concentrations (Table 3).

Only 25% of the variability of the $P1^{LM}$ was explained by the model (Table 3) because it did not predict the N_2O production from dairy cow slurries freshly collected from stocking pre-pit with varying levels of aeration. Those slurries contained very low equivalent alkalinity (EA) (49 g/kg $CaCO_3$ d.w.), the highest level of WEOC (*i.e.* above 6000 mg/kg dry weight), and the lowest pH of their category (*i.e.* 5.75) (Fig. A4-5). Soil pH has a marked effect on N_2O emissions with lower denitrification rate at low soil pH but larger N_2O/N_2 product ratio (Focht, 1974) due to severe inhibition of N_2O reduction when soil pH < 6.0 (Bergaust et al., 2010). Emissions of N_2O decrease with increasing pH in acidic soils (Nägele and Conrad, 1990). Increases in soil pH following liquid manure application have been reported (Sommer and Sherlock, 1996; Chantigny et al., 2004) and was partly attributed to the alkaline slurry and the dissociation of slurry carbonates (Sommer and Sherlock, 1996), which occurs rapidly in acidic soils (Chantigny et al., 2001). Moreover, Paul and Beauchamp (1989b) reported the pH increase following aeration of dairy cattle slurry was promoted by the oxidation of VFA that shifted the NH_4^+/NH_3 equilibrium towards NH_3 and may contribute to increased volatilization losses. In the present study, we hypothesize that addition of acidic dairy cow slurries with very low EA to the slightly acidic Kamouraska clay soil restrained the soil pH increase compared to other liquid manures, resulting in a larger N_2O yield during denitrification, lower NH_3 volatilization, and indirectly more available N for coupled nitrification-denitrification and nitrifier denitrification.

Our results suggest greater $P1^{LM}$ are expected with fresh LM compare to stored LM, as noted by Thormann et al. (2007). Moreover, slurry pH appeared as an important factor to consider in LM management for reducing N_2O emissions.

4.4-2.2.2 Solid manure

Soil N_2O emissions following poultry manure were then analyzed separately from other solid manure because S was not a significant predictor of $P1^{PM}$ contrary to other solid manures. For solid manure (poultry manure excluded), WEOC, NO_3^- , NH_4^+, EA and S were included in a robust multiple regression (Table 3). The positive slope associated with NH_4^+ and NO_3^- X WEOC may indicate that N_2O emission following manure application was the result of both denitrification and nitrification, which occurred simultaneously in soil (Paul and Beauchamp, 1993). The negative EA coefficient suggests lower EAs favour N_2O emissions. As discussed for liquid manure, lower EAs may have decreased NH_3 volatilization, and indirectly more N available for coupled nitrification-denitrification and nitrifier denitrification. The positive slope associated with S may indicated that S addition from manure decreased reduction to N_2O, as noted by Tam and Knowles (1979). Negative interaction between S and NO_3^- indicated that the possible inhibiting effect of S on denitrification decreased as NO_3^- from manure increased, probably because the mole fraction N_2O/N_2 of the denitrification products increases with increasing NO_3^- contents (Firestone et al. 1980). Finally, two outliers among replicated samples of $P1^{SM}$ were identified after emu and alpaca manure addition (Fig. 3d) and were discussed later in the present paper.

Poultry manure differentiated from other SMs with their two-fold and three-fold higher concentrations of WEOC and NH_4^+, respectively. $P1^{PM}$ was better correlated to soil CO_2 emissions (+ 0.63, $P < 0.001$) compare to $P1^{FM}$ (+ 0.28, $P < 0.001$), as noted by Pelster et al. (2012). Greater P1 after PM than other FM addition was probably caused by a change in the soil environment that was most likely related to increased C availability (Pelster et al., 2012). Predictors (e. g., NO_3^-, WEOC, NH_4^+, and EA) were highly significant in simple and interaction effects. As previously discussed for other solid manure, slope associated with predictors may indicate $P1^{PM}$ was due to both nitrification and denitrification. Generally, soil N_2O emissions induced by PM addition are similar to emissions following LM application and are associated with denitrification after rainfall or freeze/thaw events (Thornton et al., 1998; Tatti et al., 2014). Rogeri et al. (2015) also noted nitrification increased in soils within the first two days after PM addition and was faster when poultry litter was incorporated to the soil in comparison to surface applied. Our results confirm that application of poultry manure appears to promote higher P1 than other solid manure and should be considered as risky as LM in N_2O inventory reports.

4.4-2.3 Composts

Compost (CMPT) addition resulted in 0.006% of the total N applied being lost as N_2O after 48 h (Table 2). When classified by maturity stage, only immature composts significantly increased soil N_2O emissions, as noted by Takakai et al. (2010). Immature composts promoted P1 estimate around $P1^{SM}$ and above P1 of sheep and alpaca manure. Under controlled conditions, Zhu et al. (2014) also observed that immature compost induced higher soil N_2O emissions than the fresh solid fraction of pig manure. After three months of composting, $P1^{CMPT}$ is not significantly different from zero (Table 2). Such results contrast with Takakai et al. (2010) who reported soil N_2O emissions following mature compost application were lower than in unamended soil.

Larger P1 observed after immature compost addition were mostly due to vegetal compost (Table 2). In C-limited environment, $P1^{CMPT}$ is expected to be related to the WEOC that contains a portion of labile C which can stimulate soil microbial activity (Liang et al., 1996; Zhu et al., 2014). Immature composts contained more WEOC and also more NH_4^+ (Fig. A4-9a) compared to composts older than three months. In this study, NH_4^+ and pH were significant predictors of $P1^{CMPT}$ (Table 3 and S3) but not WEOC and NO_3^-. The positive slope associated with NH_4^+ may indicate N_2O emission following vegetal compost application was the result of nitrification. Several studies suggest that the N_2O product ratios of nitrification ($N_2O/(NO_2^- + NO_3^-)$) are lower in alkaline soils than in acid soils (Goodroad and Keeney, 1984; Mørkved et al., 2007). This is consistent with the negative slope associated with NH_4^+ X pH and $P1^{CMPT}$ (Table 3). Comparing different soil types, Zhu-Barker et al. (2015) concluded that addition of green waste compost (pH = 8.1) did not induce N_2O emissions in clay loam soils, likely due to the high capacity of these soils to buffer changes in biochemical properties such as nitrifier activity or pH. In our incubation, we compared 7 vegetal composts with contrasting pH varying from 6.39 to 8.26, suggesting that acidic compost may alter the buffering capacity of clay soils and provide conditions more favorable to nitrifier activity.

4.4-2.4 Organic-based meals and pellets

Exceptfor bone ash and pelletized poultry manure, estimates of P1 for organic-based meals and pellets ($P1^{PLT-ML}$) was not higher than synthetic fertiliser P1 despite the amount of WEOC added with the organic-based meals, as noted by Cayuela et al. (2010) (Table 2). The interaction of $NO3^-$ X WEOC concentrations was a significant predictor of $P1^{PLT-ML}$(Table A4-3). The positive slope associated with $NO3^-$ X WEOC concentrations and $P1^{PLT-ML}$ may indicate that N_2O emission following the application of organic-based meals was the result of denitrification (Table 3 and S3).

Bone ash P1 and pelletized poultry manure P1 were three and five times higher than synthetic fertiliser P1, respectively (Table 2). Pelletized poultry manure contained large amounts of S, e.g. 20000 mg kg^{-1} d.w., compare to other pellets and OAs (Fig. A4-1). Tam and Knowles (1979) noted that sulphide inhibited N_2O reduction in the denitrification. A possible explanation of higher P1 for bone ash and pelletized poultry manure is inhibition of N_2O reduction in the denitrification process, which can favour N_2O production rather than complete reduction to N_2. Apatite, the principal mineral constituent of bone (Sneddon et al., 2008), was found to be effective in reducing the bioavailability and leachability of Cu in soil (Ma et al., 2012). Since Cu is involved in the reduction process of denitrification (Richardson et al., 2009), accumulation of N_2O due to low Cu has been observed in pure cultures and a lake ecosystem (Glass and Orphan, 2012).

4.4-2.5 Variability of P1

Only one product, liquid seaweed, was removed from statistical analyses of P1 because of atypical behaviour, i.e., total anaerobic conditions occurring 48 h after addition (Fig A4-3g-h). Liquid seaweed contained large amount of WEOC (78246 mg kg^{-1} d.w), and S (14835 mg kg^{-1} d.w). Addition of liquid seaweed resulted in 1% of remaining O_2 in jar headspace after 48h (Fig. A4-3h), followed by N_2O net reduction (Fig. A4-3e), which contradicts the findings of Tam and Knowles (1979) about the inhibiting effect of S on soil N_2O reduction in a denitrification incubation. Magalhães et al. (2012) reported addition of dimethylsulfoniopropionate (DMSP), i.e., an abundant organic sulfur compound in marine algae, to sediments and bacterial culture resulted in accumulation of N_2O. The authors suggested possible interactions between DMSP and the denitrification pathway, although no direct inhibition on N_2O reductase activity by DMSP was observed. Sulphur-containing trace metal-binding protein has been correlated to elevated levels of trace metals in marin organisms (Engel and Brouwer, 1984). Bone ash that also produced the highest P1^{PLT-ML} (Table 2) was found to stabilize metals in a field trial with mechanisms involving microbially mediated metal sulphide formation (Sneddon et al., 2008).

Variability in P1 response was also observed for vegetal compost, and solid emu/beef cattle manure with the presence of outliers included in multiple regression analyses. Those outliers reflect the intrinsically variable nature of N_2O emissions (Butterbach-Bahl et al., 2013), probably caused by the way we incorporated the OAs into the soil. Mixing OA has been proven to increase soil N_2O emissions compared to layered addition of OAs (Zhu et al., 2014), triggering denitrification in soil microsites with reduced O_2 (Firestone and Davidson, 1989; Sey et al., 2008).

4.4-3 Short- (P2) and medium-term (P3) potentials of OAs to emit soil N_2O

The short- and medium-term POA-N_2O were nine and 25 times lower than P1, respectively, indicating that the OA-derived C and N substrates were short-lived (Rochette et al., 2008c). After 16d, P3^{CR} was 82 times lower than P1^{CR} (Table 2), as noted by Baggs et al. (2000) in field conditions which most of the emissions of N_2O (65% of total emissions) following CR incorporation occurring in the first two weeks. Liquid manure application promoted short-lived N_2O emissions because after 10 and 16d, P2^{LM} and P3^{LM} were 64 and 99 times lower than P1^{LM} (Table 2). Our results are in accordance with the maximum POA-N_2O reached the first day after dairy cattle manure application under maize, with emissions returned to near preapplication levels 7 d later (Lessard et al., 1996).

Even if short- and medium-term potentials were lower than P1 in magnitude, significant differences were detected among OAs which differ from classification of OAs provided by P1

(Table 2). MLS had the highest P2 ($P < 0.05$) of all OA categories tested, with up to 0.02% of total N applied being as N_2O after 10 d of incubation. The smaller particle size of powdered MLS compared to other OAs may have increased the contact surface of the powdered MLS, facilitating accessibility to microorganisms, enhancing soil biological activity, and the mineralization of the organic matter compared to other OAs (Tejada et al., 2014). CR also exhibited higher P2 and P3 with up to 0.007 and 0.003% of total N applied being lost as N_2O after 10 and 16 d, respectively, but no significant difference was observed among C/N ratios ranges (Table 2). Contrary to Velthof et al. (2003), SM but not LM presented a higher risk for N_2O emissions in the short- or medium-term (Table 2). The WEOC content of OAs, VFA, and mineral forms of N did not correlate well with P2 and P3 beyond the first three days, as noted by De Catanzaro and Beauchamp (1985). Other chemical characteristics such as the C/N ratio or Lignin/N were not correlated with P2 and P3. Indeed, the short duration of the experiment may not have allowed sufficient release of organic-N and available C from mineralization which impact N_2O emissions in the longer term (Liang et al., 1996; Velthof et al., 2003). Liquid manures, especially pig slurry, showed slower release of nitrogen nutrients compared to solid manure (Whalen et al.,2000). SLG and CMPT did not induce soil N_2O emissions in the short- and medium-term (Table 2), probably because of their higher biological stability index, as illustrated in Fig. A4-1j (Tremblay et al., 2010).

Two OAs stood out, bone ash and horse manure, with P2 values respectively equal to 0.05% and 0.03% of the total N applied being released as as N_2O (Table 2). Moreover, horse manure P3 reached 0.04% of the total N applied, which is 10-fold greater than the average $P3^{SM}$ of 0.004% and higher than horse manure P2. Bone ash is a liming OA characterized by high EA

(Fig. A4-7), while horse manure pH was around nine, suggesting that the liming effect caused by OAs could impact short- and medium-term soil N_2O emissions. Liming may cause a transient enhancement of microbial respiration and nitrogen mineralization (Curtin et al.,1998), which in turn enhances denitrification through O_2 consumption and nitrification through increased substrate concentrations (Mørkved et al., 2007).

4.5 Conclusions

In the Kamouraska clay soil, the POA-N_2O of OAs appeared to be immediate and short-lived, with maximum P1 reached for CR with C/N ratio < 15 and substantial N_2O emissions following LM, especially liquid dairy cattle manure. Solid manure POA-N_2O was significantly lower than $P1^{LM}$, although poultry manure differed from the group with the $P1^{PM}$ estimate being close to the P1 averages of poultry and pig slurries. In an O_2-limited environment, physico-chemical properties of OAs explained 18%, 23%, 27%, 27%, 56%, and 60% of the variability in the P1 response for lower particle-sized OA (PLT-ML), SM, LM, vegetal CMPT, PM and CR, respectively. P1 was correlated to available forms of C such as water-extractable organic C and volatile fatty acids, mineral N (NO_3^- and NH_4^+) and sometimes to S, equivalent alkalinity and pH of OAs ($P < 0.05$). In contrast, none of those chemical characteristics were correlated to P2 and P3, mostly because the enhanced N_2O emissions supported by the OA-C and N substrates were short-lived. Liquid manure P1 was five-fold greater than solid manure P1, whereas short- and medium-term N_2O emissions were higher in SM- than in LM-amended soils. Multiple robust regressions suggest $P1^{PLT\text{-}ML}$was mainly due to denitrification, $P1^{LM}$ and $P1^{SM}$ was due to both nitrification and denitrification, and $P1^{CMPT}$ was mainly due to nitrification. The mechanisms whereby S influences short-term POA-N_2O in C-limited environment may involve binding of S compounds to trace metals, resulting in an incomplete inhibition of nitrous oxide reductase in denitrification pathways, but it remains to be determined whether this mechanism can induce N_2O emissions from OA-amended soils. The assessment of POA-N_2O was conducted in a clay soil probably C-limiting for soil N_2O emissions. Further investigations are necessary to test the influence of other specific conditions, e.g., soil texture, water content, and OA application techniques, on POA-N_2O and their interactions with OA properties.

Table 1. Selected physico-chemical properties of a Kamouraska clay soil (0-20 cm) used for the development of a standard method for soil N_2O emission

Parameter		Mean	(SD)
Texture			
Clay	g kg^{-1} DM	559.6	
Silt	g kg^{-1} DM	373.3	
Sand	g kg^{-1} DM	67.1	
Before pre-incubation			
pH		6.3	(0.03)
C	g kg^{-1} DM	36.3	(0.0)
N	g kg^{-1} DM	2.7	(0.0)

C, total C content measured by dry combustion (Model TruSpec CN, Leco Corp., St-Joseph, MI)

N, total N content measured by dry combustion (Model TruSpec CN, Leco Corp., St-Joseph, MI)

pH, soil water pH

Table 2. The immediate, medium-term and long-term potentials of organic amendments to emit N_2O from the incubated Kamouraska clay soil.

			Potentials of organic amendments to emit soil N_2O								
TYPES OF INPUTS	***N***	**Application rate**	**P1, immediate** [1]			**P2, short-term** [2]			**P3, medium-term** [3]		
			ppm of N applied			ppm of N applied			ppm of N applied		
		kg N / ha	Estimate (se)	Lsd	Pr > |t|*	Estimate (se)	Lsd	Pr > |t|*	Estimate (se)	Lsd	Pr > |t|*
CROP RESIDUES	**124**	**14 - 214**	**2471 (557)**	**A**	**<.0001**	**71 (7)**	**B**	**<.0001**	**30 (7)**	**AB**	**<.0001**
C:N ratio < 15	36	138 - 214	5306 (1853)	a	<.05	52 (11)	a	<.001	20 (7)	a	<.05
C:N ratio 15-30	52	65 - 116	1659 (277)	ab	<.0001	80 (13)	a	<.0001	34 (12)	a	<.05
C:N ratio 30-70	20	30 - 50	863 (411)	b	ns	74 (15)	a	<.001	11 (11)	a	ns
C:N ratio > 70	16	14 - 24	742 (472)	b	ns	84 (18)	a	<.001	67 (32)	a	ns
FARM MANURE	**260**	**60 - 153**	**546 (78)**	**B**	**<.0001**	**31 (5)**	**D**	**<.0001**	**2 (4)**	**B**	**<.0001**
LIQUID	***116***	***60 - 124***	***857 (156)***	***A***	***<.0001***	***13 (3)***	***B***	***<.01***	***9 (3)***	***B***	***<.05***
Cattle slurry	44	60 - 123	1272 (221)	a	<.0001	13 (5)	a	<.0001	7 (1)	a	<.0001
Mixed slurry	12	121	799 (138)	a	<.0001	7 (9)	a	ns	5 (1)	a	ns
Pig slurry	36	121	702 (80)	a	<.0001	18 (6)	a	<.01	12 (1)	a	<.0001
Poultry slurry	4	124	621 (53)	a	<.0001	9 (16)	a	ns	12 (4)	a	<.05
Cow feces	12	121	592 (75)	a	<.0001	3 (9)	a	ns	5 (1)	a	ns
Cow urine	8	120	593 (122)	a	<.0001	20 (12)	a	ns	5 (1)	a	ns
SOLID	***144***	***119 - 153***	***163 (29)***	***B***	***<.0001***	***46 (8)***	***A***	***<.001***	***37 (6)***	***A***	***<.01***
Poultry manure	36	120	533 (70)	a	<.0001	70 (8)	b	<.0001	39 (6)	b	<.0001
Pig manure	8	120	286 (35)	b	<.0001	46 (11)	bcd	<.01	21 (6)	b	<.001
Horse manure	4	120	202 (33)	bc	<.0001	269 (85)	a	<.0001	401 (152)	a	<.0001
Emu manure	4	128	154 (28)	bc	<.0001	22 (7)	d	ns	8 (3)	b	ns
Beef cattle manure	28	119 - 153	152 (28)	c	<.0001	21 (2)	cd	ns	12 (2)	b	ns
Rabbit manure/poop	12	119	98 (10)	c	<.0001	18 (3)	d	ns	15 (3)	b	ns
Goat manure	28	120	100 (12)	c	<.0001	43 (5)	bcd	<.001	30 (5)	b	<.0001
Mixed manure	12	121	80 (9)	c	<.0001	10 (2)	d	ns	14 (3)	b	ns
Sheep manure	8	125	74 (10)	c	<.0001	18 (4)	d	ns	15 (4)	b	ns
Alpaga manure	4	120	53 (7)	c	<.0001	10 (3)	d	ns	13 (5)	b	ns
SLUDGES	**20**	**112**	**538 (118)**	**BC**	**<.05**	**13 (11)**	**DE**	**ns**	**24 (13)**	**ABC**	**ns**
Sewage sludge	4	121	958 (170)	a	<.0001	9 (5)	a	ns	28 (19)	a	ns
Paper mill sludge	16	80 - 120	433 (88)	b	<.001	14 (13)	a	ns	23 (15)	a	ns
ORGANIC-BASED MEALS	**12**	**130**	**229 (111)**	**CD**	**ns**	**234 (60)**	**A**	**<.001**	**27 (8)**	**AB**	**<.05**
Bone ash	4	130	396 (50)	a	<.001	508 (30)	a	<.0001	48 (29)	a	<.05
Crabmeal	4	128	152 (50)	b	<.05	110 (24)	b	<.01	19 (23)	a	<.0001
Fishmeal	4	131	138 (50)	b	<.05	83 (24)	b	<.001	15 (23)	a	<.01
PELLETS	**32**	**128**	**192 (71)**	**D**	**ns**	**32 (6)**	**CDE**	**<.0001**	**18 (4)**	**BC**	**<.001**
Acti-Sol Mother Hen	4	129	678 (50)	a	<.0001	34 (16)	a	ns	5 (12)	a	ns
Pelletized pig slurry	4	120	161 (50)	b	<.05	17 (16)	a	ns	6 (12)	a	ns
Organo-mineral pellets	20	128	131 (38)	b	<.05	37 (9)	a	<.001	26 (6)	a	<.001
Vegetative Bat Guano (10-3-1)	4	137	44 (50)	c	ns	21 (16)	a	ns	6 (12)	a	ns
COMPOSTS	**120**	**121**	**61 (23)**	**D**	**ns**	**13 (7)**	**E**	**ns**	**8 (2)**	**C**	**<.001**
AGE	**0**										
Incomplete windrow	28	121	112 (28)	a	<.001	8 (13)	a	ns	13 (3)	a	<.01
3 - 18 months	28	119	47 (28)	b	ns	4 (13)	a	ns	7 (3)	a	ns
18 - 34 months	28	120	40 (28)	b	ns	35 (13)	a	ns	7 (3)	a	ns
mature	36	121	48 (27)	b	ns	7 (11)	a	ns	7 (3)	a	ns
TYPE	**0**										
Vegetal compost	28	121	103 (28)	a	<.05	4 (4)	a	ns	9 (4)	a	<.05
Shrimp compost	8	127	61 (41)	ab	ns	1 (4)	a	ns	2 (2)	a	ns
Worm compost	8	120	41 (41)	ab	ns	2 (4)	a	ns	3 (5)	a	ns
Agrifood compost	12	120	37 (36)	ab	ns	6 (5)	a	ns	12 (5)	a	<.05
Manure compost	48	120	55 (25)	b	<.05	21 (14)	a	ns	9 (3)	a	<.01
Biosolid compost	16	119	34 (33)	b	ns	22 (18)	a	ns	8 (5)	a	ns
OTHER PRODUCTS	**20**	**108**	**148 (96)**	**D**	**<.05**	**33 (7)**	**CDE**	**<.001**	**18 (6)**	**BC**	**<.05**
Liquid seaweed *	4	**119**	**44486 ***			-6 (12)	b	ns	-4 (11)	a	ns
Shrimp waste (liquid)	4	122	331 (63)	a	<.001	35 (12)	a	< 0.01	17 (11)	a	ns
Shrimp shells	4	119	87 (63)	b	ns	32 (12)	a	<.0001	29 (11)	a	< 0.05
Cow refuse	4	60	108 (63)	b	ns	32 (12)	a	< 0.05	12 (11)	a	ns
Mouldy silage	4	120	68 (63)	b	ns	31 (12)	a	ns	15 (11)	a	ns
SYNTHETIC FERTILIZERS	**48**	**105**	**135 (49)**	**D**	**ns**	**52 (8)**	**BC**	**<.0001**	**42 (6)**	**A**	**<.0001**
Ammonium nitrate	20	27 - 121	166 (33)	a	<.0001	39 (14)	b	<.05	27 (5)	a	<.0001
Calcium ammonium nitrate	4	118	167 (54)	ab	<.01	66 (24)	ab	<.05	68 (44)	a	ns
Monoammonium phosphate	4	118	152 (54)	abc	<.05	102 (24)	a	<.001	67 (20)	a	<.01
Diammonium phosphate	4	119	138 (54)	abc	<.05	62 (24)	ab	<.05	61 (21)	a	<.01
Ammonium sulfate	4	116	131 (54)	abc	<.05	55 (24)	ab	<.05	25 (6)	a	<.001
Urea	4	115	117 (54)	abc	<.05	99 (24)	a	<.001	38 (10)	a	<.001
Environmentally Smart Nitrogen	4	123	53 (54)	bc	ns	6 (24)	b	ns	69 (31)	a	<.05
Sulfur-coated urea	4	128	32 (54)	c	ns	39 (24)	ab	ns	40 (12)	a	<.01

N, total number of observations

[1] **P1** is the immediate N_2O potential estimated over the first 48 h after addition of organic amendments into soil incubated in jars sealed during the first 72 h.

[2] **P2** is the medium-term N_2O potential estimated over a 48-h period, the second week after addition of organic amendments

[3] **P3** is the long-term N_2O potential estimated over a 48-h period, the third week after addition of organic amendments

Liquid seaweed * has been removed from the statistical analysis of P1 because of extreme observations that were discussed in the present paper.

Means sharing a capital letter are not significantly different within category of fertilization by a Lsd test (P<.05).

Means sharing a small letter are not significantly different within subcategory of fertilization by a Lsd test (P<.05).

In parenthesis are standard error of the mean (n=4).

Pr* > |t|** refers to a ***t test to test the null hypothesis that the associated population quantity equals zero (i.d., no N_2O emissions induced by OA addition)

Table 3. Linear robust regressions relating P1[a] to organic amendment properties in a Kamouraska clay soil.

		R^2	*P* > F	*N*
Crop residues (CR)				
	$\ln(P1^{CR} + 10) = -1.6683 \times \ln(C/N + 10) + 9.9071$	0.62	<0.001	124
Eq. 1	$\mathbf{P1^{CR}} = \exp[-1.6683 \times \ln(\mathbf{C/N}+10) + 9.9071 + (0.4807/2)] - 10$			
Eq. 2	$\mathbf{P1^{CR}} = 12.4270 + 18.8996 \times \mathbf{PC_1}$ (see Table A4-2 for additional details on PCA)	0.37	<0.001	60
Farm manure (FM)				
Liquid manure (LM)				
Eq. 3	$\mathbf{P1^{LM}} = 4.40E^{-03} \times \mathbf{NH_4^+} + 1.91E^{-01} \times \mathbf{NO_3^-} + 5.65E^{-03} \times \mathbf{WEOC} + 5.88E^{-03} \times \mathbf{S} - 5.81E^{-05} \times \mathbf{VFA} + 1.01E^{-09} \times \mathbf{pH} - 5.28E^{+06} \times \mathbf{(NH_4^+ * pH)} + 3.30E^{+04} \times \mathbf{(NO_3^- * VFA)} - 5.28E^{+05} \times \mathbf{(NO_3^- * S)} - 7.38E^{+03} \times \mathbf{(WEOC * S)} - 106.263$	0.27	<.001	104
Solid manure [b] (SM)				
Eq. 4	$\mathbf{P1^{SM}} = -3.53E^{-05} \times \mathbf{EA} + 1.14E^{-03} \times \mathbf{S} - 3.77E^{-05} \times \mathbf{WEOC} + 1.15E^{-03} \times \mathbf{NO_3^-} + 5.51E^{-04}\ \mathbf{NH_4^+} - 1.35E^{+03} \times \mathbf{(S * NO_3^-)} + 1.27E^{+03} \times \mathbf{(WEOC * NO_3^-)} - 13.589$	0.23	<.001	108
Solid poultry manure				
Eq. 5	$\mathbf{P1} = 2.00E^{-03} \times \mathbf{NH_4^+} - 4.79 \times \mathbf{NO_3^-} - 3.60E^{-03} \times \mathbf{WEOC} + 2.00E^{-04} \times (\mathbf{WEOC * NO_3^-}) - 4.00E^{-04}\ \mathbf{\times\ EA} + 127.84$	0.56	<.0001	36
Pellets and organic-based meals (PLT-ML)				
Eq. 6	$\mathbf{P1^{PLT\text{-}ML}} = -2.79E^{-03} \times \mathbf{NO_3^-} + 1.86E^{-05} \times \mathbf{WEOC} + 1.18E^{+03} \times (\mathbf{NO_3^- * WEOC}) - 0.4905$	0.18	<0.05	40
Composts (CMPT)				
Vegetal composts				
Eq. 7	$\mathbf{P1^{CMPT}} = 0.05 \times \mathbf{NH_4^+} + 5.08 \times \mathbf{pH} - 0.01\ \mathbf{(NH_4^+ * pH)} - 41.79$	0.27	<0.01	28

[a] **P1**	immediate potential of organic amendments (OA) to induce soil N_2O emissions (POA-N_2O), micrograms N_2O-N kg^{-1} dry soil induced 48h after OA addition (control emissions subtracted).
[b]	Poultry manure was excluded from the group and analysed separately.
C/N	C/N ratio
Propionic	Propionic acid (volatile fatty acid)
Isobutyric	Isobutyric acid (volatile fatty acid)
EA	Equivalent Alkalinity (micrograms $CaCO_3$ kg^{-1} soil)
WEOC	Water-extractable organic carbon (micrograms kg-1 soil)
BSI	Biological Stability Index

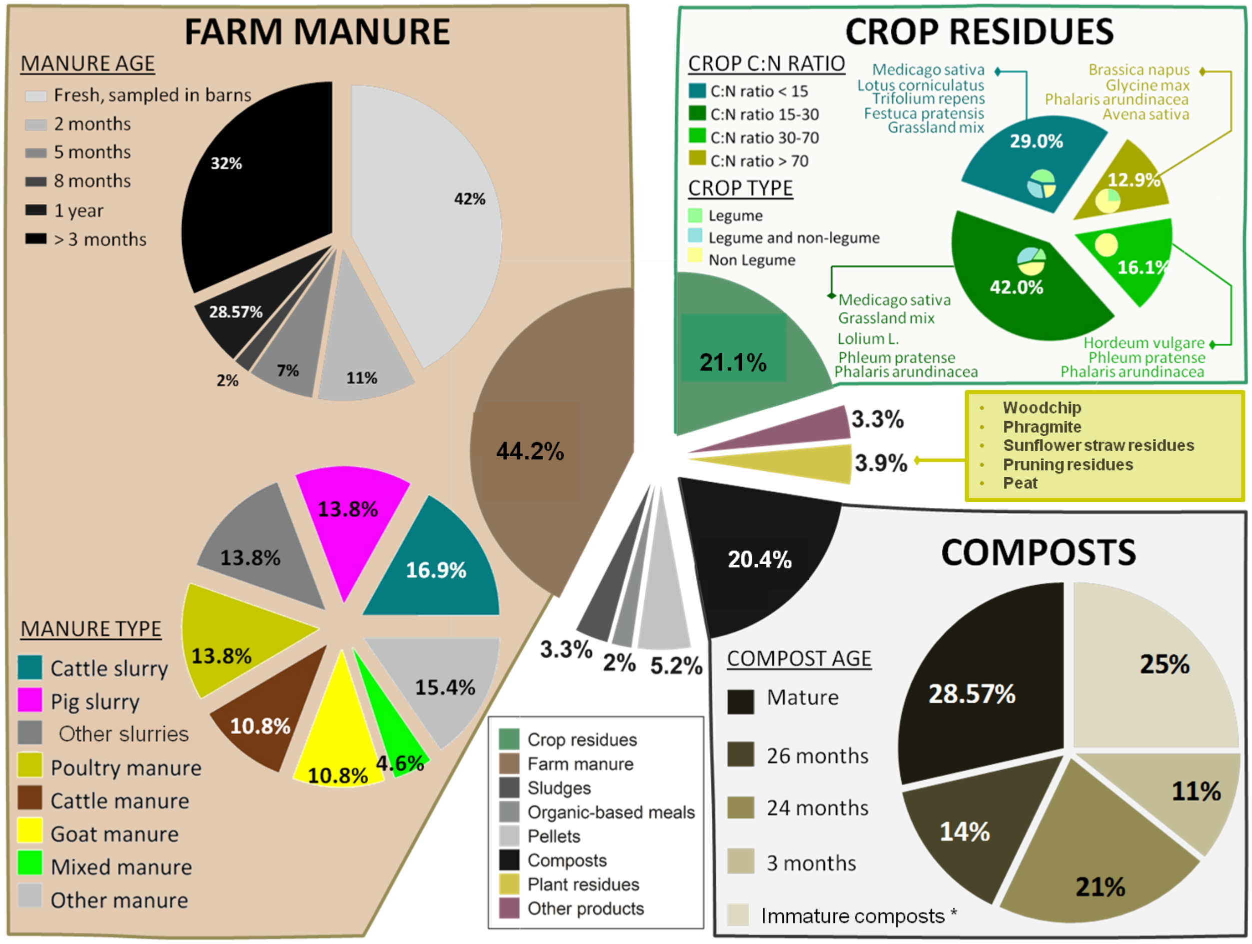


Fig 1. Collection of amendments and organic-based tested for their potentials to induce soil N_2O emissions in controlled conditions (n = 147).

* Immature composts are piles under construction (compost age < 3 months).

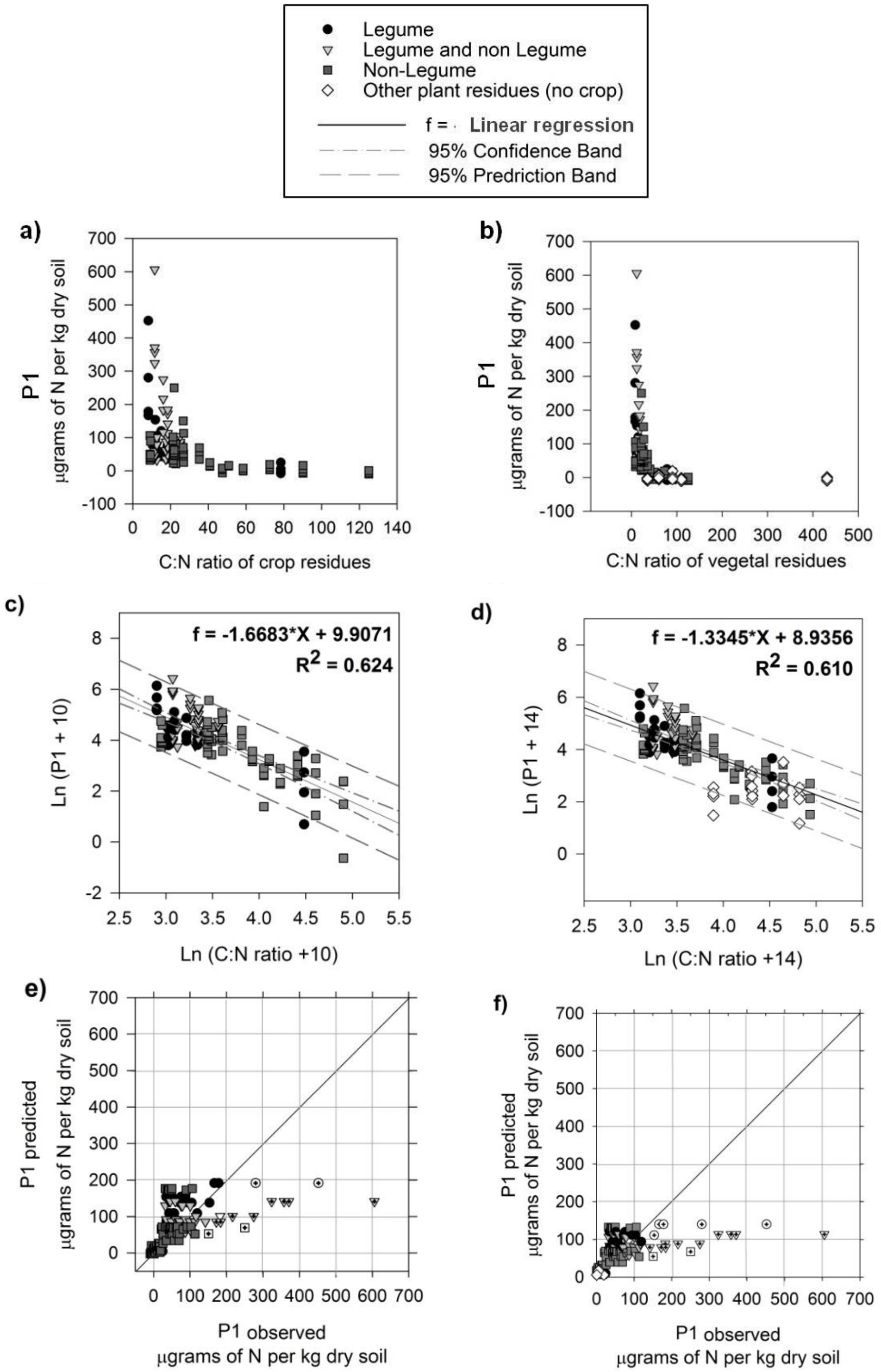


Fig 2. Carbon: Nitrogen ratio as predictor of immediate potential of crop residue to induce soil N_2O emissions* (P1)

a) Observed P1 as a function of crop residues C/N ratios; **b)** Linear regression analysis of log-transformed variables; **c)** Predicted values of crop residue P1* using simple linear regression model based on C/N ratio; **b-d-f)** Peat, woodchip, sunflower straw residues, pruning residues and phragmites were added in the regression approach. Outliers' symbols are represented in x-hair.

*P1, micrograms N_2O-N kg^{-1} dry soil induced 48h after OA addition (control emissions subtracted), *Lotus corniculatus* was removed from the regression (outlier) and discussed in the present paper. (See additional details in Table 3).

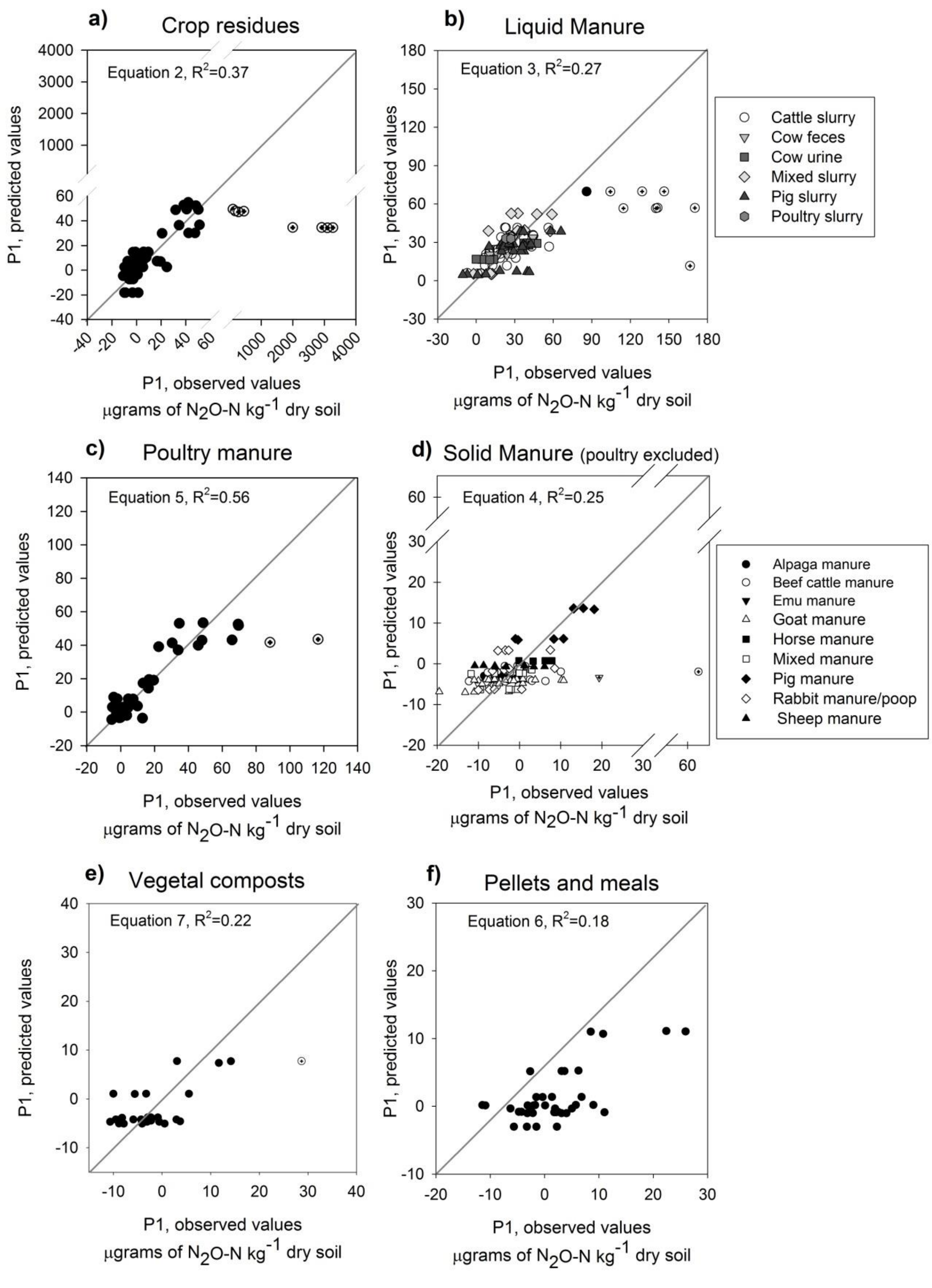


Fig. 3. P1* prediction using robust regressions based on organic amendment properties

(See equation details in Table 3, S3, S4, and S5). Outliers' symbols are represented in x-hair.

*P1, immediate potential of organic amendments (OA) to induce soil N_2O emissions (POA-N_2O), micrograms N_2O-N kg^{-1} dry soil induced 48h after OA addition (control emissions subtracted)

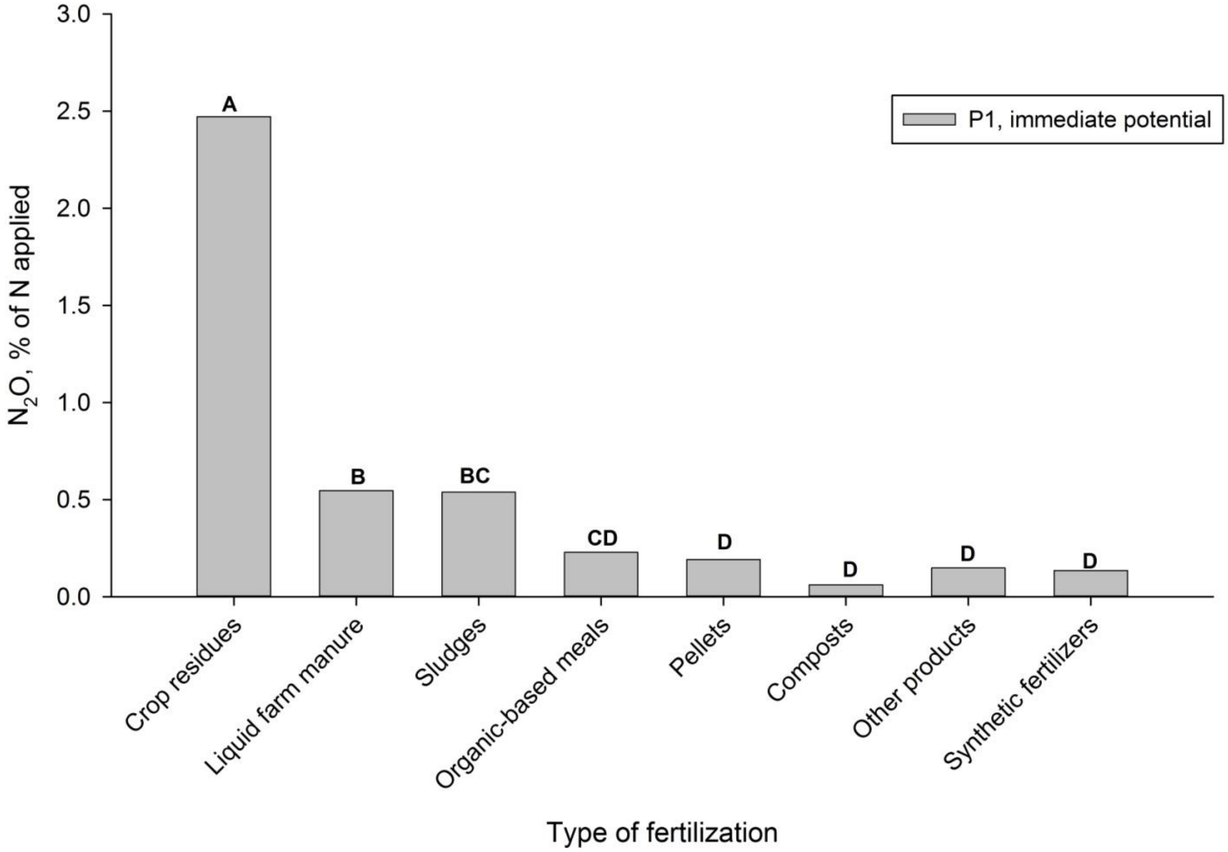


Fig. 4. Type of organic amendment (OA) influenced the immediate potential of organic amendments to emit N_2O from the incubated Kamouraska clay soil.

P1 is the immediate potential of organic amendments (OA) to induce soil N_2O emissions (POA-N_2O) 2d after OA addition (control emissions subtracted). Means sharing a letter are not significantly different within category of fertilization by a Lsd test (P<.05)

GENERAL CONCLUSIONS

Over the past decades, several attempts have been made to improve the Tier1 default IPCC methodology for soil N_2O inventory considering the type of N source (Bouwman et al., 2002b; Chen et al., 2013). However, previous studies focused either on a narrow range of OAs (manure, crop residues), or a particular geographical area, and none has proven robust enough for broad acceptance.

The primary goal of this thesis was to gain a better understanding of the influence of physico-chemical properties of OAs on soil N_2O emissions shortly after their addition, and other controlling factors (incubation parameters, soil properties, climatic and management-related factors) as a prerequisite for developing more accurate predictions of N_2O emission factors.

Three experiments were conducted to achieve this goal. In the meta-analysis Chapter (Chapter 2), confronting three analytical approaches allowed us to distinguish and estimate EF for soil N_2O emissions from OAs, alone and combined with synthetic fertilizers. We demonstrated that the IPCC EF1 value was too high when considering the N_2O contribution from agricultural soils amended with composts, but too low to represent the EF of N_2O in agricultural soils receiving liquid manure (mostly pig slurry) combined with synthetic fertilizers. We propose a global default EF for organic sources, EF_{org}, equal to 0.57 ± 0.30% and encourage the use of FertiClasses or FertiRiskClass categories to account for the N_2O emissions from specific OA sources or groups of OAs with similar characteristics. We improved the accuracy of EF_{org}, especially for agricultural soils receiving high-risk and low-risk organic amendments, with the identification of three new N_2O risk classes of OAs (and their related global EF): the high-risk group including animal manures, waste waters and biosolids (1.09 ± 0.17%); the medium-risk group including composts + fertilizers and crop residues + fertilizers (0.46 ± 0.22%); and the low-risk group including composts, crop residues, paper mill sludge and pellets (0.25 ± 0.20%). Finally, we confirmed that variations in N_2O EFs in OA-amended soils are influenced mainly by the mineral N content and the C/N ratio of OAs, rainfall (expressed as TAP), soil texture and drainage. We recommend site-specific EFs that consider organic amendment chemistry, soil characteristics, climate conditions and whether the organic amendment is applied alone or in combination with synthetic fertilizers.

In the second experiment (Chapter 3), a comparative incubation study helped to identify optimal laboratory conditions for the expression and measurement of the POA-N_2O. At the mesocosm scale, varying O_2 availability is necessary to adequately assess the potential of OAs to enhance soil N_2O emissions. This is because oxic conditions favor substrate accumulation in soil, and those substrates become available to denitrifiers that are activated when conditions become anoxic (e.g., after a rainfall event). The duration of the oxic phase altered the magnitude of the OA effect on N_2O emissions under anoxia. The progressive decline of O_2 below ambient in the headspace of the sealed-jar system permitted the evaluation of OAs role in enhancing soil N_2O in a O_2-limited environment (oxic phase ceased at 5% O_2 concentration), which is not possible with the open-jar method. For the purpose of the last experiment, we selected a laboratory method that involved intermittent aerations of a sealed-jar system. An initial 72-h measurement period was followed by repeated 48-h periods of O_2-limited conditions to assess the short-term (72-h) and medium-term (multiple 72-h periods) potential of OAs to induce soil N_2O emissions.

In Chapter 4, the laboratory assessment of POA-N_2O was conducted in a clay soil, probably C-limiting for soil N_2O emissions. Soil N_2O emissions were immediate and short-lived, with maximum POA-N_2O reached for CR with C/N ratio < 15 and substantial N_2O emissions following LM, especially liquid dairy cattle manure. Solid manure POA-N_2O was significantly lower than liquid manure POA-N_2O, although poultry manure differed from the group with an estimate close to P1 averages of poultry and pig slurries. In O_2-limited environments, physico-chemical properties of OAs explained 18%, 23%, 27%, 27%, 56%, and 60% of variability in the immediate POA-N_2O response for fine particle-sized OA (PLT-ML), SM, LM, vegetal CMPT, PM and CR, respectively. The immediate POA-N_2O was correlated to available forms of C such as water-extractable organic C and volatile fatty acids, mineral N (NO_3^- and NH_4^+) and sometimes to S, equivalent alkalinity and pH of OAs ($P < 0.05$). Our results suggested that the immediate POA-N_2O of fine particle-sized OAs (meals and pellets) was mainly due to denitrification, was due to both nitrification and denitrification for farm manure, and for composts was mainly due to nitrification. The mechanisms whereby S influences short-term POA-N_2O environment remain to be determined for OAs.

Overall, the incubation study led to contrasting results compared to the meta-analysis. While the meta-analysis concluded OAs were generally at lower N_2O risk compare to synthetic N sources, the incubation study concluded OAs were generally at higher N_2O risk compare to synthetic N sources. The assessment of POA-N_2O in controlled conditions was conducted in a clay soil probably C-limiting for soil N_2O emissions. By contrast, agricultural soils generally received high fertilizer inputs to get maximum crop yield which eventually increases SOC, and N availability (Thangarajan et al., 2013). Soil moisture and temperature can constitute the main drivers of denitrification regardless of the scale, while proximal factors are oxygen supply influenced by substrate concentration, available energy, and distal factors refer to plant N uptake influenced by soil texture (Butterbach-Bahl et al., 2013). Further investigations are necessary to test the influence of other specific conditions, e.g., soil texture, water content, OA application techniques on POA-N_2O and their interactions with OA properties. In conclusion, a more accurate soil N_2O inventory requires deeper investigation of the interactions between the physico-chemical properties of OAs and soil properties with the systematic consideration of additional chemical properties of C and N substrates, such as OA pH, equivalent alkalinity and S.

Finally, the IPCC methodology should be revised to consider the nature of N sources. The database assembled and the approach followed in the meta-analysis could therefore be used to update the IPCC EFs for soil N_2O emissions resulting from the application of OAs to agricultural soils. The results from this thesis showed that the chemical properties of OAs highly impact soil N_2O emissions immediately after their addition in agricultural soils, confirming that N_2O mitigation strategies should focus on OA application techniques adapted to the OA and specific soil types. Properties of OAs have lesser impact in the short- and medium-term because N_2O potentials depends on complex interactions between OA C- and N-derived substrates and soil properties. Therefore, models describing soil N_2O emissions should handle complex interactions between the chemical properties of OAs and soil properties for a significant step towards soil N_2O mitigation in agroecosystems.

CONTRIBUTIONS TO KNOWLEDGE

The research conducted in this thesis provides the following important contributions to knowledge:

1. I conducted the first meta-analysis that specifically focused on global emission factors (EF) of OAs from field experiments following the addition of OAs alone or combined with synthetic fertilizers.
    a. My research demonstrated that the IPCC EF_1 for N_2O inventory value was too high when considering the N_2O contribution from agricultural soils amended with composts, but too low to represent the EF of N_2O in agricultural soils receiving liquid manure (mostly pig slurry) combined with synthetic fertilizers.
    b. My research led to the proposition of a new global default EF for organic sources, EF_{org}, equal to 0.57 ± 0.30%, and which is lower than the IPCC default EF of 1% for synthetic fertilizer. I also improved the accuracy of EF_{org} with the identification of three new N_2O risk classes of OAs (and their related global EF): the high-risk group including animal manures, waste waters and biosolids (1.09 ± 0.17%); the medium-risk group including composts + fertilizers and crop residues + fertilizers (0.46 ± 0.22%); and the low-risk group including composts, crop residues, paper mill sludge and pellets (0.25 ±0.20%).
    c. I demonstrated that EF_{org} was modulated by the amendment's C/N ratio, soil properties (texture, drainage, organic C and N) and climatic (precipitation) factors.

2. A comparative laboratory study showed a better discrimination of OAs related to their POA-N_2O using the sealed-jar method that created transient conditions from oxic to anoxic (compared to the open-jar method).

3. In a second laboratory experiment, more than 130 OAs were concomitantly assessed in the same incubation study for their POA-N_2O and were compared to synthetic fertilizer emissions.

    a. According to multiple regression analyses, the physico-chemical properties of OAs explained 18% to 60% of variability in immediate POA-N_2O (< 48 h).

    b. My research confirmed that the immediate POA-N_2O was positively correlated to available forms of C such as water-extractable organic C and volatile fatty acids, mineral N (NO_3^- and NH_4^+). Moreover, my research demonstrated that other chemical properties were significant. I showed that OA pH and equivalent alkalinity had a significant effect on soil N_2O emissions in controlled conditions regardless of the category of OAs, and that the significant effect of OA sulphur content on soil N_2O emissions is not confined to specific crop residues such as alfalfa residues but may applied for all OAs, especially in slightly alkaline clay soil type and O_2-limited environment.

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APPENDICES - CHAPTER 2.

Table A2-1 a Selection procedure for papers from the Scopus research database[3].

Search statement	**Concepts and Keywords**

	Soil	AND	N_2O	AND	Organic amendment
General	soil*		nitrous oxide		organic amendment*
		OR	N_2O	OR	residue
				OR	waste
				OR	refuse
				OR	by-products
				OR	organic waste
				OR	organic by-products
				OR	organic fertilizer
				OR	fertilizer

AND

	Soil	AND	N_2O	AND	Organic amendment
Vegetal residues	soil*		nitrous oxide		vegetal residues
		OR	N_2O	OR	residue
				OR	forage
				OR	crop residue
				OR	forage crop
				OR	crop debris
				OR	crop refuse
				OR	mulch
				OR	surface trash

AND

	Soil	AND	N_2O	AND	Organic amendment
Livestock manures	soil*		nitrous oxide		manure
		OR	N_2O	OR	slurry, slurries
				OR	muck slurry
				OR	slurr*
				OR	dung
				OR	mud

AND

	Soil	AND	N_2O	AND	Organic amendment
Sludges	soil*		nitrous oxide		sewage
		OR	N_2O	OR	sludge
				OR	biosolid*
				OR	ooze
				OR	effluent

AND

	Soil	AND	N_2O	AND	organic amendment
Composts	soil*		nitrous oxide		compost
		OR	N_2O	OR	decayed organic matter

RESULTS	**959 references including 23 duplicates related to the CAB query**

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[3] The detailed review of literature was carried out until June 13 2014.

Table A2-1 b Selection procedure for papers from the CAB Abstract research data base[4].

Search statement	Keywords	Results
General 1	(nitrous oxide or N_2O).af.	10433
AND		
General 2	soil*.af.	1288490
AND		
General 3	organic amendment*.af.	9873
AND		
RESULTS	**145 references including 23 duplicates related to the Scopus query**	

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[4] The detailed review of literature was carried out until June 13 2014.

Table A2-2. Properties of organic and synthetic sources reported in the database, classified by FertiTypes and FertiClasses[5] (mean ± standard deviation).

				Total N input			Organic amendment properties						mineral N, mg/kg dry basis	
			N	**Min**	**-**	**Max**	**Dry Matter, %**		**C/N ratio**		**pH**			
FERTITYPES		**Organic sources**	**251**	19	-	800	15.9	± 23.9	8.3	± 11.5	7.6	± 0.7	66847	± 75520
		Organic and synthetic sources	**72**	87	-	817	24.9	± 31.3	21.4	± 27.1	7.7	± 0.1	217026	± 90354
		Synthetic sources (S)	**99**	50	-	480	n/a	n/a	n/a	n/a	n/a	n/a	353040	± 94554
FERTICLASSES	**High risk**	**All high-risk**												
		Liquid manure + S	31	130	-	460	4.0	± 3.1	4.2	± 3.7	8.0	± 0.4	237042	± 78864
		Biosolid, CR + S	6	120	-	142	n/a		n/a		n/a		n/a	
		Waste water	8	24	-	231	3.5	± 2.2	9.5	± 6.1	6.0	± 2.1	3716	± 5989
		Liquid manure	149	35	-	480	4.0	± 2.5	4.2	± 2.6	7.6	± 0.6	89896	± 79178
		Biogas residues	10	160	-	480	4.9	n/a	4.6	n/a	7.6	n/a	42000	n/a
		Biosolid + S	6	87	-	300	42.5	± 3.1	26.9	± 5.4	5.1	± 1.5	83502	± 16
		Solid manure + S	3	240	-	392	19.1	n/a	15.4	n/a	n/a		n/a	
		Solid manure	29	72	-	800	44.2	± 20.7	12.2	± 4.4	7.6	± 1.6	4535	± 4584
	Medium risk	**All medium-risk**												
		Compost + S	14	150	-	817	53.5	± 11.7	12.6	± 10.5	n/a		83745	n/a
		Crop residues + S	12	135	-	271	64.9	± 35.3	66.1	± 23.5	n/a		n/a	
	Low risk	**All low-risk**												
		Paper mill sludge + CR	6	220	-	243	n/a		n/a	± 0.0	n/a		n/a	
		Compost	29	125	-	672	35.7	± 21.7	10.8	± 3.3	7.6	± 0.3	4822	± 9865
		Pellets	5	508	-	510	97.4	± 0.0	9.9	± 0.7	n/a		n/a	
		Crop residues (CR)	8	19	-	108	95.8	± 5.9	32.1	± 40.5	n/a		n/a	
		Liquid manure + CR	1	178	-	178	6.5	n/a	35.9	n/a	n/a		2353	n/a
		Paper mill sludge	6	519	-	519	35.0	± 0.0	24.6	n/a	6.9	n/a	n/a	

N, Total # of observations; **n/a**, not available

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[5] **FertiType**, type of fertilization: organic, synthetic fertilizers, organic and synthetic fertilizers
FertiClass, nature of organic sources ± synthetic sources (Table 3, Chapter 2)
FertiRiskClass, N_2O risk classes of organic sources ± synthetic sources (Table 3, Chapter 2)

Table A2-3. Properties of organic sources combined or not with synthetic sources (mean ± standard deviation).

Mineral nitrogen content % dry weight	N	Application rate kg N ha^{-1} Min	-	Max	Dry Matter %		C/N ratio		pH	
0.0 - 0.3	**31**	**114**	**-**	**672**	**17.9**	**± 21.8**	**18.3**	**± 6.9**	**7.9**	**± 1.2**
Compost	13	129	-	672	25.7	± 18.3	17.2	± 2.6	7.7	± 0.1
Liquid manure[†]	10	114	-	114	0.6	± 0.1	n/a	n/a	8.6	± 0.5
Solid manure	5	170	-	480	41.3	± 27.9	15.3	± 3.7	n/a	n/a
Waste water	2	197	-	231	4.7	± 4.2	18.4	± 4.0	5.1	± 2.0
Liquid manure + CR	1	178	-	178	6.5	n/a	35.9	n/a	n/a	n/a
0.3 - 1.0	**7**	**126**	**-**	**672**	**32.4**	**± 7.8**	**8.0**	**± 2.2**	**6.7**	**± 1.7**
Solid manure	7	126	-	672	32.4	± 7.8	8.0	± 2.2	6.7	± 1.7
1.0 - 10	**72**	**35**	**-**	**480**	**9.6**	**± 13.6**	**6.4**	**± 4.6**	**7.4**	**± 0.3**
Liquid manure[ŧ]	54	35	-	480	5.6	± 1.7	5.4	± 2.0	7.3	± 0.3
Biogas residue	10	160	-	480	4.9	± 0.0	4.6	± 0.0	7.6	± 0.0
Compost	3	125	-	300	56.2	± 27.8	12.0	± 1.9	7.2	± 0.6
Biosolid + S	2	300	-	300	41.3	± 3.2	26.3	± 0.0	n/a	± 0.0
Waste water	1	117	-	117	4.8	n/a	5.3	n/a	7.8	n/a
Solid manure	1	416	-	416	43.2	n/a	5.2	n/a	n/a	n/a
Compost + S	1	300	-	300	36.1	n/a	12.8	n/a	n/a	n/a
10 - 25	**45**	**130**	**-**	**300**	**2.9**	**± 1.8**	**3.0**	**± 1.4**	**7.9**	**± 0.3**
Liquid manure + S[Ϫ]	12	130	-	130	4.4	± 2.8	3.6	± 1.9	7.9	± 0.4
Liquid manure[Ϫ]	33	130	-	300	2.3	± 0.7	2.8	± 1.1	7.9	± 0.3
> 25	**11**	**130**	**-**	**130**	**1.4**	**± 0.3**	**1.5**	**± 0.6**	**8.2**	**± 0.2**
Liquid manure + S[Ϫ]	8	130	-	130	1.5	± 0.4	1.6	± 0.7	8.2	± 0.2
Liquid manure[Ϫ]	3	130	-	130	1.3	± 0.3	1.3	± 0.4	8.2	± 0.3

S, synthetic sources
CR, crop residues
N, total # of observations
n/a, not available

[†] cattle by-products (dairy cow)

[ŧ] 57% of the observations were pig slurry by-products and 43% were cattle by-products.

[Ϫ] pig slurry by-products, combined or not with synthetic fertilizers referring to raw slurry or (anaerobically) digested material, thin fraction, or decanted, filtered, flocculated fractions.

Table A2-4. Measures of association for soil parameters reported in the database

		Soil properties				
		Silt	**Total N**	**Organic C**	**C/N ratio**	**pH**
Silt	**Rho**	1.000	-0.038	-0.086	-0.320	0.258
	Pr > |r|		ns	ns	<.0001	<.0001
	N_{ob}	260	237	248	237	260
Total N	**Rho**		1.000	0.939	0.353	-0.461
	Pr > |r|			<.0001	<.0001	<.0001
	N_{ob}		306	306	306	296
Organic C	**Rho**			1.000	0.587	-0.558
	Pr > |r|				<.0001	<.0001
	N_{ob}			340	306	330
C/N ratio	**Rho**				1.000	-0.572
	Pr > |r|					<.0001
	N_{ob}				314	296
pH	**Rho**					1.000
	Pr > |r|					
	N_{ob}					344

Rho, Spearman's rank correlation coefficient
Rho = +1 indicates a perfect positive association of ranks,
Rho = 0 indicates no association between ranks
Rho = -1 indicates a perfect negative association of ranks
The closer Rho is to zero, the weaker the association between the ranks.
Pr> |r|, H0: Rho=0
N_{ob}, total # of observations

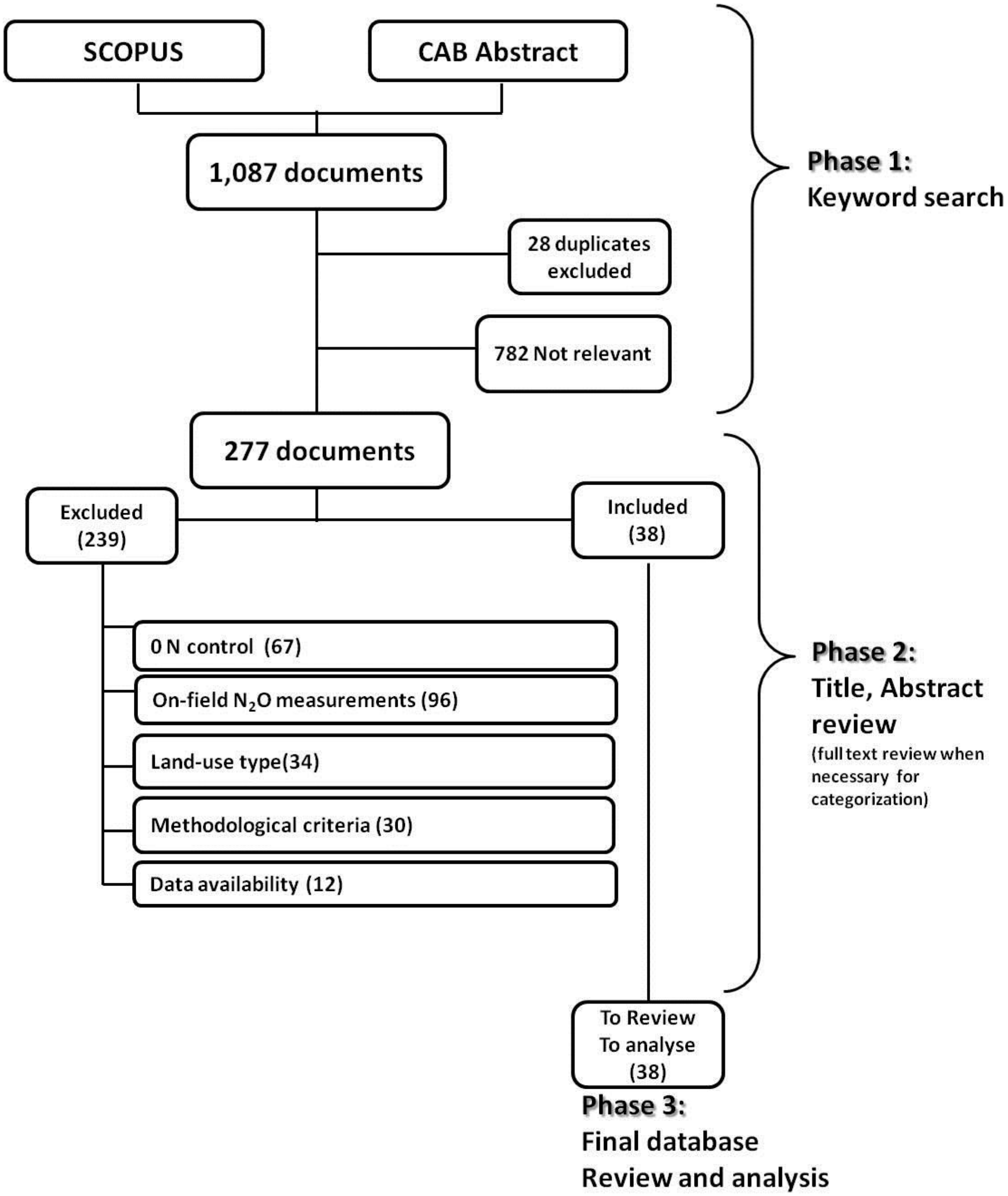

Figure A2-1. Summary of the procedure for document selection from the Scopus and CAB Abstracts research databases

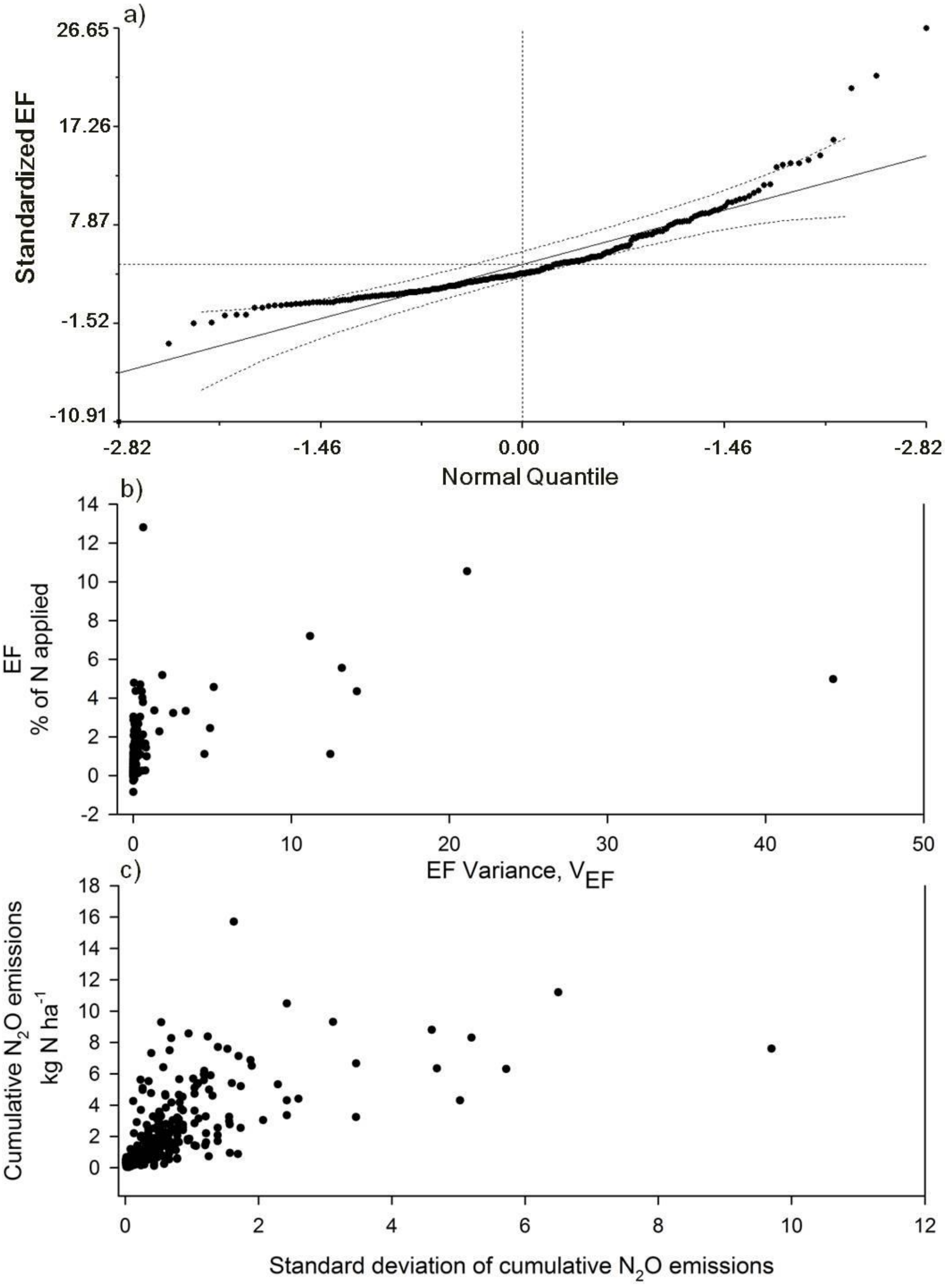

Figure A2-2. Distribution of N_2O emission factor and its variance.
a) Asymmetric distribution of N_2O emission factors from selected studies (n=316),
b) Emission factor (EF) of N_2O, expressed as the fraction of the N applied, plotted against the variance of emission factor (EF) from selected studies (n=316),
c) Cumulative N_2O emissions related to the standard deviation of these emissions from selected studies (n=409).

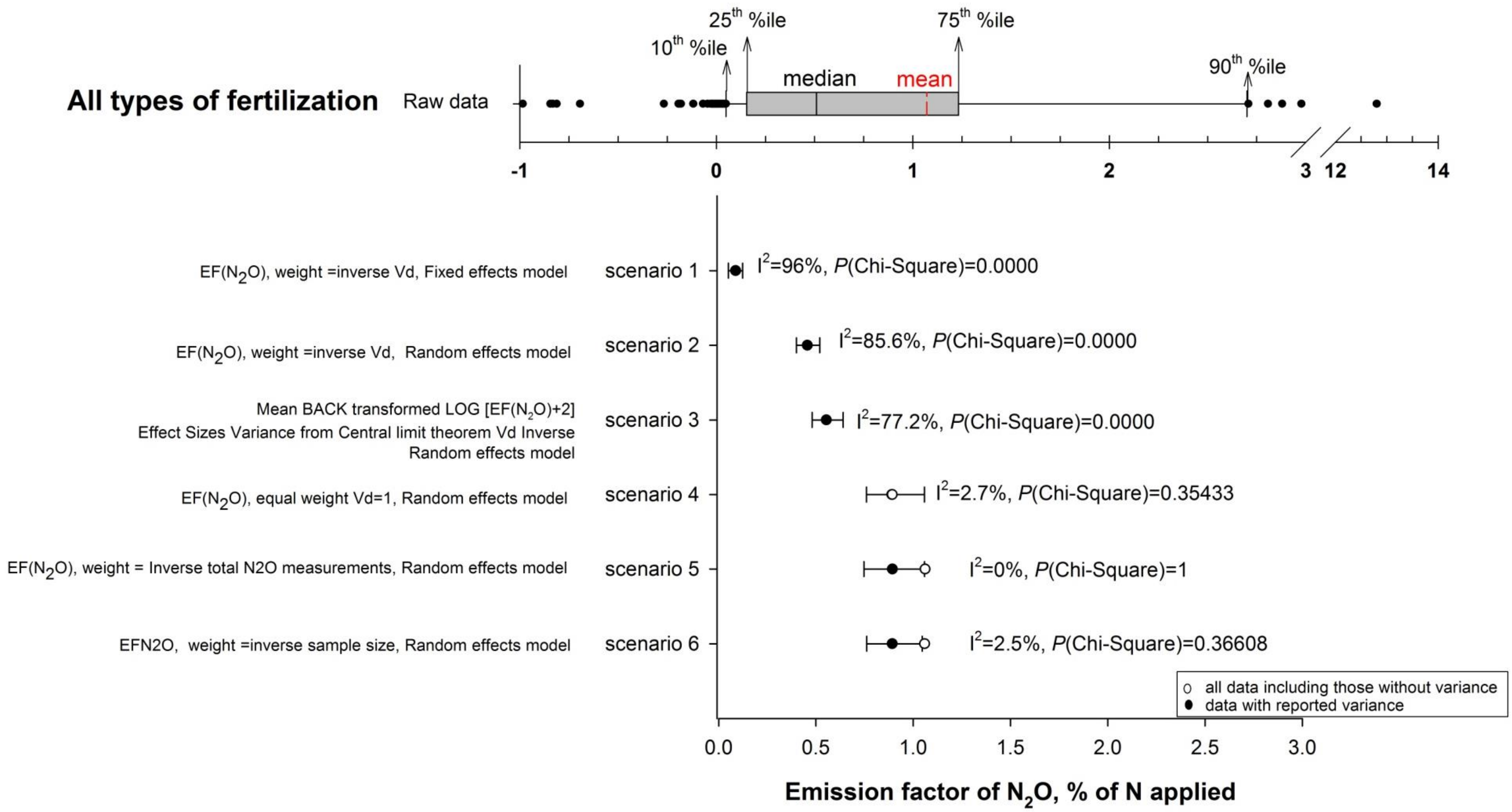

Figure A2-3. Adjustment of the random-effects model according to Borenstein (2009), comparing the model performance following different weighting procedures. Scenario 2 model provided best performance with the highly significant Chi-Square, which means it is recommended the random-effects model would use the inverse of EF variance (1/Vd) as a weighting factor.

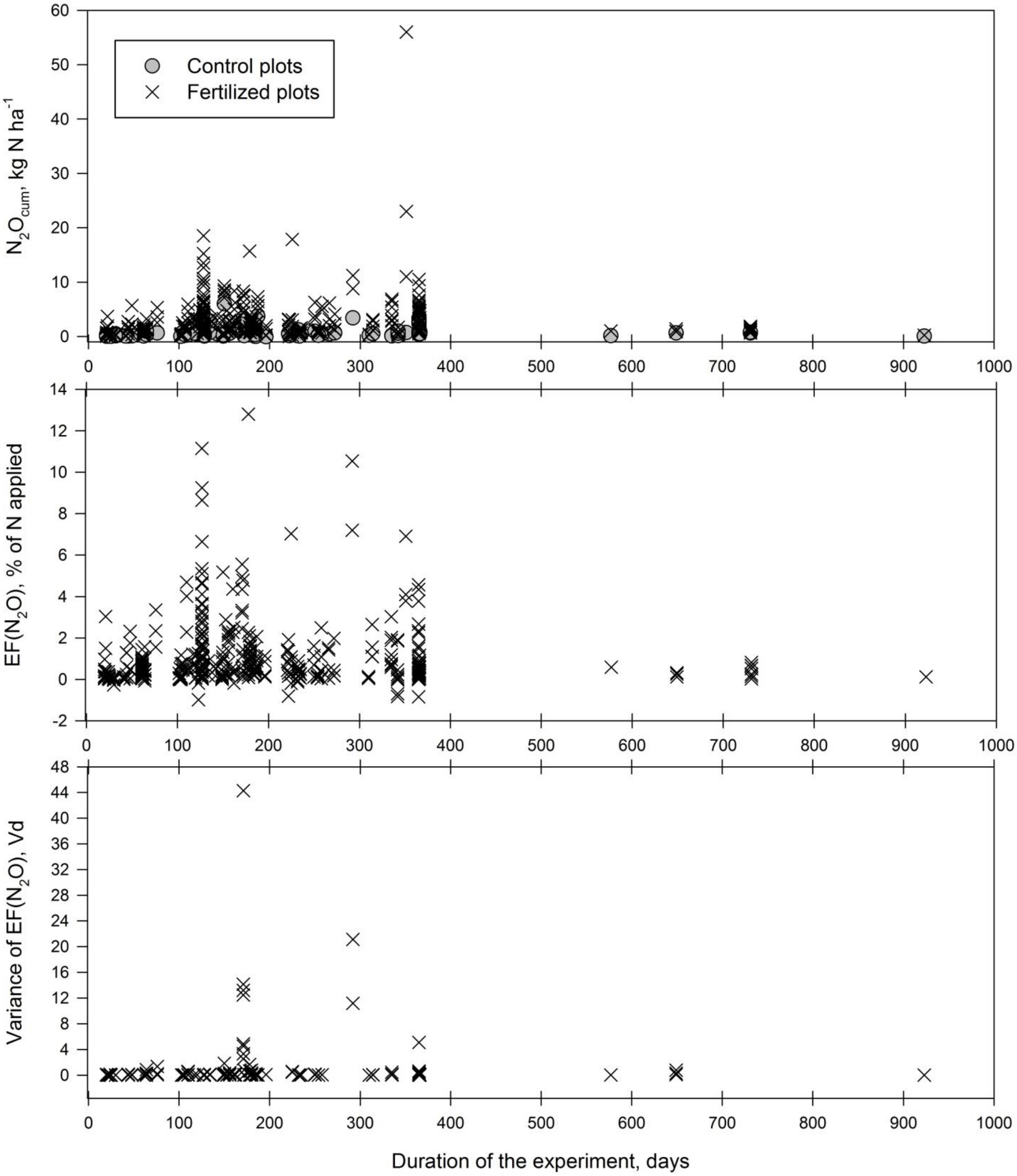

Figure A2-4. The influence of study duration on N_2O response variables.
The parameter EF (N_2O) represents N_2O emission factor and the variance of EF(N_2O) represents the variance of N_2O emission factor.

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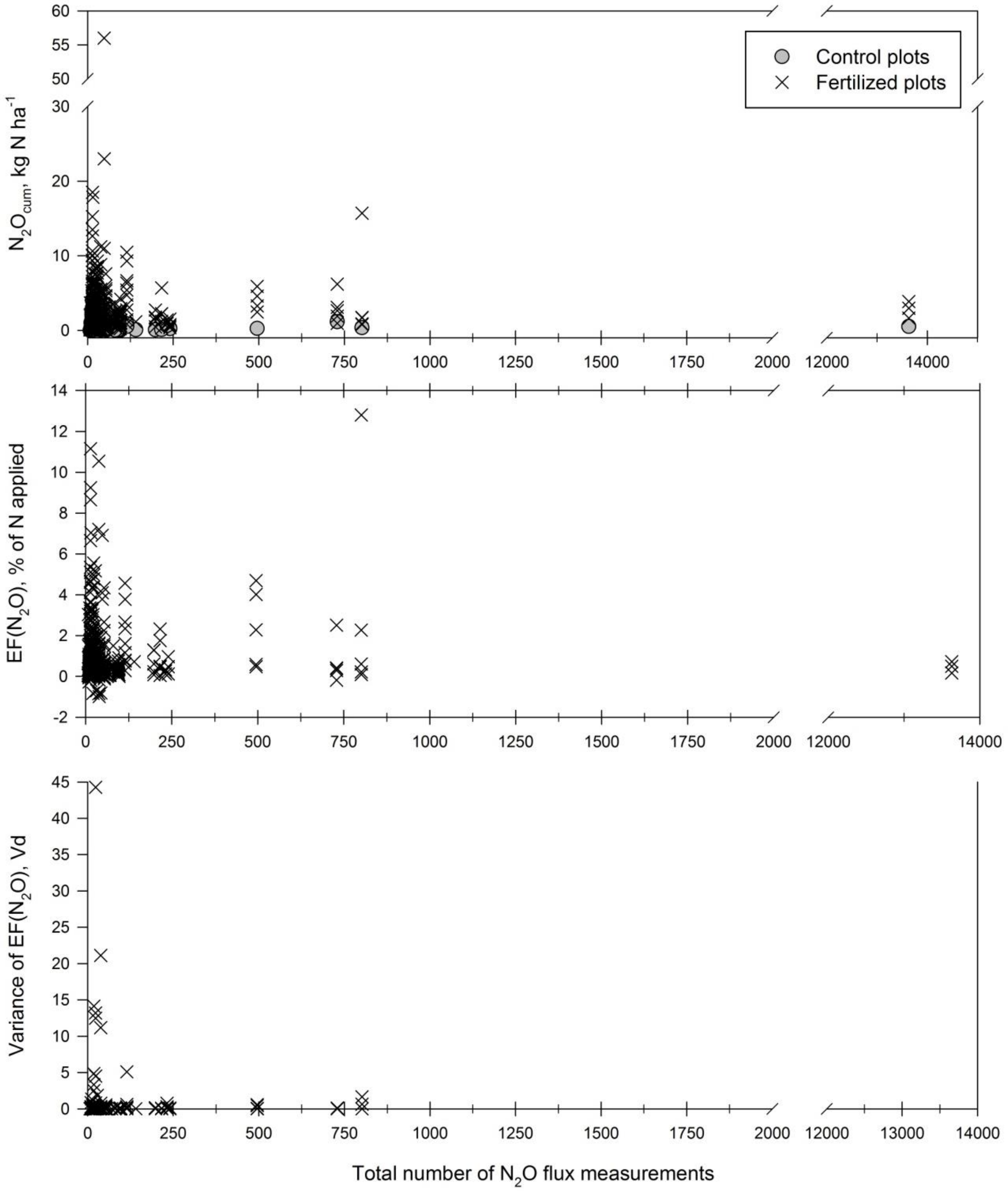

Figure A2-5. The influence of total number of flux measurements on N_2O response variables.

The parameter N_2Ocum represents cumulative N_2O emissions, EF (N_2O) represents N_2O emission factor and the variance of EF(N_2O) represents the variance of N_2O emission factor.

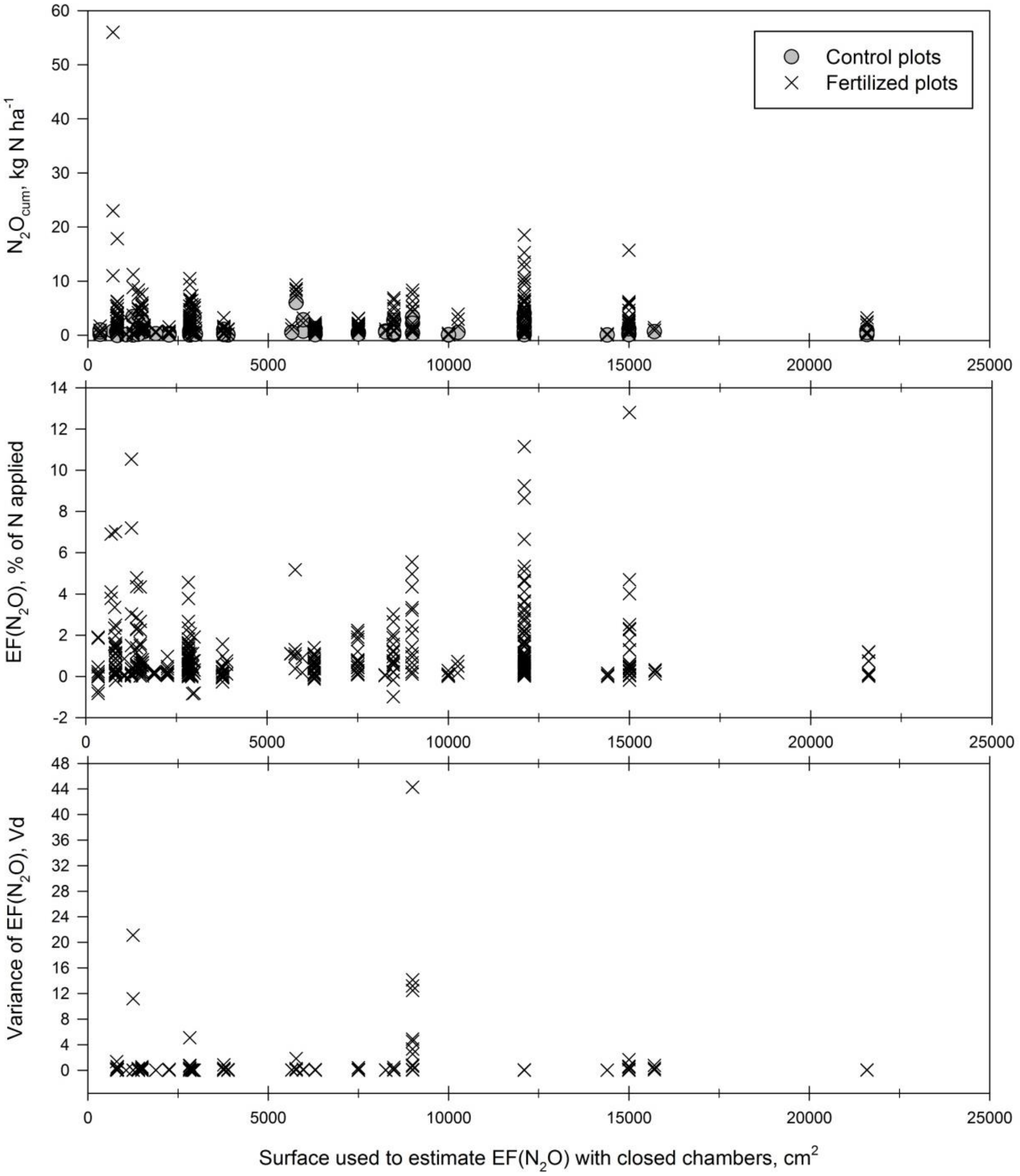

Figure A2-6. The influence of total surface area within closed chambers used for flux measurements on N_2O variables.

The parameter N_2Ocum represents cumulative N_2O emissions, EF (N_2O) represents N_2O emission factor and the variance of EF(N_2O) represents the variance of N_2O emission factor.

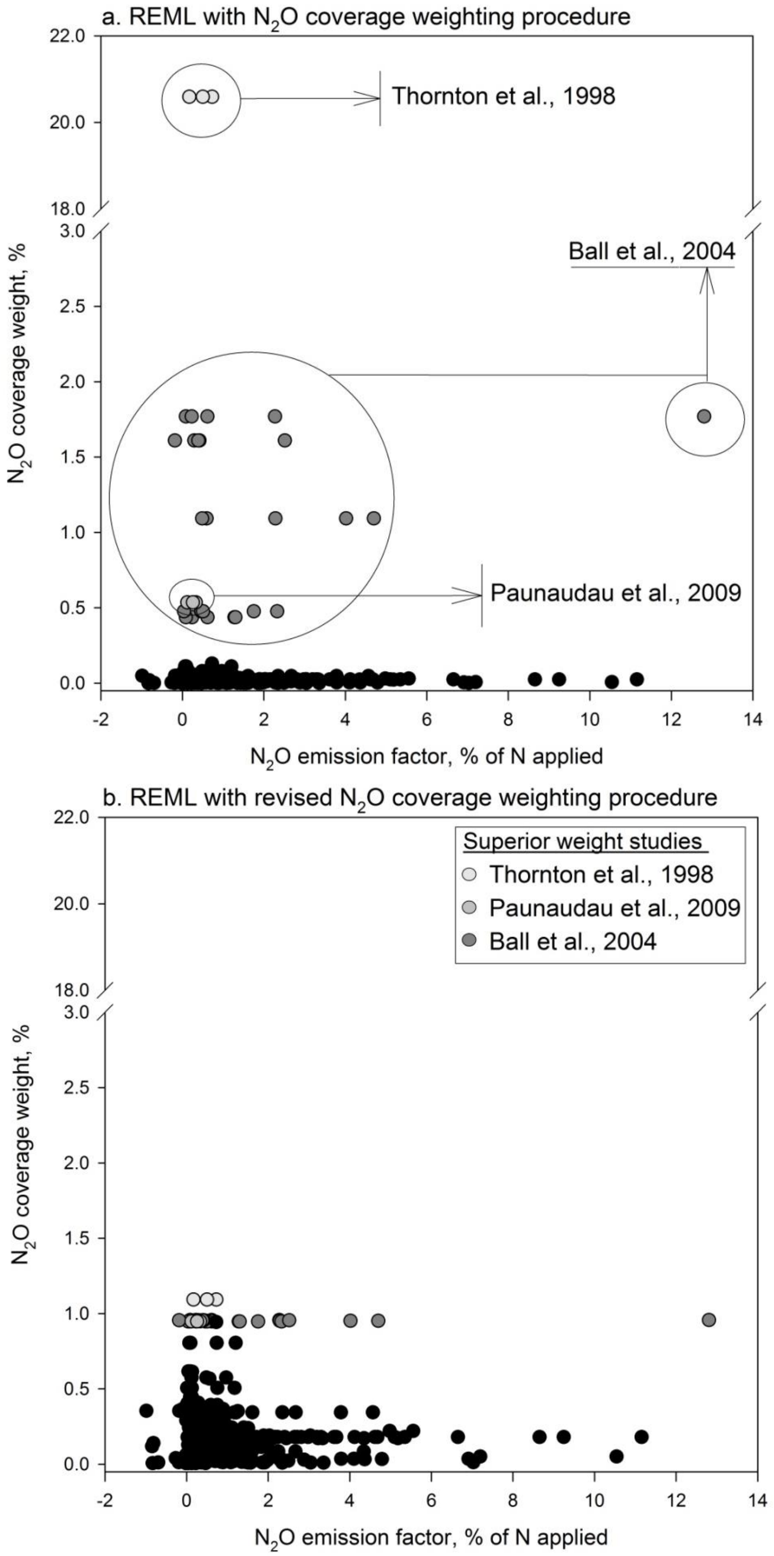

Figure A2-7.Revising the REML weighting procedure with detection of superior weight studies. Superior weight studies were defined as studies whose weight of N_2O observations was twice greater than the average weight of all N_2O observations (0.24%).

APPENDICES - CHAPTER 3.

Table A3-1. Fate of mineral N in the Kamouraska soil under four different incubation methods

Amendment	Method	At the beginning of the incubation				At the end of the oxic phase				At the end of the incubation			
		soil $NH_4^{+\,§}$		soil $NO_3^{-\,§}$		soil NH_4^{+}		soil NO_3^{-}		soil NH_4^{+}		soil NO_3^{-}	
		mg N kg^{-1} dry soil											
CTL	**O^{w}/S^{+}**	2.70	(0.24)	3.79	(2.76)	0.44^{a}	(0.06)	20.74^{a}	(2.15)	9.92^{b}	(0.30)	0.00^{b}	(0.00)
	S/S^{+}					0.13^{b}	(0.06)	12.82^{b}	(1.16)	12.62^{a}	(0.25)	0.02^{b}	(0.02)
	S/S^{-}									7.16^{c}	(1.03)	0.01^{b}	(0.01)
IF	**O^{w}/S^{+}**	59.30	(0.05)	20.15	(0.01)	0.51^{a}	(0.13)	78.72^{a}	(3.10)	10.01^{b}	(0.90)	0.03^{b}	(0.03)
	S/S^{+}	59.39	(0.06)	20.17	(0.02)	2.63^{a}	(1.48)	56.14^{b}	(9.98)	14.62^{a}	(0.66)	0.04^{b}	(0.04)
	S/S^{-}	59.39	(0.06)	20.17	(0.02)					2.50^{c}	(0.10)	9.03^{b}	(4.00)
AR	**O^{w}/S^{+}**	8.83	(0.04)	56.47	(0.36)	0.57^{b}	(0.08)	49.17^{a}	(1.32)	11.40^{c}	(0.10)	0.00^{b}	(0.00)
	S/S^{+}	8.83	(0.03)	56.51	(0.28)	3.98^{a}	(0.75)	23.69^{b}	(1.49)	20.59^{a}	(0.67)	0.02^{b}	(0.04)
	S/S^{-}	8.83	(0.05)	56.48	(0.47)					13.24^{b}	(0.57)	0.01^{b}	(0.01)
PM	**O^{w}/S^{+}**	22.75	(0.03)	3.80	(0.00)	0.62^{b}	(0.14)	57.70^{a}	(1.21)	12.32^{b}	(0.55)	0.00^{b}	(0.01)
	S/S^{+}	23.68	(0.03)	3.80	(0.00)	7.81^{a}	(1.03)	27.50^{b}	(1.51)	24.98^{a}	(1.91)	0.00^{b}	(0.01)
	S/S^{-}	23.67	(0.03)	3.80	(0.00)					14.40^{b}	(0.47)	0.04^{b}	(0.00)
PS	**O^{w}/S^{+}**	80.74	(1.52)	3.83	(0.00)	0.87b	(0.33)	45.48^{a}	(1.37)	12.40^{b}	(0.38)	0.00^{b}	(0.00)
	S/S^{+}	71.43	(1.74)	3.83	(0.00)	7.91^{a}	(0.82)	20.03^{b}	(1.34)	28.38^{a}	(5.96)	0.02^{b}	(0.01)
	S/S^{-}	67.50	(1.73)	3.83	(0.00)					15.50^{b}	(0.97)	0.02^{b}	(0.02)
SMC	**O^{w}/S^{+}**	2.73	(0.00)	3.94	(0.00)	0.58^{a}	(0.21)	16.18^{a}	(1.68)	9.87^{b}	(0.28)	0.00^{b}	(0.00)
	S/S^{+}	2.73	(0.00)	3.94	(0.00)	0.22^{b}	(0.08)	12.90^{b}	(0.81)	12.25^{a}	(0.48)	0.01^{b}	(0.01)
	S/S^{-}	2.73	(0.00)	3.94	(0.00)					7.54^{c}	(0.37)	0.01^{b}	(0.01)
WSR	**O^{w}/S^{+}**	2.77	(0.00)	3.85	(0.00)	0.54^{a}	(0.06)	2.9^{b}	(0.52)	6.83^{b}	(3.81)	0.13^{b}	(0.21)
	S/S^{+}	2.77	(0.00)	3.85	(0.00)	0.20^{b}	(0.11)	5.63^{a}	(0.72)	15.15^{a}	(1.12)	0.13^{b}	(0.24)
	S/S^{-}	2.77	(0.00)	3.85	(0.00)					11.77^{a}	(0.27)	0.04^{b}	(0.05)

Means that share a letter are not significantly different within method type by a Tukey-Kramer test (α=0.05). In parenthesis are standard deviation values (n=4).

[§] Values were calculated adding the NH_4^{+} and NO_3^{-} inputs to the soil NH_4^{+} and soil NO_3^{-} contents of the CTL jar, respectively.

Means that share a letter are not significantly different within method type by a Tukey-Kramer test (α=0.05). In parenthesis are standard deviation values (n=4).

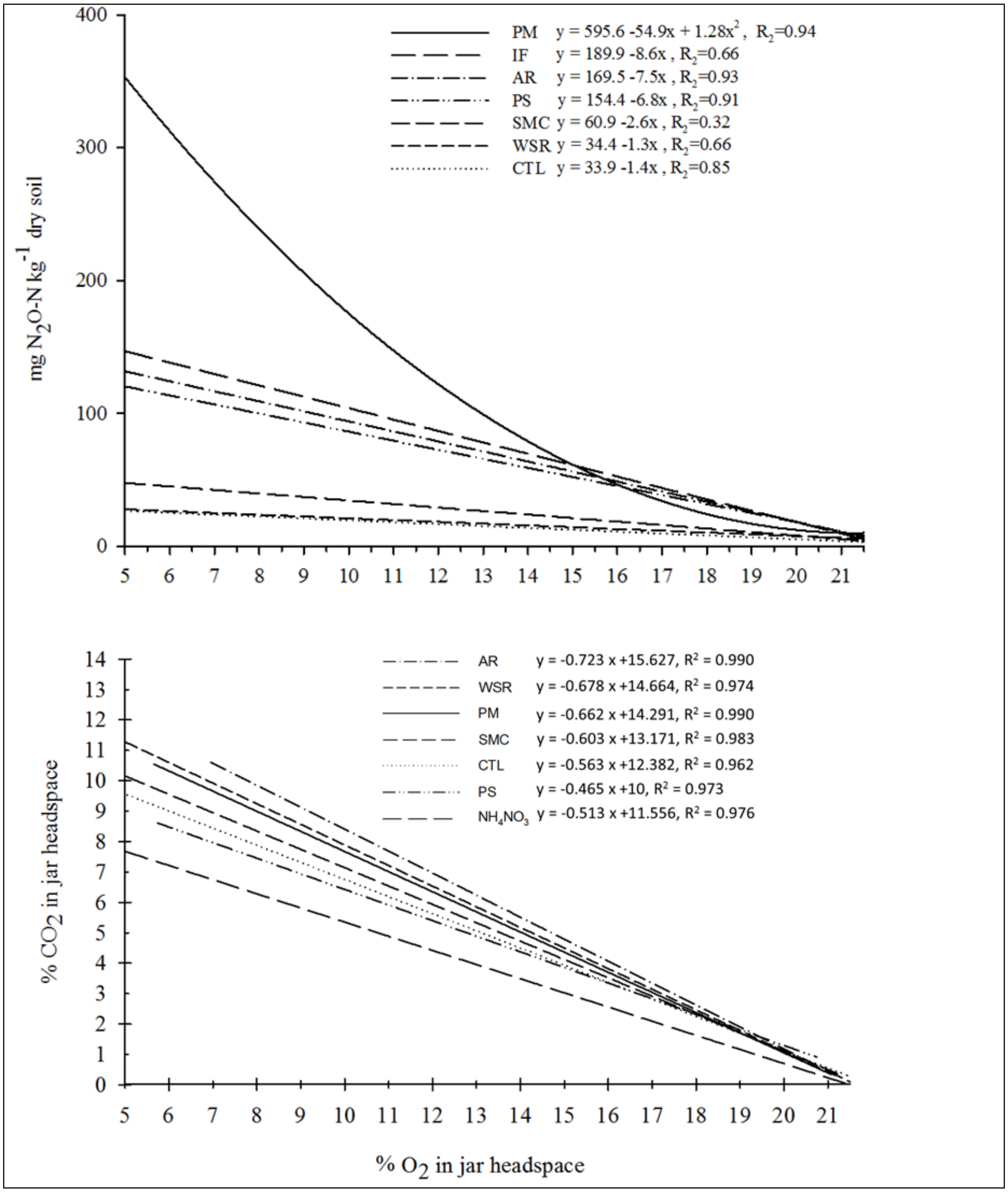

Figure A3-1. Soil N_2O emissions under O_2 –limited concentrations with the S methods

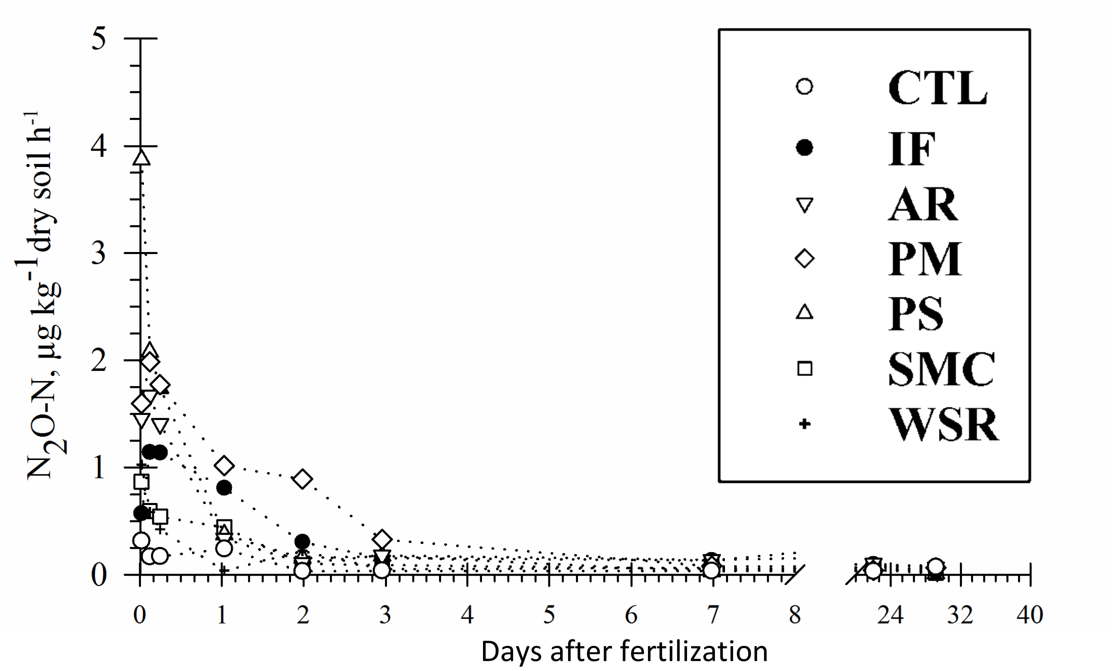

Figure A3-2. Fluxes of soil N_2O emissions after fertilization with the opened-jar method

Abbreviations for fertilization treatment are as follows: CTL, control (unamended soil); IF, inorganic fertilizer (NH_4NO_3); AR, alfalfa residues; PM, poultry manure; PS, pig slurry; SMC, sheep manure compost and WSR, wheat straw residues.

APPENDICES - CHAPTER 4.

Table A4-1. High level of collinearity between chemical properties of crop residues indicated by Pearson's correlations (n=64).

	C/N ratio	NH_4^+	NO_3^-	BSI	WEOC	S
C/N ratio	1.00000	-0.52692	-0.32083	0.28566	-0.51611	-0.61983
		***	**	*	***	***
NH_4^+		1.00000	0.48347	-0.52938	**0.81314**	**0.95165**
			***	***	*******	*******
NO_3^-			1.00000	-0.30703	0.53979	0.50887
				*	***	***
BSI				1.00000	-0.58126	-0.52587
					***	***
WEOC					1.00000	**0.82518**
						*******
S						1.00000

Table A4-2. Robust regression model relating $P1^{CR}$[*] to chemical properties of crop residues based on principal component (PC) scores.

Chemical properties [†]	PC_1	PC_2	PC_3	PC_4	PC_5	PC_6	CE[x̄]
S	0.25						0.90
NH_4^+	0.24						0.85
WEOC	0.24						0.83
NO_3^-	0.16						0.40
BSI	-0.17						0.43
C/N ratio	-0.17						0.43
Eigenvalues	3.85	0.74	0.70	0.48	0.19	0.04	
Variance proportion	0.64	0.13	0.12	0.07	0.03	0.01	
Cumulative variance	0.64	0.77	0.89	0.96	0.99	1.00	
Multiple Linear Regression	**$P1 = 12.4270 + 18.8996 \times PC_1$ $R^2 = 0.37$, $P<0.001$**						

[*] $P1^{CR}$, immediate potential of crop residues to induce soil N_2O emissions, micrograms N_2O-N kg^{-1} dry soil induced 48h after OA addition (control emissions subtracted)

[†] Chemical properties: S, sulphur; NH_4^+, ammonium; WEOC, water-extractable organic carbon; NO_3^-, nitrate; BSI, Biological Stability Index

[x̄] CE, Total communality estimates

Table A4-3. Multiple robust regressions relating P1[*] to properties of organic amendments

Robust Parameter Estimates (method MM estimation)				
Predictors	**df**	**Estimate**	**Chi-Squared**	**Pr > ChiSq**
Liquid manure				
NH_4^+	1	4.40E^{-03}	6.93	0.0085
NO_3^-	1	1.91E^{-01}	0.58	0.4445
WEOC	1	5.65E^{-03}	12.39	0.0004
S	1	5.88E^{-03}	9.67	0.0019
VFA	1	-5.81E^{-05}	2.56	0.1098
pH	1	1.01E^{-09}	1.94	0.1632
NH_4^+*pH	1	-5.28E^{+06}	6.38	0.0116
NO_3^- * VFA	1	3.30E^{+04}	25.4	<.0001
NO_3^- *S	1	-5.28E^{+05}	1.96	0.1619
WEOC * S	1	-7.38E^{+03}	10.5	0.0012
Solid manure (poultry manure excluded)				
EA	1	-3.53E^{-05}	10.76	0.001
S	1	1.14E^{-03}	28.32	<.0001
WEOC	1	-3.77E^{-05}	2.41	0.1203
NO_3^-	1	1.15E^{-03}	2.48	0.1152
NH_4^+	1	5.51E^{-04}	33.46	<.0001
S*NO_3^-	1	-1.35E^{+03}	9.88	0.0017
WEOC*NO_3^-	1	1.27E^{+03}	4.79	0.0286
Solid poultry manure				
EA	1	-4.00E^{-04}	40.33	<.0001
NH_4^+	1	2.00E^{-03}	46.06	<.0001
NO_3^-	1	-4.79	35.04	<.0001
WEOC	1	-3.60E^{-03}	36.44	<.0001
NO_3^- * WEOC	1	2.00E^{-04}	28.55	<.0001
Vegetal composts				
NH_4^+	1	0.0471	5.13	0.0235
pH	1	5.0844	1.08	0.2985
NH_4^+*pH	1	-0.0060	4.32	0.0377
Pellets				
NO_3^-	1	-2.96E^{-03}	2.54	0.1109
WEOC	1	1.58E^{-05}	0.18	0.6686
NO_3^- * WEOC	1	1.11E^{+03}	7.08	0.0078

[*] P1, immediate potential of organic amendments (OA) to induce soil N_2O emissions (POA-N_2O), micrograms N_2O-N kg^{-1} dry soil induced 48h after OA addition (control emissions subtracted)

NO_3^-, nitrate; WEOC, water-extractable organic carbon; S, Sulphur; VFA, Volatile Fatty Acids; EA, Equivalent Alkalinity; NH_4^+, ammonium

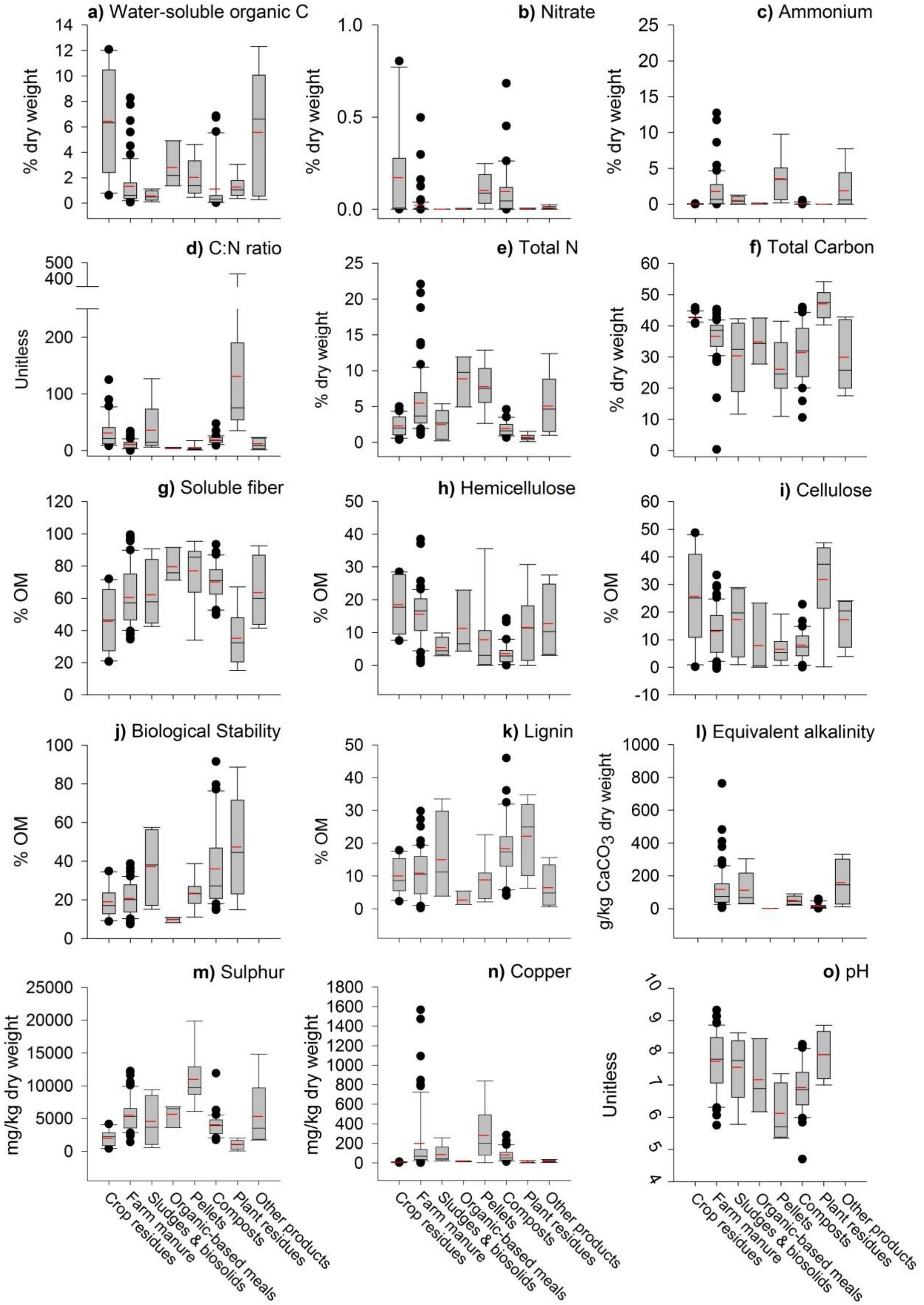

Fig. A4-1. Variations in chemical properties according to the organic amendment categories

The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.

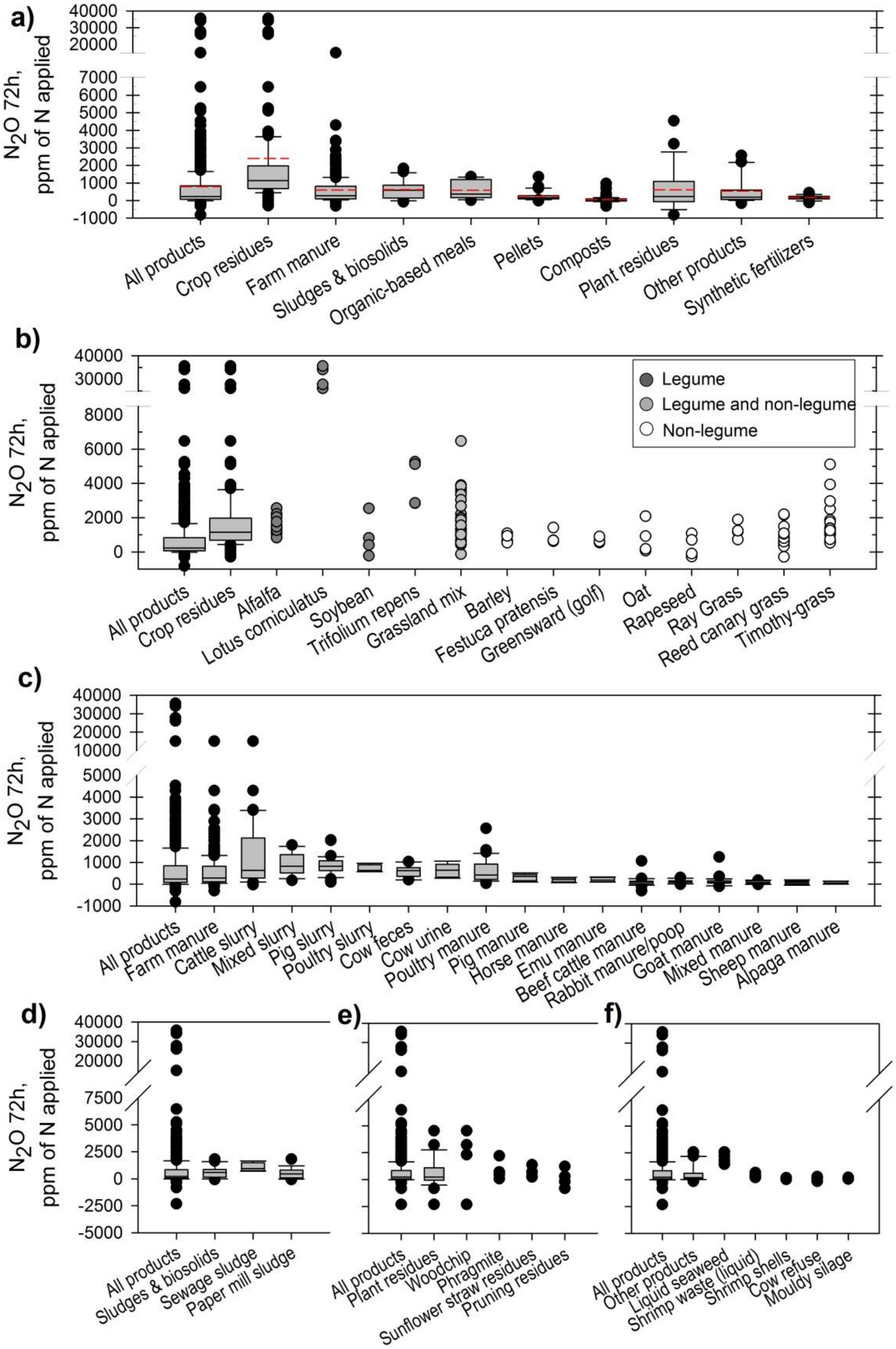

Fig. A4-2. Variability in N$_2$O emissions 72h after organic amendment addition

(control emissions subtracted). The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.

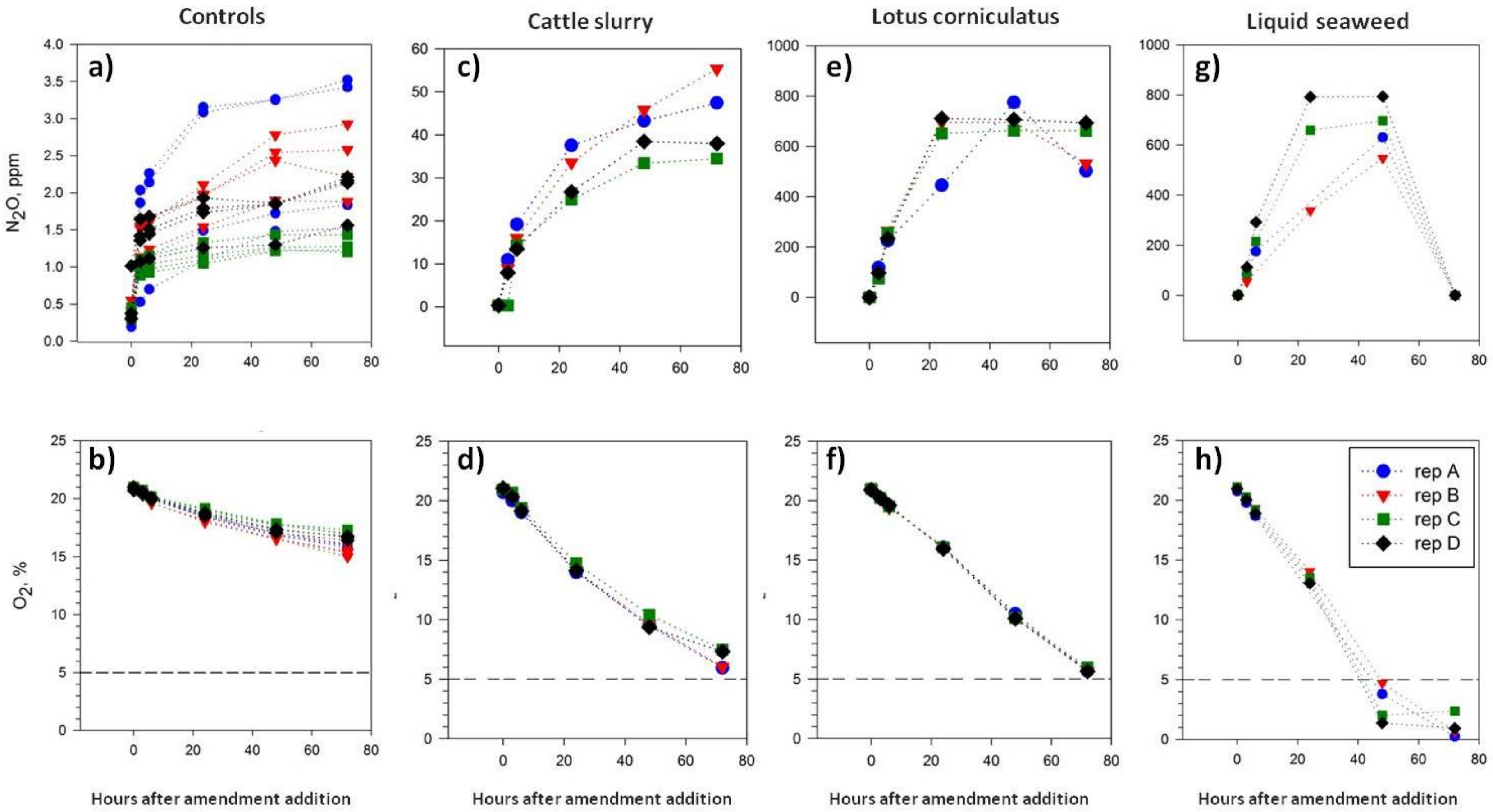

Fig. A4-3 Dioxygen and N_2O concentrations in jar headspace of unamended controls and soils mixed with reactive amendments.

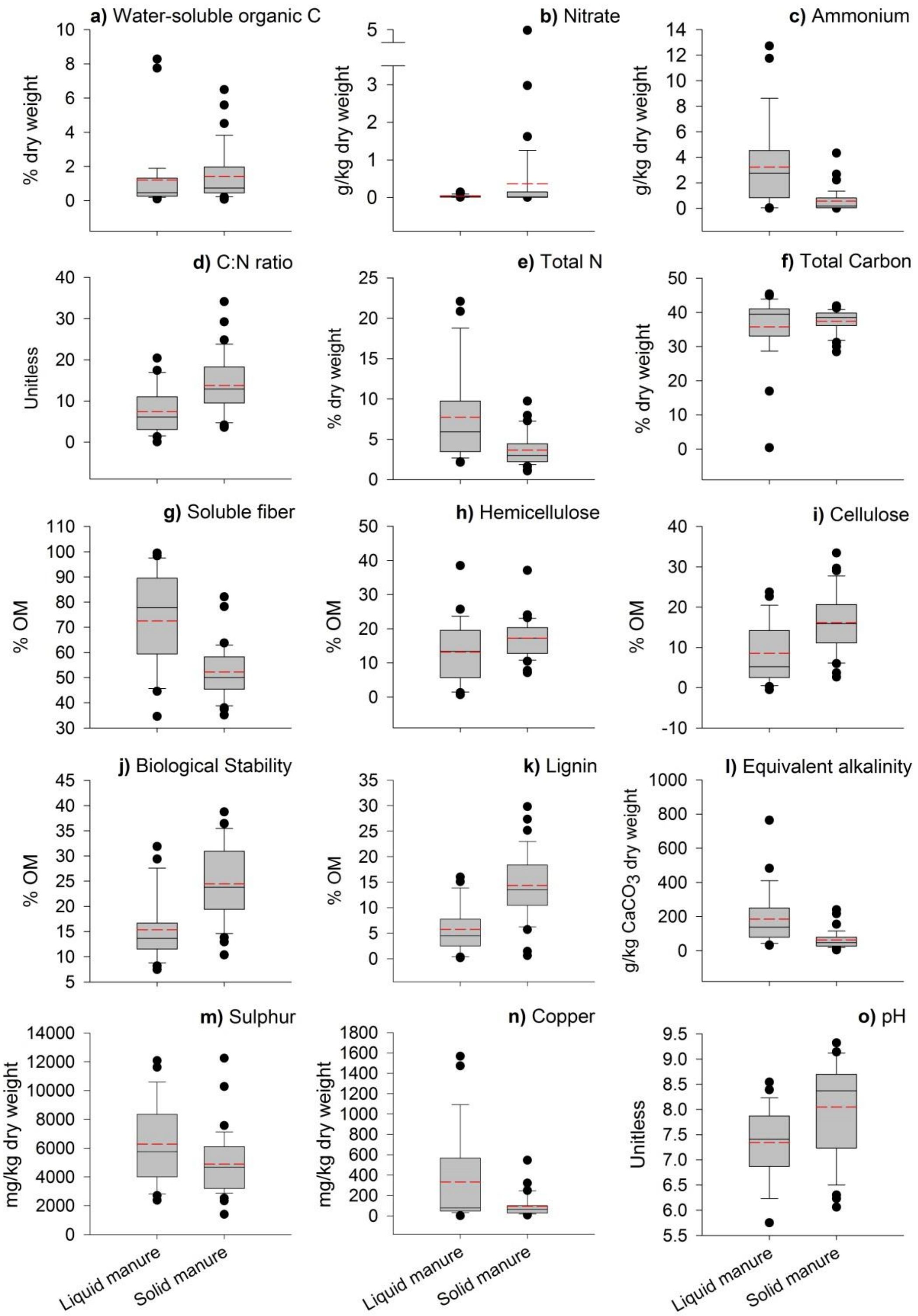

Figure A4-4. Variations in chemical properties according to manure type (liquid vs. solid)
The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.

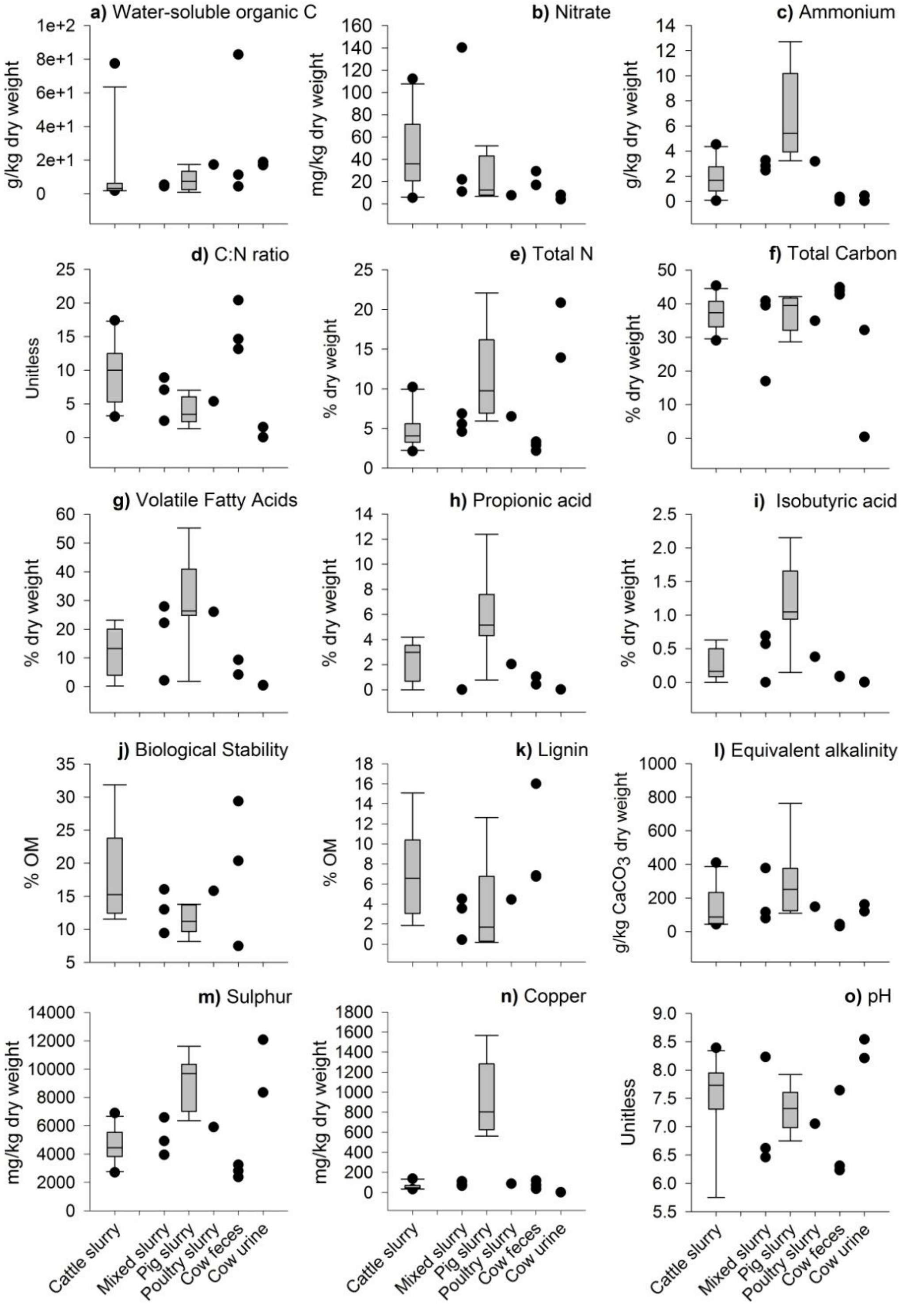

Figure A4-5. Variations in chemical properties according to liquid manure type

The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.

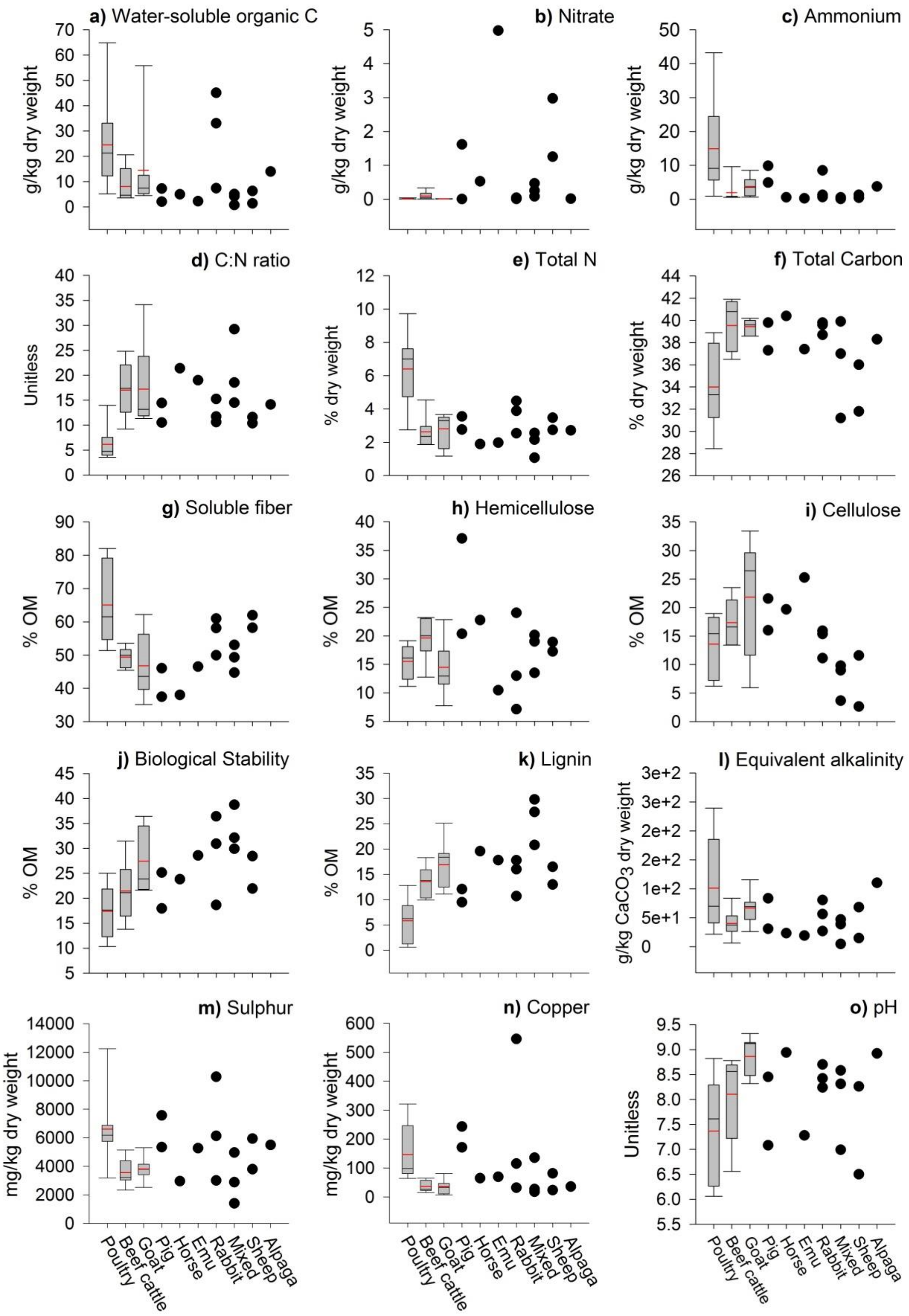

Figure A4-6. Variations in chemical properties according to manure nature (animal type)

The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.

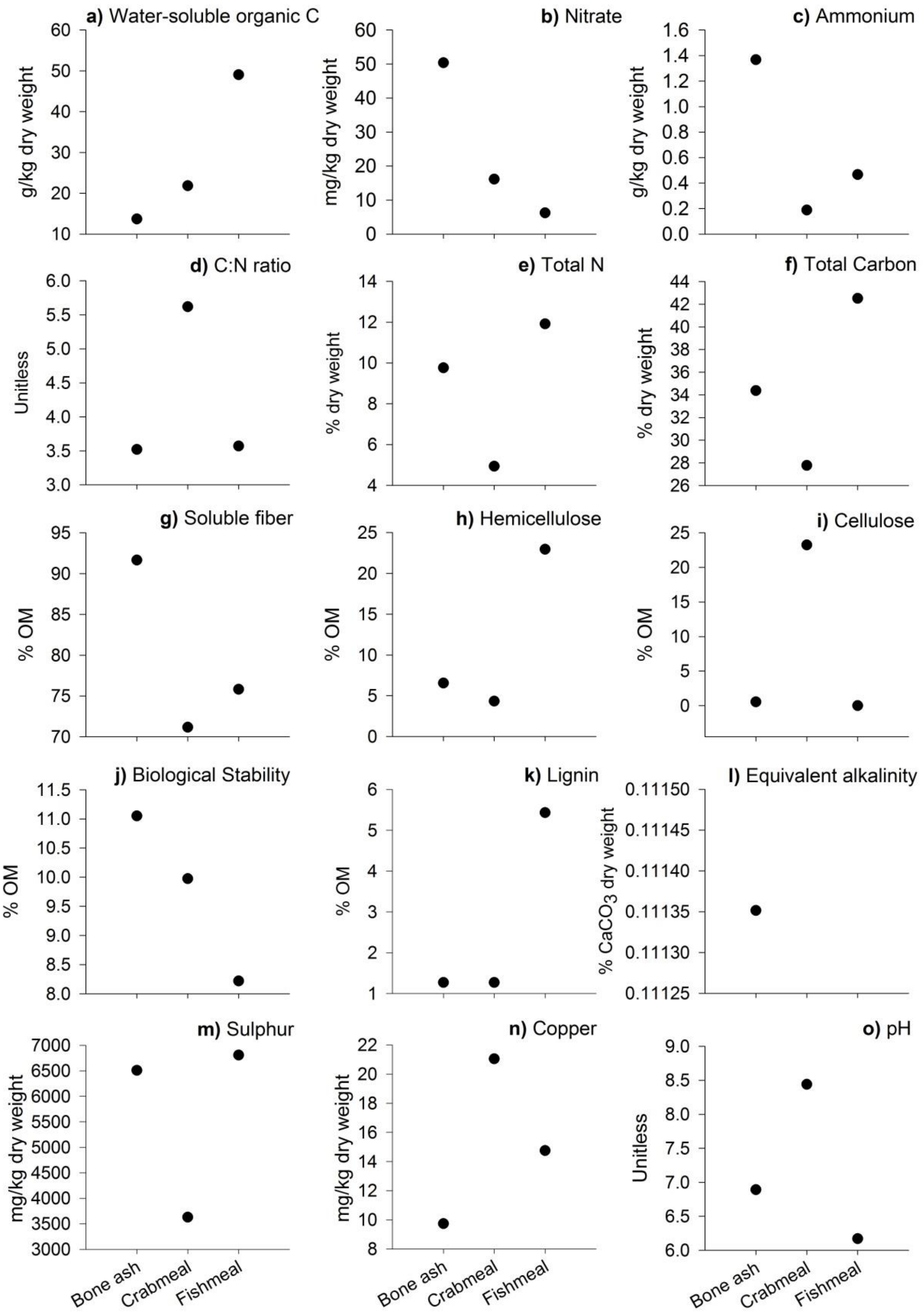

Figure A4-7. Variations in chemical properties according to the type of organic-based meal

The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.

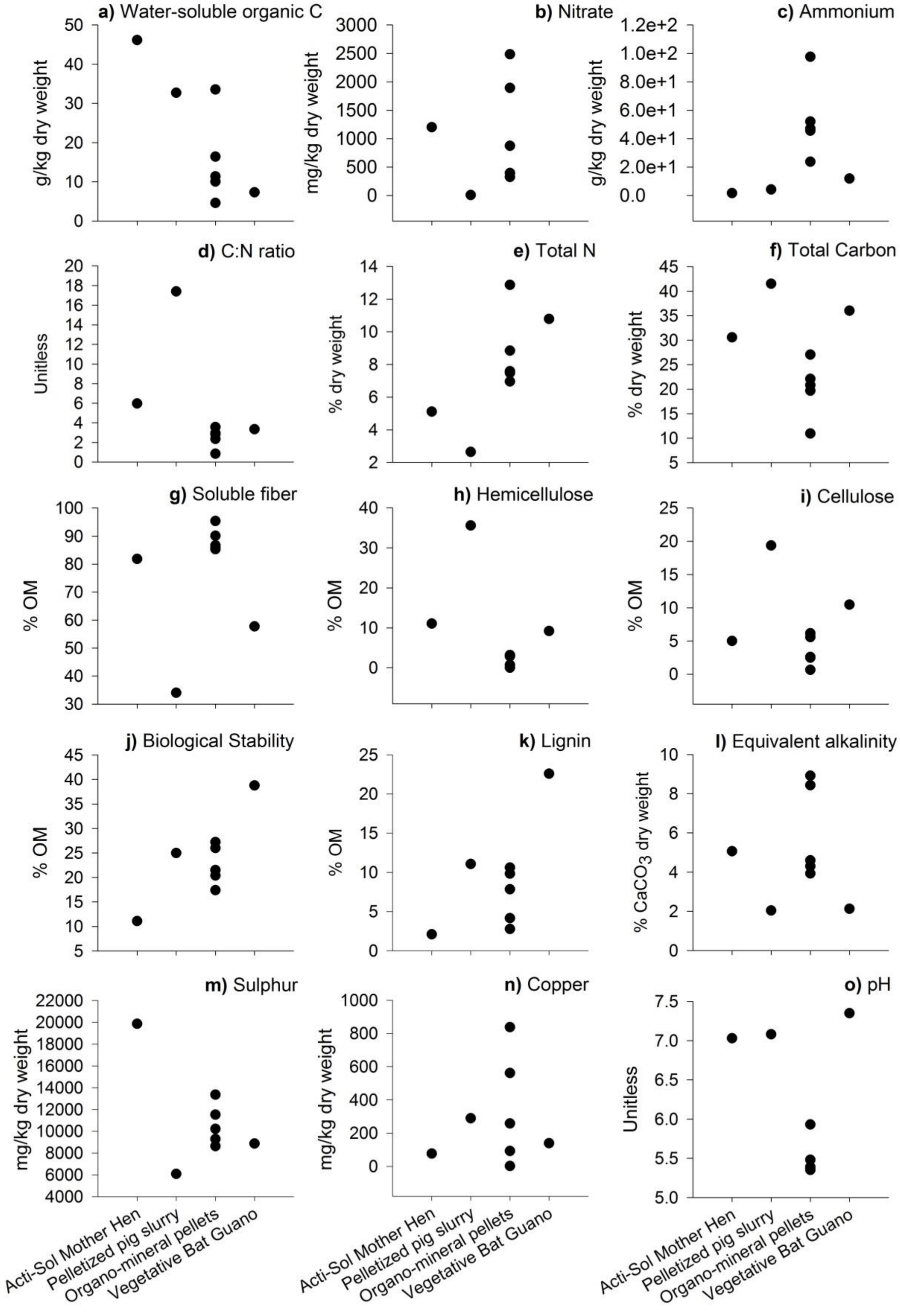

Figure A4-8. Variations in chemical properties according to pellet type.

The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.

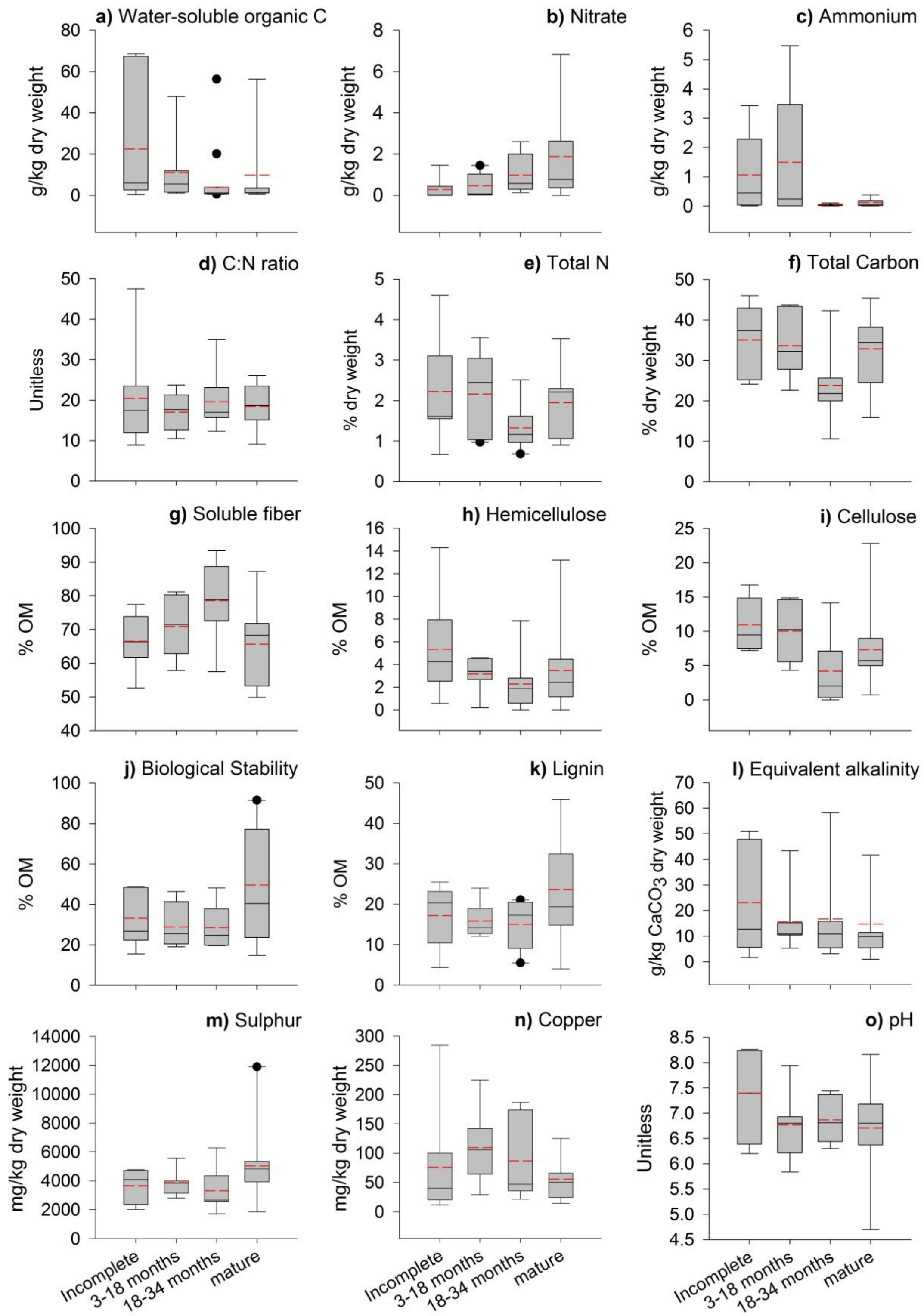

Figure A4-9. Variations in chemical properties according to compost age.

The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.

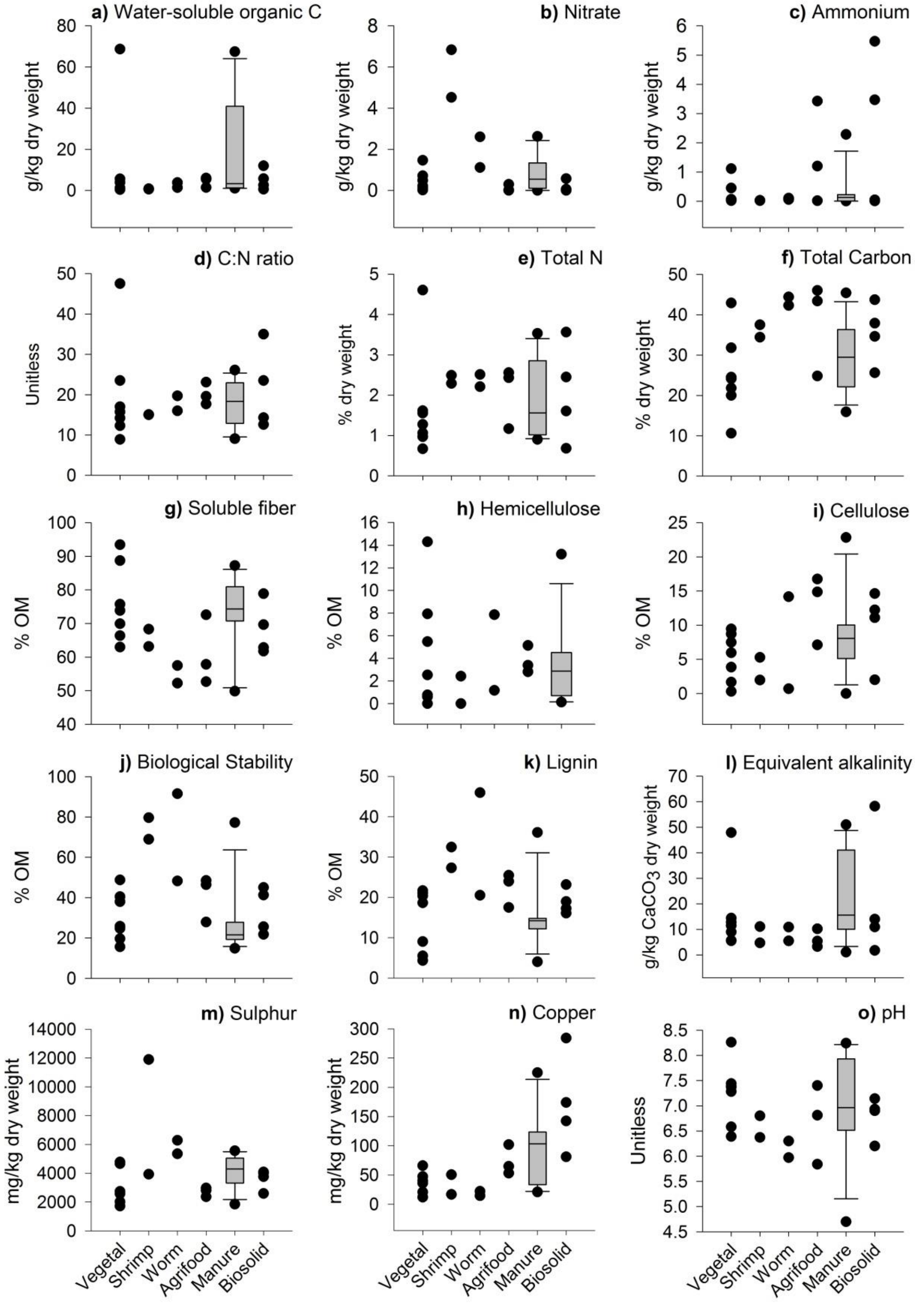

Figure A4-10. Variations in chemical properties according to compost type.

The boundary of the box closest to zero (Y axis) indicates the 25th percentile and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. The solid line within the box marks the median and the dashed red line marks the mean. Outlying points are represented for each organic amendment type.