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Estimating Greenhouse Gas Emissions from Land-Applied Biosolids in Canada: A Mathematical Modelling Approach

By

Okenna Obi-Njoku

Supervisors

Dr. O. Grant Clark (McGill University)

Dr. Gordon Price (Dalhousie University)

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Abstract

Municipal wastewater biosolids are increasingly used to fertilize crops on Canadian farmland with the attendant effect of greenhouse gas (GHG) emissions. As part of their national inventories to the United Nations Framework Convention on Climate Change, countries are required to estimate GHG emissions from the land application of biosolids and report them using Intergovernmental Panel on Climate Change (IPCC) protocols. However, Canada currently does not have N_2O emission factors to accurately model emissions from biosolids because of scarce empirical data. This study therefore measured emissions, generated emissions factors, and refined models of biosolids-induced GHG emissions to improve Canada's national GHG inventory. To do this, laboratory and field experiments were used to assess three types of biosolids (i.e., composted, mesophilic anaerobically digested called "digested", and alkaline-stabilized).

In an incubation experiment, soil samples were amended with the three biosolids to assess the rate of C and N mineralization under 29% and 49% water-filled pore space (WFPS) soil moisture conditions. Under 49% WFPS, 79%, 52%, and 8% of C was mineralized in the digested, alkaline-stabilized, and composted biosolids, respectively. A first-order mathematical equation was fitted to the cumulative CO_2-C and N_2O-N emissions data, with $R^2 > 0.98$ and $p < 0.05$. This study also highlighted the potential of composted biosolids to sequester carbon in soil and mitigate soil N_2O emissions. The results of this experiment helped to calibrate the DeNitrification and DeComposition (DNDC) model to simulate C and N dynamics in a biosolids-fertilized corn (*Zea mays* L.) field in Quebec from 2017 to 2019. Pearson's correlation coefficients between measured and simulated data ranged between 0.3 and 0.8 for crop yield, daily and cumulative CO_2 and N_2O emissions, and soil organic carbon, while being 0.1 for total soil N. In addition to the Quebec (mixed wood plains) site, DNDC was then used to simulate N_2O emissions from two other sites in

Nova Scotia (Atlantic maritime) and Alberta (prairie). Overall, N_2O emissions were highest for digested biosolids and overall emissions were influenced by site-specific factors, with emissions magnitudes following the order: Quebec > Nova Scotia > Alberta. The DNDC simulations were contrasted with IPCC Tier 1 and Tier 2 methods, and root mean-square error and coefficient of determination values between measured and simulated values showed that the DNDC (Tier 3) approach was more accurate than the Tier 1 and 2 methods. Empirically derived correction factors for each of the biosolids were proposed to improve the accuracy of Tier 2 method, which fits the proposed update to the Canadian GHG inventory methodology.

This study resulted in improved estimates of biosolids-induced N_2O emissions from Canadian farmlands, with the option to use an improved Tier 2 method to report such emissions in the national GHG inventory until the Tier 3 method is implemented.

Resumé

Les biosolides des eaux usées municipales sont de plus en plus utilisés pour fertiliser les cultures sur les terres agricoles canadiennes avec l'effet concomitant des émissions de gaz à effet de serre (GES). Dans le cadre de leurs inventaires nationaux de la Convention-cadre des Nations Unies sur les changements climatiques, les pays sont tenus d'estimer les émissions de GES provenant de l'épandage de biosolides et de les déclarer en utilisant les protocoles du Groupe d'experts intergouvernemental sur l'évolution du climat (GIEC). Cependant, le Canada ne dispose pas actuellement de facteurs d'émissions de N_2O pour modéliser avec précision les émissions des biosolides en raison de la rareté des données empiriques. Cette étude a donc mesuré les émissions, généré des facteurs d'émissions et affiné les modèles d'émissions de GES induites par les biosolides afin d'améliorer l'inventaire national des GES du Canada. Pour faire cela, des expériences en laboratoire et sur le terrain ont été utilisées pour évaluer trois types de biosolides (composté, mésophile digéré en anaérobie dit “digéré”, et stabilisé aux alcalins).

Dans une expérience d'incubation, des échantillons de sol ont été modifiés avec les trois biosolides pour évaluer le taux de minéralisation du C et du N dans des conditions d'humidité du sol à espace interstitiel rempli d'eau à 29 % et à 49 %. Sous 49 % de WFPS, 79 %, 52 % et 8 % du C a été minéralisé dans les biosolides digérés, stabilisés alcalins et compostés, respectivement. Une équation mathématique de premier ordre a été ajustée aux données d'émissions cumulées de CO_2-C et N_2O-N, avec $R^2 > 0,98$ et $p < 0,05$. Cette étude a également mis en évidence le potentiel des biosolides compostés à séquestrer le carbone dans le sol et à atténuer les émissions de N_2O du sol. Les résultats de cette expérience ont permis de calibrer le modèle de DéNitrification et Décomposition (DNDC) pour simuler la dynamique du C et du N dans un champ de maïs (*Zea mays* L.) fertilisé aux biosolides au Québec de 2017 à 2019. Les coefficients de corrélation de

Pearson entre les données mesurées et simulées variaient entre 0,3 et 0,8 pour le rendement des cultures, les émissions quotidiennes et cumulatives de CO_2 et de N_2O et le carbone organique du sol, tout en étant de 0,1 pour le N total du sol. En plus du site du Québec (plaines à forêts mixtes), la DNDC a ensuite été utilisée pour simuler les émissions de N_2O de deux autres sites en Nouvelle-Écosse (Atlantique maritime) et en Alberta (prairie). Dans l'ensemble, les émissions de N2O étaient les plus élevées pour les biosolides digérés et les émissions globales étaient influencées par des facteurs propres au site, les magnitudes des émissions suivant l’ordre : Québec > Nouvelle-Écosse > Alberta. Les simulations DNDC ont été comparées aux méthodes de niveau 1 et 2 du GIEC, et l'erreur quadratique moyenne et les valeurs de coefficient de détermination entre les valeurs mesurées et simulées ont montré que l'approche DNDC (niveau 3) était plus précise que les méthodes de niveau 1 et 2. Des facteurs de correction empiriquement dérivés pour chacun des biosolides ont été proposés afin d'améliorer l'exactitude de la méthode de niveau 2, qui correspond à la mise à jour proposée de la méthodologie canadienne d'inventaire des GES.

Cette étude a permis d'améliorer les estimations des émissions de N_2O induites par les biosolides des terres agricoles canadiennes, avec la possibilité d'utiliser une méthode de niveau 2 améliorée pour déclarer ces émissions dans l'inventaire national des GES jusqu'à ce que la méthode de niveau 3 soit mise en œuvre.

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Original Contributions to Knowledge

This thesis addresses knowledge gaps related to our understanding of the contribution of agricultural use of municipal biosolids to greenhouse gas (GHG) emissions. The main contributions to knowledge from this work include the following:

1. IPCC Tier 2 correction factors were developed, as required by ECCC to report nationwide emissions of N_2O from land-application of biosolids from 1990 to date.
2. A suite of empirical data on GHG emissions from land-application of municipal biosolids have been generated across Canada. Prior to this study, no such comprehensive data was available to policymakers and scientists to understand such emissions.
3. For the first time, a process-based model, in this case DNDC, has been calibrated and validated for simulating C and N dynamics in biosolids-amended agroecosystems across three different Canadian ecozones (mixedwood plains, Atlantic maritime, and the prairies). As such, DNDC.vCAN can now be used under different management and climate scenarios by Agriculture and Agri-Food Canada (AAFC) and Environment and Climate Change Canada (ECCC) and researchers to estimate and report biosolids-related soil GHG emissions, predict crop yields, and investigate the different N pathways in such agroecosystems.
4. Beyond generating GHG emissions datasets, this study also differentiates the N_2O mitigation potential of land-applied composted biosolids relative to the mesophilic anaerobically digested and alkaline-stabilized biosolids given its lower emission factor across the three field experiments (Quebec, mixedwood plains; Nova Scotia, Atlantic maritime; and Alberta, prairies) and slower rate of degradation in the laboratory experiment.

These contributions benefit the international community of modellers, policy makers, farmers, and scientists who require these tools for simulation. The work has also increased our understanding of C and N dynamics under different biosolids management, agroecosystems, and climatic scenarios.

Contributions of Authors

This manuscript-based thesis describes empirical experiments and computational modelling drawing from multiple disciplines such as mathematics and soil and plant sciences. The research was funded under the second phase of the Agricultural Greenhouse Gas Program (Project AGGP2-033) by the Ministry of Agriculture and Agri-Food Canada. Empirical data used in this experiment were generated by a team of research collaborators working at three research sites at McGill University, Montreal (Quebec), Dalhousie University, Truro (Nova Scotia) and the University of Alberta, Edmonton (Alberta). The empirical experiments were designed by the principal investigators who were Professors Grant Clark, Joann Whalen, David Burton, Gordon Price, and Guillermo Hernandez Ramirez, and Dr. Michael Boh who doubled as project manager and supervised research activities at the Montreal site. As a Ph.D. candidate, I participated in setting up and managing the field experiments at the Montreal site. In Truro, Zheya Lin and Gurwinder Singh managed the research fields, collected data on GHG emissions under the supervision of Prof. Gordon Price and Prof. David Burton. In Edmonton, Carmen Roman-Perez managed the fields under the supervision of Prof. Guillermo Hernandez Ramirez. Researchers from all three sites were involved in initial cleaning, interpretation and evaluation of the datasets that were used for the modelling exercise described in this work. Their contributions have been duly acknowledged in the manuscripts contained in this thesis, as described below.

I drafted the initial version of all the three manuscripts with the guidance of Dr. Boh and supervision provided Prof. Clark and Prof. Price. All three researchers participated in developing the study objectives and the broad research questions, analysis of results, writing and reviewing various drafts of the manuscripts. Andrea Gonzalez Pavia contributed to the design, management, data collection, and interpretation of the incubation experiment and co-authored chapter 3. As a co-author of chapter 4, Dr. Naseer Hussain led the collection and laboratory analyses of GHG emissions data at the Montreal site under the supervision of Prof. Whalen. He assisted in data interpretation and reviewed various drafts of the manuscript. Dr. Ward Smith and Brian Grant were co-authors of chapters 4 and 5. They shared scientific principles and expert views on model parameterization and evaluation, assisted in adapting DNDC to model biosolids-related carbon and nitrogen dynamics, and assisted in drafting the manuscript. Corey Flemming, who was a co-author on Chapter 5, shared his experience on methodological approaches for accounting and reporting GHG emissions in the national inventory and assisted in drafting the manuscript. Carmen Roman-Perez and Gurwinder Singh were students while Professors Guillermo Hernandez-Ramirez and David Burton were principal investigators, who were co-authors on chapter 5, shared datasets from the University of Alberta and Dalhousie University, respectively, and provided insights on the interpretation of results and feedback on drafts of the paper.

Manuscripts and Presentations Related to this Thesis

Scientific Manuscripts included in this Thesis

Chapter 3. Okenna Obi-Njoku, Gordon W. Price, Michael Yongha Boh, Andrea Gonzalez Pavia, O. Grant Clark (***under review***). Carbon and nitrogen mineralization kinetics of three different types of biosolids applied to an agricultural soil. Submitted for review to the Soil Science Society of America Journal.

Chapter 4. Okenna Obi-Njoku, Ward Smith, Brian Grant, Michael Yongha Boh, G.W. Price, Naseer Hussain, Joann Whalen, O. Grant Clark (***under review***). Greenhouse gas emissions following biosolids application to farmland: Estimates from the DeNitrification and DeComposition model. Submitted for review to the Journal of Agriculture, Ecosystems and Environment.

Chapter 5. Okenna Obi-Njoku, Ward Smith, Brian Grant, Michael Yongha Boh, Corey Flemming, Carmen Roman-Perez, Gurwinder Singh, Guillermo Hernandez-Ramirez, David Burton, G.W. Price, O. Grant Clark (***in preparation***). Comparing IPCC Tier 1, 2, and 3 methodologies for estimating nitrous oxide emissions from biosolids-amended soils in three different climatic ecozones. In preparation for submission to the Journal of Agriculture, Ecosystems and Environment.

Related Scientific Manuscript

The study below was conducted during my Research Affiliate Program (RAP) at Environment and Climate Change Canada.

Okenna Obi-Njoku, Arumugam Thiagarajan, Corey Flemming, Douglas MacDonald, O. Grant Clark (***in preparation***). Developing a time series of biosolids production and land application in Canada from 1990 to 2018. In preparation for submission to the Canadian Journal of Soil Science.

Conference and Workshop Presentations

Obi-Njoku, **O.**, Smith, W., Grant, B., Boh, M. Y., Price, G.W., Clark, O. G. 2017. Modelling crop yield, nitrogen uptake, and greenhouse gas emissions from land applied biosolids in Canada. Presentation at the Agricultural Greenhouse Gas Program (AGGP) Workshop, University of Alberta, Edmonton, Alberta, Canada, November 14-16, 2017.

Obi-Njoku, **O.**, Smith, W., Grant, B., Boh, M. Y., Price, G.W., Clark, O. G. 2018. Calibrating the Denitrification and Decomposition (DNDC) model to estimate crop yield and greenhouse gas emissions from land applied biosolids in Canada. Presentation at the CSBE/SCGAB 2018 Annual Conference, University of Guelph, Guelph, Ontario, Canada, July 22-25, 2018.

Obi-Njoku, **O.**, Smith, W., Grant, B., Boh, M. Y., Price, G.W., Clark, O. G. 2018. A process-based modelling approach to evaluate soils amended with biosolids. Presentation at the Symposium on "Land-Applied Biosolids: Greenhouse Gas Emissions and Crop Yields", McGill University, Macdonald Campus, Ste. Anne de Bellevue, Quebec, Canada, August 9, 2018.

Obi-Njoku, **O.**, Smith, W., Grant, B., Boh, M. Y., Price, G.W., Clark, O. G. 2018. Calibrating the DeNitrification and DeComposition (DNDC) model to estimate crop yield and greenhouse gas emissions from land applied biosolids in Canada. Presentation at the Canadian Biosolids and Residuals Conference (CBRC) 2018, World Trade and Convention Centre, Halifax, Nova Scotia, Canada, 9-12 September 2018.

Obi-Njoku, **O.**, Smith, W., Grant, B., Boh, M. Y., Price, G.W., Clark, O. G. 2019. Modelling greenhouse gas emissions, nitrogen uptake and crop yield from biosolids-fertilized soils using the DeNitrification and DeComposition (DNDC) model. Presentation at the ASABE Conference, Boston, Massachusetts, USA, July 7-10, 2019.

Obi-Njoku, **O.**, Gonzalez Pavia, A., B., Boh, M. Y., Price, G.W., Clark, O. G. 2020. Mineralization of carbon in soils amended with composted, alkaline-stabilized, and mesophilic anaerobically digested biosolids. Presentation at the 2020 Canadian Society of Bioengineering (CSBE) Webinar, September 25, 2020.

Obi-Njoku, **O.**, Smith, W., Grant, B., Boh, M. Y., Price, G.W., Clark, O. G. 2021. Estimating nitrous oxide emissions from land application of biosolids across Canada. Presentation at the 2021 Canadian Society of Bioengineering (CSBE)/CIGR Webinar, May 11-14, 2021.

Obi-Njoku, **O.**, Smith, W., Grant, B., Flemming, C., Boh, M. Y., Roman-Perez, C., Singh, G., Hernandez-Ramirez, G., Burton, D., Price, G.W., Clark, O. G. 2021. Estimating nitrous oxide emissions from land application of biosolids across Canada. 2021. Presentation at the Symposium on "Land-Applied Biosolids: Greenhouse Gas Emissions and Crop Yields", McGill University, Macdonald Campus, Ste. Anne de Bellevue, Quebec, Canada, May 21, 2021.

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Nomenclature

Commonly used abbreviations, acronyms, and symbols are listed below. Other symbol definitions appear with equations in the text.

Acronym		Full meaning
AAFC	-	Agriculture and Agri-Food Canada
APSIM	-	Agricultural Production Systems sIMulator
BEAM	-	Biosolids Emissions Assessment Model
CAST	-	Council for Agricultural Science and Technology
CCME	-	Canadian Council of Ministers of the Environment
CWWA	-	Canadian Water and Wastewater Association
CEC	-	Cation Exchange Capacity
CERES-EGC	-	Crop Environment REsource Synthesis - Environnement et Grandes Cultures
CMC	-	Complementary Mineralization Coefficient
CO_2e	-	Carbon Dioxide Equivalent
COP	-	Conference of the Parties to the United Nations Framework Convention on Climate Change (UNFCCC)
DNDC	-	Denitrification and Decomposition Model
DOC	-	Dissolved Organic Carbon
DS	-	Dissolved Solid
EC	-	Electrical Conductivity
ECCC	-	Environment and Climate Change Canada
EF	-	Emission Factor

EPA - Environmental Protection Agency

EPIC - Environmental Policy Integrated Climate

GHG - Greenhouse Gas

GWP - Global Warming Potential

IPCC - Intergovernmental Panel on Climate Change

MSF - Most Significant Factor

NIR - National Inventory Report

NMC - Net Mineralization Coefficient

OM - Organic Matter

PBM - Process-Based Model

RZWQM2 - Root Zone Water Quality Model

SOC - Soil Organic Carbon

SOM - Soil Organic Matter

SON - Soil Organic Nitrogen

TC - Total Carbon

TN - Total Nitrogen

UNFCCC - United Nations Framework Convention on Climate Change

USEPA - United States Environmental Protection Agency

WFPS - Water-Filled Pore Space

WMO - World Meteorological Organization

WNMM - Water and Nitrogen Management Model

Chapter 1. General Introduction

1.1. Background of the Research

Agriculture, through soil-plant-animal processes associated with intensive farming, is directly linked to the global increase in atmospheric concentrations of three principal greenhouse gases (GHG): carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) (IPCC, 2000). Intensive agricultural systems arose from the need to meet the increasing global demand for food, feed, and fuel triggered by the industrial revolution of the 18th Century (CAST, 2004; IPCC, 2014). Since then, atmospheric concentrations of GHGs have increased, and with this increase come the attendant effects of global warming and climate change (IPCC, 2014). For instance, atmospheric CO_2 concentration increased from a pre-industrial level of 280 ppm to more than 410 ppm at the time of writing, with at an annual rate of 0.5–0.7 ppm (IPCC, 2014; Lindsey, 2019). Even more concerning are the increases in atmospheric N_2O and CH_4 concentrations, which have ~300 and ~25 times the global warming potential (GWP) of CO_2, respectively (CAST, 2004). The atmospheric concentration of N_2O in 2020 stood at ~331 ppb with a 0.2–0.3% annual increase, while CH_4 was at 1,869 ppb with an annual increase of 0.2–0.3% annually (World Meteorological Organization, 2020). To monitor these GHG emissions, Annex 1 Parties (industrialized countries such as Canada, USA, and France) to the United Nations Framework Convention on Climate Change (UNFCCC) are mandated to submit annual national inventories of sources and sinks of GHGs.

Agricultural GHG emissions occur either directly on-farm or indirectly off-farm (Figure 1.1), and in 2015 contributed approximately 5 Pg CO_2e(~11%) of total global GHG emissions (Tian et al., 2020). Agriculture contributed around 52% of the 17 Tg CO_2e of total global N_2O emissions in 2015 (Tian et al., 2020). These agricultural GHG emissions result mainly from enteric fermentation by ruminants, soil management, manure management and storage, energy generation, and transport (Smith et al., 2008; ECCC, 2017). One of the major sources of agricultural GHG emissions is the industrial production and agricultural use of commercial fertilizers such as urea in intensive crop production systems (Chai et al., 2019). To mitigate these emissions, agricultural best management practices are being promoted in industrialized (Annex 1) countries, like Canada, including recycling plant nutrient sources (e.g. livestock manure and biosolids), increasing efficiency of plant nutrient use, and conservation tillage (Desjardins et al., 2001; Dace, et al, 2015).

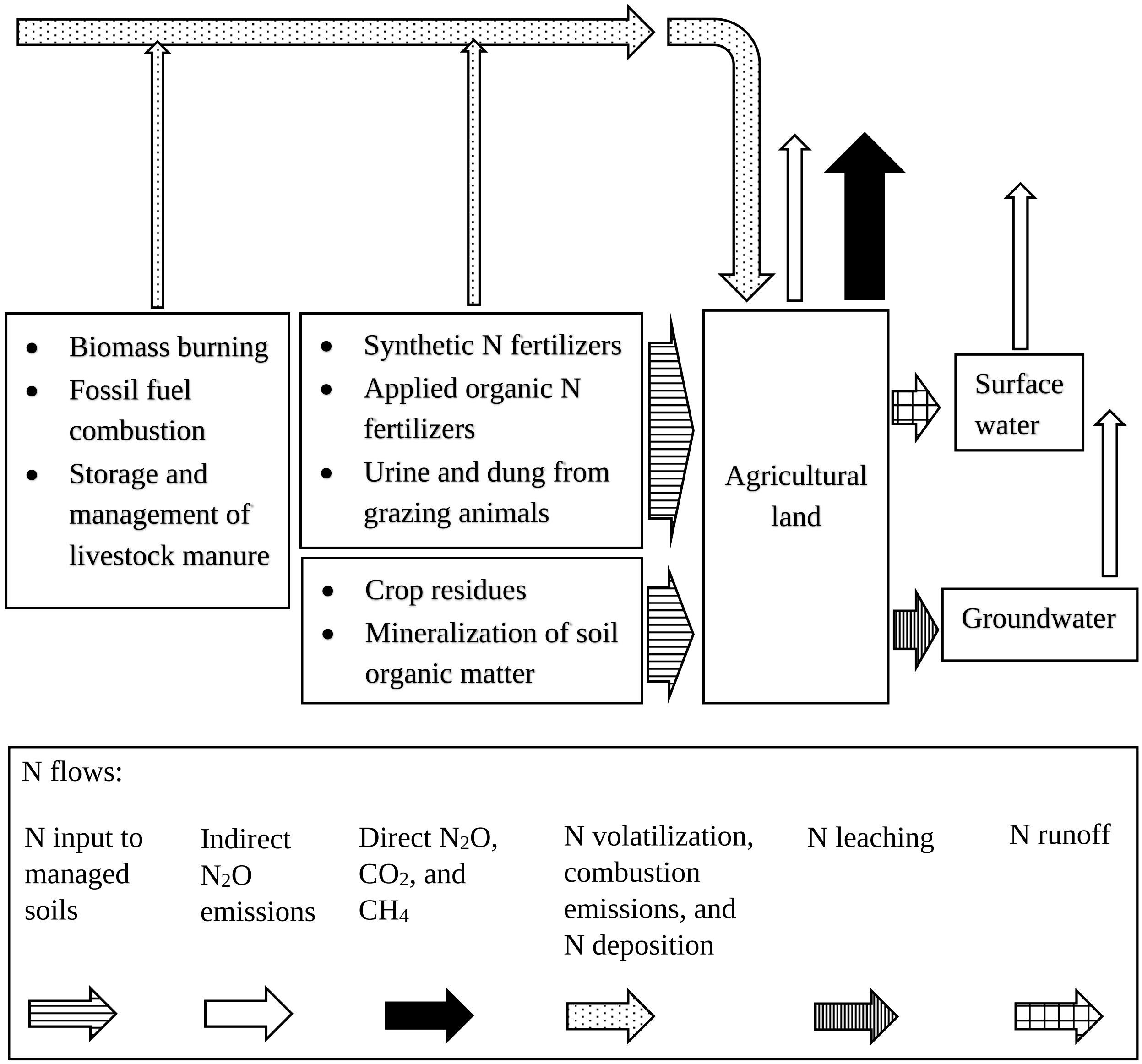

Figure 1.1. Schematic diagram illustrating the sources and pathways of N that result in direct and indirect N_2O emissions from on-farm agricultural activities. Adapted from IPCC (2006)

GHG emissions from soils contribute significantly to Canada's agricultural GHG budget, partly due to intensive use of N fertilizers (Lokupitiya & Paustian, 2006). In 2015, ~40% of Canada's 60 Tg CO_2e agricultural emissions were from soils (ECCC, 2017). Canadian soils receive

N through application of synthetic N fertilizers (e.g. urea) and organic amendments (e.g. livestock manure, urine, crop residues, and municipal biosolids) (Desjardins et al., 2001; CCWA, 2007; ECCC, 2017). Organic amendments, in particular, improve soil C sequestration and provide slow-release plant-required N in the form of nitrate (NO_3^-) and ammonium (NH_4^+) (Rowell et al., 2001). The excess NO_3^- and NH_4^+ remaining after plant uptake, together with soil C, provide feedstock for microbe-mediated redox reactions that produce N_2O, CO_2, and CH_4 emissions (Bouwman, 1996; Rigby et al., 2016).

Soil biochemical reactions are influenced by climatic and soil conditions (Tian et al., 2016). Research has shown that soil GHG production pathways are determined by soil aeration status, which is in turn influenced by rainfall- and/or irrigation-induced soil moisture and by tillage (Bateman & Baggs, 2005; Trumbore, 2006). This explains the relatively lower N_2O emissions in the semi-arid prairies of western Canada than in the more humid eastern Canada, and also between conventional tillage, reduced tillage, and no-till practices (Rochette et al., 2008). Under aerobic soil conditions, CO_2 and N_2O emissions occur as a result of soil organic carbon (SOC) decomposition and NH_4^+ nitrification, respectively (Trumbore, 2006; Kim et al., 2010; Norton & Stark, 2011). Under short-term anaerobic soil conditions, oxygen depletion occurs due to consumption by soil organisms (e.g. decomposers) when there is minimal diffusion of oxygen into the soil (Smith et al., 2008). This oxygen depletion stimulates denitrifying bacteria to use NO_3^- as an oxidizer; thus, NO_3^- becomes sequentially reduced to nitrite (NO_2^-), nitric oxide (NO), N_2O, and dinitrogen (N_2) (Bouwman, 1996; Lokupitiya & Paustian, 2006). The escape of N_2O into the atmosphere during these biochemical processes leads to net N_2O emission from the soil. If anaerobic conditions persist for several days, activities of methanogens dominate, resulting in CH_4 production and emission (Smith et al., 2008).

Biosolids are nutrient-rich by-products of wastewater treatment used by Canadian farmers to improve soil structure, pH, water-holding capacity, air, and water transport, and provide macronutrients (C, H, O, N, P, K, Ca, Mg, S) and micronutrients (B, Cu, Fe, Mn, Zn, Mo, Cl, Co, Ni) for plant growth and development (CCME, 2012; Fan et al., 2019). In Canada, biosolids are generally produced from sewage sludge by thermal treatment, aerobic or anaerobic digestion, co-composting with carbonaceous bulking agents, or the addition of alkaline-stabilized admixtures (Cheminfo Services Inc., 2018). These treatment processes stabilize the organic matter content, reduce the pathogen load, and make biosolids easy to handle as a plant fertilizer and soil amendment (EPA, 2000; CCME, 2012). The selection of a biosolids processing method often depends on the intended beneficial use, for example as a liming agent, to build SOM, improve soil quality, or as a source of plant nutrients (CCME, 2012). The biochemical composition and physical attributes of biosolids and their decomposition rates vary according to their processing (Peters & Lundie, 2002). For instance, O_2 availability in soil microsites could be modulated by relatively wet biosolids because their addition saturates soil micropores and provides labile C in the short term (Peters & Lundie, 2002). Such differences in the physico-chemical characteristics of biosolids due to differences in the selected processing techniques will likely result in varying rates of GHG emissions.

The production and land-application of biosolids have been increasing in most Canadian provinces, yet GHG emissions resulting from their use remain unreported in Canada’s National Inventory Reports to the UNFCCC (ECCC, 2018; Cheminfo Services Inc., 2018). Canada’s biosolids production is driven by population growth, improved wastewater treatment technology, and more stringent government regulations sanctioning the disposal of untreated sewage sludge (CCME, 2010; Cheminfo Services Inc., 2018). Sludge production from municipal wastewater treatment plants increased by 60%, from 500 to 780 dry Tg between 1990 and 2015 with 57% of the treated sludge being land applied as biosolids (Cheminfo Services Inc., 2018). Quantities of land-applied biosolids are expected to increase further in the coming years as provincial legislation is encouraging diversion of biosolids and other organics from landfills to soils (McCarthy, 2016). However, there is a scarcity of spatially explicit empirical data on GHG emissions from agricultural land application of biosolids across Canada relative to other organic materials (e.g., manure). Considering that methods for processing digested, alkaline-stabilized, and composted biosolids differ, and that the climatic conditions and biosolids application methods vary across Canada, we can hypothesize that: (1) the resulting N_2O emissions during the growing season would be highest for digested biosolids due to its relatively lower C/N than those of other biosolids, (2) the magnitude of N_2O emissions will be higher in sites with higher precipitation during the growing season, and (3) higher N_2O emissions will be recorded when biosolids are surface spread than when incorporated into soil. These hypotheses are supported by the observed effects of environmental variables and physico-chemical composition on GHG emissions from soils amended with different types of organic materials (Griffis et al., 2017). Meanwhile, the existing tool for estimating GHG emissions from biosolids management in Canada, the Biosolids Emissions Assessment Model (BEAM), does not account for relationships between biotic and abiotic factors that drive biosolids-induced GHG emissions (Sylvis, 2009). Therefore, an in-depth understanding of the interactions between soil, climate, crop, and applied biosolids in different Canadian ecological zones is critical for improving methods for estimating the GHG fluxes associated with land-application of biosolids.

The Intergovernmental Panel on Climate Change (IPCC) developed protocols and guidelines for accounting and reporting national GHG fluxes to the UNFCCC (IPCC, 2006). The protocols are categorized into three tiers based on increasing levels of accuracy from Tier 1 to 3 (Grewer et al., 2016). This accounting system can be used to estimate GHG fluxes by multiplying an emission factor, which represents a fraction of the applied fertilizer N lost as N_2O, by the activity data, which is the anthropogenic activity during a given period. Tier 1 methods for estimating national and subnational N_2O emissions use aggregated, internationally derived emission factors; Tier 2 uses regional or country-specific emission factors to estimate disaggregated GHG emissions; and Tier 3 methods make use of high-resolution site-specific data and/or process-based models. In the 2001 UNFCCC inventory year, about 56%, 26%, and 0% of the Annex 1 countries used IPCC Tier 1, Tier 2, and Tier 3 methods, respectively, and 18% did not estimate or report N_2O emissions. In addition, more than 65% of the countries failed to report CO_2 emissions from the cultivation of mineral soils, organic soils, or liming and removals (e.g., sequestration in soil and woody biomass) (Lokupitiya and Paustian, 2006). The failure to include this information in the reports has been associated with a lack of detailed, spatially-explicit data, and disaggregated emission factors (Paustian et al., 2006). During the last decade, some Annex 1 countries such as New Zealand, UK, and USA have made efforts to use Tier 2 and Tier 3 methodologies for GHG accounting (Olander et al., 2011; ECCC, 2018).

Process-based models such as the Denitrification and Decomposition (DNDC) model (Li et al., 1992) and DayCent (Parton et al., 1994) are useful tools for implementing Tier 3 methods and have been used to estimate spatially disaggregated GHG fluxes for a variety of agroecosystems. These models consider the roles of climate, vegetation, soil, and crop management on C and N dynamics in agroecosystems. DNDC has been shown to reliably estimate GHG emissions under various land use systems (Brilli et al. 2017; Ehrhardt et al., 2018). However, its suitability under Canadian conditions and specifically for use in modelling municipal biosolids as a soil amendment has not been evaluated.

The variability in climate, soils, and agricultural practices across ecozones make it necessary to develop a Canada-specific methodology for estimating GHG from land-applied biosolids. This will fill the knowledge gap about the contribution of the agricultural use of biosolids to GHG emissions and improve the quality of data reported in Canada's annual GHG inventory. This is of importance to Agriculture and Agri-Food Canada (AAFC) and Environment and Climate Change Canada (ECCC), which are both committed to improving Canada's GHG accounting and to cutting anthropogenic GHG emissions to 30% below 2005 levels by 2030 (ECCC, 2020).

Currently, Canada's national GHG inventory includes soil emissions estimated per province on an ecodistrict scale of ca. 150,000 ha, using a regression-based Tier 2 approach that accounts for inorganic N, crop residue, and manure application (Rochette et al., 2008; ECCC, 2018). However, the data used for developing the Tier 2 equations did not include the agricultural use of municipal biosolids. In addition, datasets from Eastern Canada were based on empirical measurements from the provinces of Ontario and Quebec alone, which have similar climates and grow similar crops. Eastern Canada is humid and includes mixed wood plains (~12% of croplands) and Atlantic maritime ecozones (ECCC, 2018). Croplands in eastern and western Canada differ in terms of soil, climate, and vegetation. Western Canada includes areas of semi-arid prairies, sub-humid prairies, and boreal plains, which comprise 83% of croplands in Canada (ECCC, 2018). Compared to soils in eastern Canada, N_2O emissions in the Black and Brown soil regions of the Canadian Prairies are respectively ~4 and ~10 times lower for a given fertilizer rate (Rochette et al., 2008). This indicates lower denitrification activity in the semi-arid prairies of western Canada than in humid eastern Canada. Therefore, it is critical to develop an approach for deriving emission factors that takes into consideration variability in climate and soils after the agricultural application of biosolids.

1.2. Research Objectives

The general objective of this research was to generate GHG emission factors associated with agricultural land application of different types of municipal biosolids to improve the quality and completeness of Canada’s national GHG inventory reporting. The specific objectives were:

1. To assess the kinetics of C decomposition and N mineralization from loam soil amended with urea and/or biosolids and incubated under different soil moisture conditions.
2. To evaluate the capability of the DNDC model to simulate C and N dynamics in a typical Canadian agroecosystem amended with municipal biosolids. Calibrate and validate DNDC with daily and cumulative GHG emissions, crop yield, soil organic C, and total soil N from field experiments conducted over three growing seasons in Ste-Anne-de-Bellevue, Quebec.
3. To compare estimates of N_2O fluxes from agricultural soils amended with biosolids in Canada’s mixedwood plain, Atlantic maritime, and prairie ecozones using Tier 1, Tier 2 (Canadian), and Tier 3 (Denitrification and Decomposition model [DNDC]) methodologies. Then, recommend the most accurate and compatible methodology for the accounting of N_2O emissions from land-applied biosolids in the national GHG inventory.

Since the majority (>85%) of biosolids that are land-applied in provinces in Eastern and Western Canada are produced either using anaerobic digestion, co-composted with carbonaceous bulking agents, or treated with alkaline admixtures (Cheminfo Services Inc., 2017; 2018), this research was focused on these biosolids. This research also was conducted in sites that broadly represent agricultural conditions in humid and semi-arid agrizones in Canada, to establish a baseline upon which further studies can be conducted to improve biosolids-induced GHG accounting.

1.3. Thesis Structure

Chapter 1 of the thesis is a general introduction which provides background information about the research topic, describes the research problem under investigation, and identifies the pertinent research objectives which were pursued. Chapter 2 is a literature review describing the state of knowledge on biosolids composition, land-application and regulations, and emissions. In this chapter, the methodologies are reviewed for quantifying and scaling up GHG estimates for Canadian national inventories. It also describes how the DNDC model was applied as a tool for simulating GHG and for generating emission factors under different cropping systems. Chapters 3, 4, and 5 address objectives 1, 2, and 3 above, respectively. Each of these chapters is in the form of a research paper for publication in a peer-reviewed scientific journal. The thesis is formatted according to the requirements of Library and Archives Canada. References are located at the end of each chapter of the thesis.

Chapter 2. Literature Review

2.1. Introduction

This literature review is aimed at describing the state-of-the-knowledge, regarding GHG emissions resulting from land-application of biosolids in Canada. This chapter begins with a review of the physico-chemical composition of commonly used biosolids in Canada and how, in conjunction with biotic and abiotic factors, their composition influences the kinetics of decomposition of land-applied biosolids. The methods for estimating GHG emissions following the decomposition of biosolids are reviewed in the context of reporting national GHG inventories, particularly in Canada. Also, the benefits and challenges associated with each method of estimating GHG emissions are briefly highlighted, including some details on the use of process-based models. Finally, the structure of process-based models, their uses, benefits, and limitations across different GHG estimation scenarios are discussed, mostly in the context of conducting sensitivity and uncertainty analysis, calibrating, and validating the models to minimize estimation errors.

2.2. Composition of Biosolids

Biosolids vary in their physico-chemical characteristics depending on the wastewater treatment process, age, and source of the biosolids (Arulrajah et al., 2011). In biosolids just like in other organic materials, C and N are bound in the form of water-soluble substances, polymer carbohydrates (e.g. pectin, hemicellulose, and holocellulose), lignin and other aromatic compounds, hydrophobic lipids, and proteins (e.g. hydroxyproline-rich glycoproteins) (Wang et al., 2007; Bisaria & Kondo, 2014). The process and extent of stabilization (physical, biological, and chemical) alters the morphology (e.g., shape, bulkiness, surface area) and quality (e.g. C to N ratio [C/N], and carbon, lignin, hot water-soluble materials, and nutrient contents), which have an impact on biosolids mineralization rates (Rubio-Loza & Noyola, 2010; Rigby et al., 2016; Case et al., 2016). Treatment methods such as alkaline-stabilized stabilization, composting, and anaerobic digestion all vary in terms of process duration, temperature, biochemical pathway, physical conditions, and type of additive used for co-composting, co-digestion, or alkalizing (EPA, 2000; Barbarick & Ippolito, 2009; Rubio-Loza & Noyola, 2010; Cheminfo Services Inc., 2018). For instance, during the production of commercial-grade alkaline-stabilized biosolids (N-Viro®, Walker Environmental, Goffs, NS), the addition of alkaline-stabilized admixtures to the biosolids increases the pH of the biosolids above 12, which may result in rapid ammonia (NH_3) loss (Christie et al., 2001). Also, the addition of carbon-based bulking agents during composting results in an overall increase in the carbon content of the final product (Ippolito et al., 2010; Dentel & Qi, 2013). As can be expected, N losses during composting and alkaline-stabilized stabilization account for the generally lower N concentrations in these biosolids compared to digested biosolids (Sullivan et al., 2015).

2.3. Kinetics of Carbon and Nitrogen Mineralization

An understanding of the kinetics of C and N mineralization of land-applied biosolids help farmers and regulatory authorities determine the amounts and timing of biosolids application during the growing season. Given the difference in composition between a variety of biosolids and manures, some researchers have suggested that the mineralization rate in soils fertilized with livestock manure is much higher than in soils fertilized with municipal biosolids (Barbarick & Ippolito, 2007; Cogger et al., 2011; Thangarajan, 2013; Sayem, 2014). The different manures (e.g., swine, poultry, and dairy) vary in their C/N ratios, total N concentrations, and moisture contents, hence cannot be compared directly with biosolids in general. Also, it is not clear how these findings are applicable in the Canadian context where variations in mineralization rates and availability of crop-required N can be expected due to differences in the prevailing climatic and soil conditions as reported by Mendoza et al. (2006) and Robinson & Polglase (2000). Mendoza et al. (2006) showed that N losses through leaching may occur if the rate of N release during degradation of biosolids exceeds the rate of crop N uptake. These losses could be further exacerbated by high rainfall or meltwater which move N beyond the reach of plant roots into deeper soil layers. These considerations differ due to notable variations in soil moisture regimes induced by precipitation differences across Canadian landscapes, soils, and vegetations in the different ecozones. Also, N losses through leaching can be mitigated if biosolids degrade slowly and release N at a rate slower than the crop N uptake rate. However, the crop N requirement may not be met, and N release may continue after crop harvest, leading to N leaching (Haynes et al., 2009). Therefore, the degradation rate and application method of the biosolids, as well as site characteristics (e.g. soil type and climate) are considered when determining the biosolids application rate, to minimize N losses, increase C sequestration, and meet crop N needs (Öğüt & Er, 2015; Charles et al., 2017).

2.3.1. Effect of Biosolids Composition on Mineralization Rate

The degradation rate of biosolids depends in part on the composition of the biosolids (Wang et al., 2007; Pei et al., 2019). In general, organic matter degradation varies as a function of its quality and morphology, biotic activity, exogenous nutrient inputs, and stage of decomposition (Harmon et al., 1999). Depending on the morphology and particle size of the biosolids, initial degradation occurs quickly and later at a slow rate following stabilization (Gilmour et al., 2003; Cabrera et al., 2005). Morphology refers to size, nature, and structure of carbonaceous material (e.g. lignin) in the particles of organic matter and determines the exposure and availability of organic molecules to microbial activity (Schowalter, 2016). Typically, the exposed labile cellulose and hemicellulose contained in the organic matter is first consumed by decomposers before the lignin-protected cellulosic and hemicellulosic organic substrates (Harmon et al., 1999; Zmora-Nahum et al., 2007). This partly explains the initial slow mineralization of C in biosolids with a relatively high C/N (e.g., ≥30).

2.3.2. Effect of Environmental Factors on Mineralization Rate

In addition to the physico-chemical characteristics of biosolids, biotic and abiotic conditions of the soil also influence the kinetics of C and N mineralization after application (Kaboneka et al., 1997). Humidity, precipitation, and soil temperature are among the most influential factors (Benbi et al., 2014; Blagodatsky et al., 2011). For example, decomposition rates are typically higher in warm, humid ecosystems than in temperate, arid ones (Gregorich et al. 2016; Bell et al., 2018). Soil temperature and moisture can jointly influence abiotic factors which control SOM decomposition, with implications for GHG emissions (Solly et al. 2014; Gregorich et al., 2017). Solar radiation, air temperature, and precipitation are the dominant climatic features that influence soil temperature and moisture. All these factors influence the rate of decomposition due to their effect on soil microbiota (Li, 2007; Blagodatsky et al., 2011). This can be seen in the rate of CO_2 and N_2O evolution resulting from soil microbial activity, as well as the higher SOM in arid climates as compared with humid ones (Knapp et al., 1983; Van de Werf & Verstraete, 1987; Rowell et al., 2001; Gregorich et al., 2017; Pei et al., 2019).

Also, local soil conditions can further amplify the effect of climatic conditions on decomposition of SOM and N mineralization (Bouwman et al., 1993; Dou et al., 1996; Thangarajan et al., 2013). For instance, higher denitrification rates have been associated with finer soil texture compared to coarser soil texture (Sey, 2006) and higher soil pH until about 7 leads to increased soil respiration (Kunhikrishnan et al., 2016). Furthermore, soil management practices also influence degradation rates; e.g. tillage aerates the soil, accelerating microbial activity (Beyaert & Voroney, 2011).

2.4. Methods for Estimating Greenhouse Gas Emissions from Agricultural Soils Amended with Biosolids

The Intergovernmental Panel on Climate Change (IPCC) established a three-tier framework for estimating GHG emissions from agricultural soils to support internationally standardized estimation and reporting of national GHG emissions to the United Nations Framework Convention on Climate Change (UNFCCC). The implementation of these methods is guided by the IPCC Good Practice Guidance (IPCC, 2000a, 2003), the IPCC 2006 Guidelines for National Greenhouse Gas Inventory (IPCC, 2006), and the 2019 refinements (IPCC, 2019).

2.4.1. Tier 1 Method

The IPCC Tier 1 method involves using simple equations and default emission factors which do not take into consideration country-specific data. In this methodology, the emission factor is multiplied by the activity data (e.g., amount of N applied) to estimate N_2O emissions (Eq. 2.1). Since the *1996 IPCC Guidelines for National Greenhouse Gas Inventories*, the aggregated Tier 1 emission factor has undergone several refinements. The Tier 1 emission factor for estimating direct N_2O emissions was refined from 1.25 to 1.0% N_2O-N per kg N applied in the 2006 version without accounting for country- or region-specific climatic conditions or management practices other than N application rate. In the current *2019 Refinement to the 2006 IPCC Guidelines for*

National Greenhouse Gas Inventories, two approaches were provided: (1) an aggregated emission factor of 1.0 ± 0.8%, irrespective of climate, management practices other than N application rate, or soil differences; and (2) a set of emission factors disaggregated according to climate into wet (ratio of annual precipitation: potential evapotranspiration > 1) and dry (ratio of annual precipitation: potential evapotranspiration < 1), as well as the fertilizer type (synthetic and organic) (IPCC, 2019). In wet climates, the recommended emission factors for synthetic N and other forms of N (e.g., organic N) are 1.6 ± 0.3% and 0.6 ± 0.5%, respectively, while in dry climates, irrespective of the fertilizer type, the emission factor is 0.5 ± 0.5%. These refinements to the emission factors for direct soil N_2O emissions are based on recent scientific studies conducted around the world, which are yet to be validated for biosolids-induced soil N_2O emissions within the Canadian context. Meanwhile, to estimate indirect N_2O emissions, it is assumed that the fraction of volatilized NOx and NH_3 are constant irrespective of geographical location and climatic conditions. This approach is a mere simplification which serves as a baseline for estimating difficult-to-monitor indirect N_2O emissions.

$$N_2O\_N = EF \times N_{inputs} \qquad \text{Eq. 2.1}$$

$N_2O\text{-}N$ is the amount of N emitted as N_2O; EF is the emission factor for this Tier which is expressed as kg N_2O-N kg^{-1} N; and N_{inputs} is the amount of synthetic or organic N applied in kg.

Since the Tier 1 emission factor was derived from a dataset biased towards mid-latitude and temperate regions, it is likely to over- or under-estimate country- or region-specific soil GHG fluxes when applied in countries or regions with different conditions (Bouwman et al., 2002; IPCC, 2006). According to a meta-analysis of global N_2O emissions from land-application of livestock manures and a combination of biosolids and crop residues, the global emission factor for organic materials was reported to be 0.57 ± 0.30% (Charles et al., 2017). This value falls within the range of climate-disaggregated Tier 1 emission factors recommended by the IPCC in the 2019 refinement of the IPCC (2006) emission factor. Charles et al. (2017) also estimated an emission factor of 1.21 ± 0.14% for animal slurries, waste waters, and biosolids combined with crop residue. These organic materials while being different in their physico-chemical characteristics were surprisingly estimated to fall within the same range of emission factors, as well as being similar to that of the aggregated Tier 1 method. Meanwhile, crop residues + fertilizers (0.59 ± 0.27%) had an emission factor similar to the disaggregated Tier 1 emission factor. However, for most other organic materials, the disaggregated IPCC Tier 1 emission factor for organic N sources was generally higher than the mean values of the emission factors reviewed by Charles et al. (2017) as follows: solid manure, composts + fertilizers, and crop residues + fertilizers had emission factor of 0.35 ± 0.13%; and composts, crop residues, paper mill sludge and pellets had emission factor of 0.02 ± 0.13%. Only the emission factor from liquid manures + fertilizers (2.14 ± 0.53%) was higher than the Tier 1 emission factor. The resulting emission factors had less uncertainty (ranging from 0.13% up to 0.59% of the applied N emitted as N_2O) than the aggregated IPCC Tier 1 emission factors. The recent Tier 1 emission factors could be considered an improvement given that their values are comparable with those found in recent scientific studies. Also, the uncertainties associated with their values were minimal compared to those found in a Canadian study where uncertainties were at least 15% of the applied N (Hutchinson et al., 2007). Such uncertainties could be due to differences in soil, climate, and fertilizer type, as well as possible shortcomings of the available measurement techniques (Butterbach-Bahl et al., 2013).

Given the influence of temperature, moisture, and C/N on N_2O emissions, as well as the spatial variability of Canada’s vegetations, the Tier 1 method is limited as it ignores spatial variability in the variables that drive emissions at national and regional scales. Also, this approach is top-down (i.e., estimating from global to local scale) and is likely to over- or under-estimate soil GHG fluxes at ecoregion, ecoprovince, and ecozone scales. On the contrary, bottom-up approaches, which disaggregate these spatial variabilities on a local scale, are typical of Tier 2 and 3 methods and are expected to produce better GHG estimates.

2.4.2. Tier 2 Method

A comparison between the Tier 1 (using the IPCC (2006) default value) and Tier 2 methods revealed that their emission factor estimates varied in some instances at regional and national scales. For instance, Lesschen et al. (2011) showed that, across Europe, Tier 2 emission factors were estimated to range between 0.25–0.75% of the applied N and predicted the actual emissions better than the IPCC Tier 1 method. Their results also showed that, by accounting for regional differences in N input sources, precipitation, land use, and soil type, the Tier 2 method had lower errors than the Tier 1 method in reference to empirical measurements. In China, the Tier 2 emission factor estimates ranged between 0.56% and 1.54% of the applied N with a mean of 0.92% of applied N for non-rice crops (mainly wheat and maize) (Shepherd et al., 2015). The mean value of the estimated Tier 2 emission factor for China was similar to the aggregated IPCC Tier 1 emission factor but with higher uncertainty ranges. Also, in the study by Shepherd et al. (2015), regional differences in emission factors were found for wheat but not maize crop. In summary, these variations in emission factors across China were not only due to differences in climate, fertilizer type, and soil texture, but crop type as well.

Canada's annual direct N_2O emissions from agricultural soils are currently reported in the National Inventory Reports to the UNFCCC based on a Tier 2 methodology developed by Rochette et al. (2008a) (ECCC, 2006; 2018). This method uses empirical data from Canadian cropping systems to estimate direct N_2O-N emissions from applied N, adjusted according to climate and farm management practices. The estimates of soil N_2O emissions account for: applied N; mineralization associated with loss of soil organic matter; decomposition of animal manure on pasture, range, and paddock; tillage intensity; summer fallow; soil texture (including organic soils); topography; and irrigation. In this method, the emission factors were first derived at the regional scale based on the relationship between N_2O emissions and N fertilizer rate for unirrigated, well-drained soils under conventional tillage practices. Only three regions had sufficient field measurements for this analysis: Quebec-Ontario (n = 72 site-years), and the Brown-Dark Brown (n = 155 site-years) and Black (n = 48 site-years) soil regions in the Canadian Prairies. The regional emission factor values were then refined at the ecodistrict scale (~150,000 ha) to reflect the effects of local conditions on N_2O emissions (Eq. 2.2).

$$EF_{eco} = 0.022 \times \frac{P}{PE} - 0.0048 \qquad \text{Eq. 2.2}$$

EF_{eco} is the emission factor per ecodistrict (kg N_2O-N per kg N); P is the precipitation during the growing season; and PE is the potential evapotranspiration during the growing season. EF_{eco} depends on the ratio of precipitation to potential evapotranspiration (P/PE) during the growing season (May to October).

In Canada's Tier 2 method, N_2O emissions are estimated using a bottom-up approach. Here N_2O emissions are estimated per ecodistrict by multiplying the derived ecodistrict-specific emission factor (EF_{eco}) by the corresponding activity data (e.g., N amount). The N_2O emissions are then corrected for the effects of soil texture, crop type (annual or perennial), and tillage type, and aggregated incrementally at the ecoregion, ecoprovince, and ecozone scales to determine the overall national N_2O emissions. Using this methodology, the estimated emission factor varied from less than 0.25% in semi-arid ecozones to about 1.7% in humid ecozones (Rochette et al., 2008b). Two weakness of this method that limit its use for estimating N_2O emissions from land-application of biosolids on a national scale are: (1) the dataset was based on four out of ten Canadian provinces (Quebec, Ontario, Saskatchewan and Alberta); and (2) wastewater biosolids were not accounted for in this methodology.

An updated Tier 2 methodology was proposed by Rochette et al. (2018) but, at the time of writing, had yet to be implemented in the National Inventory Report. In the updated method, datasets for developing the Tier 2 regression equations cover three more provinces (New Brunswick, Manitoba, and British Columbia) than in the earlier version. In addition, the number of site observations in the dataset for synthetic fertilizer N application in the semi-arid Prairies increased from 48 to 126 sites. Organic N datasets, however, still came from studies in Ontario and Quebec, representing limited variability in soil texture, precipitation, potential evapotranspiration, and crop type. As shown in Eq. 2.3, emission factor for organic materials (EF_{org}) was estimated using two parameters: soil clay content and the ratio of precipitation to potential evapotranspiration during the growing season.

$$N_2OEF_{org} = -1.4 + e^{[2.07+0.003CLAY-2.01PPE]} \qquad \text{Eq. 2.3}$$

N_2OEF_{org} is the N_2O emission factor with organic N application (kg N_2O-N per kg N); $CLAY$ is clay content (g kg^{-1}); and PPE is the ratio of the growing season precipitation to potential evapotranspiration.

Meanwhile, as seen in Eq. 2.4, emission factor for mineral N (EF_{min}) was estimated using four parameters.

$$N_2OEFmin = -1.4 + e^{[-0.2982+0.00095P+0.0198Corg+0.0732Tair-0.4264Crop]} \qquad \text{Eq. 2.4}$$

N_2OEF_{min} is the N_2O emission factor with mineral N application (kg N_2O-N per kg N), P is the precipitation during the growing season from May to October (mm); C_{org} is the soil organic C content (g C kg^{-1}); T_{air} is the air temperature (^{o}C); and *Crop* is crop type (annual and perennial).

Liang et al. (2020) described how the updated Tier 2 methodology would be integrated into the GHG inventory, with preliminary results showing improvements in N_2O estimation over the previous version of Canada's GHG inventory methodology. Given the limitations of the Tier 2 method in estimating N_2O emissions from organic N sources, particularly in Canada's Prairies, discrepancies between Tier 2 estimates and empirical measurements of N_2O emissions are still expected. Methods for estimating N_2O emissions from land-applied biosolids need to be based on empirical measurements representative of the Canadian ecodistricts where biosolids are used in agriculture.

2.4.3. Tier 3 Method: Process-Based Modelling Approach for Estimating Nationwide Soil Greenhouse Gas Fluxes

Tier 3 methods use site-specific measurements and/or process-based models that simulate the physical processes that underly GHG emissions (IPCC, 2006; IPCC, 2019). Process-based models range from simple, N-cycling models like NEMIS (Hénault & Germon, 2000) to complex C and N-cycling models like DNDC (Li et al., 1992), DailyDayCent (Parton et al., 1994), the Environmental Policy Integrated Climate (EPIC) model (Izaurralde et al., 2006), Root Zone Water Quality Model (RZWQM2) (Ma et al., 2012), Ecosys (Grant, 1995), SWAT-N_2O (Arnold et al., 1998), APSIM (Agricultural Production Systems sIMulator) (Thorburn et al., 2010), the Water and Nitrogen Management Model (WNMM) platform for field-scale simulation (Li et al., 2005), Crop Environment REsource Synthesis - Environnement et Grandes Cultures (CERES-EGC) (Gabrielle et al., 1995), and more expansive whole-farm models. These models have been used to simulate and study ecosystems processes such as plant growth and development (Justes et al., 1994; Lipiec et al., 2003; Puntel et al., 2018), the impacts of management practice on soil C dynamics (Zhang et al., 2015; Zhang et al., 2017), SOM turnover (Paustian et al., 1992; Li et al., 1994), land use change (Meiyappan et al., 2014), gas exchange at the soil-plant-atmosphere interface (Coleman et al., 1997; Gabrielle et al., 2006; Misselbrook et al., 2006; Nguyen et al., 2014), soil water dynamics (Lascano, 1991), denitrification (Saggar et al., 2013), climate change impacts on crop systems (Graux et al., 2013), and nitrification and denitrification in lab-scale trials (Xing et al., 2011). Several of these models, including DNDC, have been tested and validated using datasets measured from forest, grassland, and agricultural ecosystems (Beheydt et al., 2007). Amongst all the numerous studies, only a few studies in Europe and the USA focused on process-based modelling of C and N dynamics in agricultural soils amended with sewage sludge/biosolids (e.g. Fumagalli et al., 2013). However, no such modelling studies have been carried out on Canadian soils receiving biosolids.

Tier 3 reporting methods that use process-based models are required by the IPCC to follow seven steps: model selection or development, calibration, evaluation, collection and collation of input data, implementation, assessment of uncertainty, and verification of inventory estimates with independent data (IPCC, 2019).

2.4.3.1. Process-Based Modelling Approach for Estimating Regional Soil GHG Fluxes

Process-based models can be used together with inventories of measurements that capture variability in climatic, soil, vegetation, and farm management conditions within a region (e.g. nation) (IPCC, 2019). This approach involves dividing a region into spatial sub-units for which the input parameters are assumed to be homogeneous and running the model for each sub-unit. For instance, Del Grosso et al. (2005) used DayCent in a Tier 2 emission factor methodology to estimate direct and indirect N_2O emissions for major non-rice cropping systems in the USA. The croplands in the USA were stratified into 63 sets according to similarities in vegetation and soil type prior to DayCent parameterization and simulation. Also, Smith et al. (2002) and de Vries et al. (2005) used DNDC to estimate N_2O emissions over different landscapes and crop management practices in Canada and the Netherlands, respectively, to produce more accurate estimates than the IPCC Tier 1 methodology. In Poland, Syp & Faber (2017) used DNDC to simulate N_2O emissions, but their results did not differ significantly from the established Tier 2 method. This method has been used in other studies to quantify GHG fluxes in the UK (Brown et al., 2002), across Europe (Britz & Leip, 2009; Leip et al., 2011), the Netherlands (De Vries et al., 2011), China (Cai et al., 2003), and Italy (Lugato et al., 2010). The Tier 2 method has many limitations. For instance, soil heterogeneity is a critical factor in modelling spatial variability in GHG fluxes, but soil data at fine spatial resolutions are difficult to obtain (Gottschalk et al., 2007; Nol et al., 2010). Therefore, extensive data collection is required for model parameterization, or data limitations may undermine the scaling up of model estimates from site to regional scales (Olander et al., 2011; Fitton et al., 2017).

2.4.3.2. Estimating Regional GHG Emissions Using Meta-models

A process-based modelling approach can also be used to estimate N_2O emissions, and a simplified model may be fitted to those simulated data (e.g. using regression modelling) as a way to estimate emission factors with lower computational and data requirements, for use in National Inventory Reports (de Vries et al., 2005; Li et al., 2001; Lesschen et al., 2011). Here, a combination of models or a range of outputs from multiple range of inputs in a single model are often used to produce meta-models, which are domain-specific (e.g., region or vegetation) and preserve the relationships between the key inputs and response variables. This method involves parameterization of the selected model(s), Monte Carlo simulations over the full range of input variables, and multiple regression analysis to produce simplified meta-models of emission factor. This method was used by Giltrap & Ausseil (2016) to produce simplified meta-models of the simulated N_2O emission factor for grazed pastures in New Zealand; by Britz & Leip (2009) to calculate marginal N_2O emission factor for a 1 kg ha^{-1} increase of N fertilizer rate for specific crops in Western Europe; and by Giltrap et al. (2008) to directly estimate N_2O emissions from agriculture in the Manawatu-Wanganui region in New Zealand. The advantage of meta-models over process-based models is that they are less data intensive. However, like other models, meta-models cannot be extrapolated beyond the range of input values originally simulated. This is especially important when estimating non-CO_2 GHG (e.g. N_2O) emissions in agroecosystems, as non-CO_2 emissions exhibit higher spatial and temporal variability than CO_2 emissions (Gottschalk et al., 2007; Hastings et al., 2010; IPCC, 2019).

2.5. The DeNitrification and DeComposition (DNDC) Model

2.5.1. Overview of DNDC

The DNDC model was originally developed in the USA to simulate soil N_2O emissions but has since been improved to simulate C and N cycling in entire agroecosystems across the globe (Gilhespy et al., 2014). The original DNDC model consists of six sub-models (Figure 2.1.): soil climate, decomposition, nitrification, denitrification, fermentation, and crop growth (Li & Frolking, 1992; Giltrap et al., 2010). These sub-models are grouped into two components. The first component consists of the soil climate, crop growth, and decomposition sub-models, while the second component consists of nitrification, denitrification, and fermentation sub-models. The first component simulates the soil environment and drives the simulation of C and N cycling by the second component.

Since its development, DNDC has evolved to simulate complex C and N dynamics in whole-farm systems. For instances, DNDC has been adapted to simulate soil C and N cycling (Li et al., 1994; Li, 2000), crop growth based on phenology (Zhang et al., 2002), soil water and N movement (Li et al., 2006), ammonia volatilization (Congreves et al., 2016; Dutta et al., 2016), and OM turnover and gas emissions in livestock systems with full farm facilities (Li et al., 2012). It has also been tested and adapted to meet user-specific needs by different researchers in several countries, including Canada (Gilhespy et al., 2014). DNDC produces results that are consistent and compatible with other models used in compiling GHG inventories (Brilli et al., 2017). It also allows for the quantification and reduction of uncertainty relative to Tiers 1 and 2 methods (Li et al., 2001), to improve the simulation of C and N transformations in the soil (Myrgiotis et al., 2018).

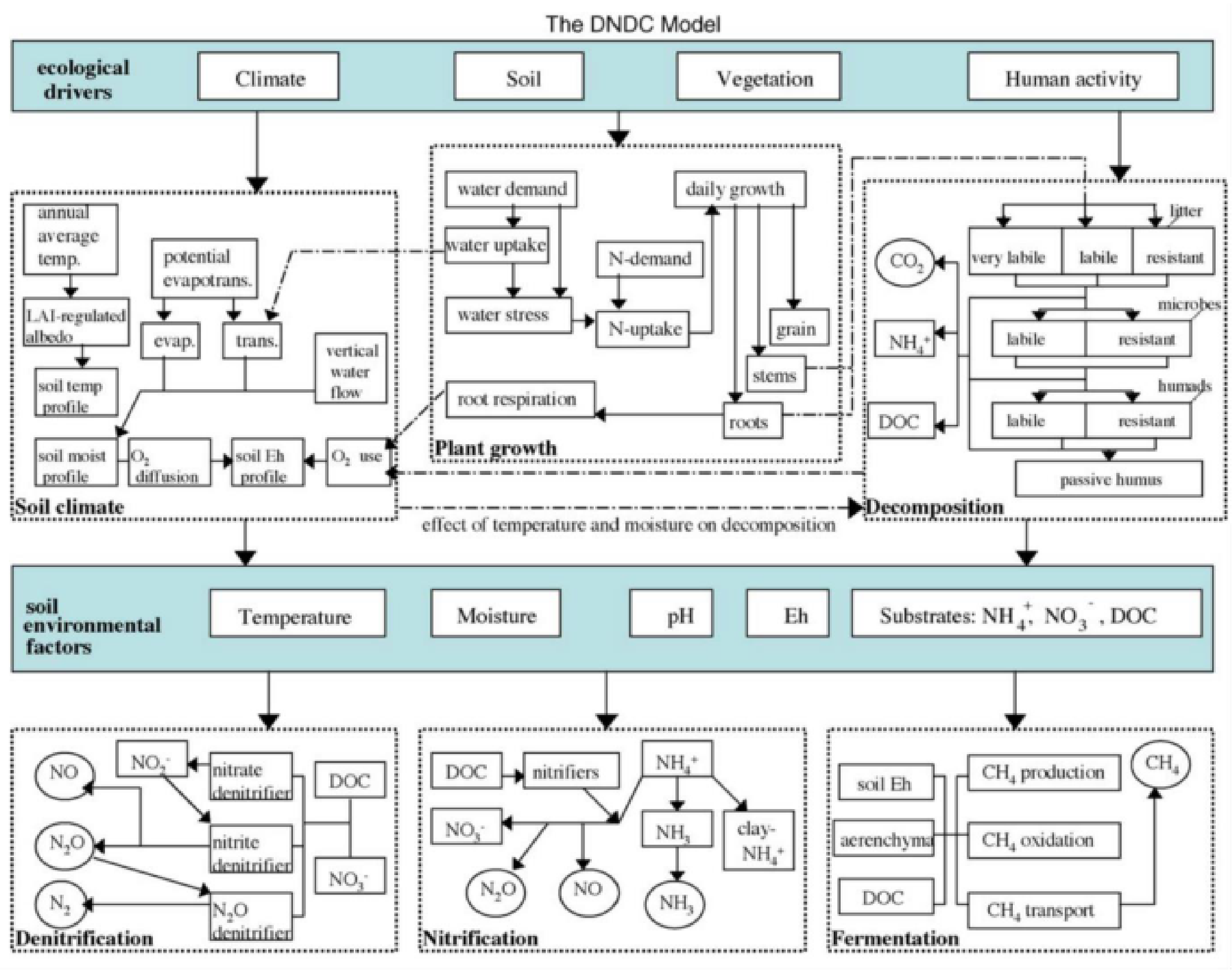

Figure 2.1. DNDC model structure showing the 6 sub-models and processes linking ecological and soil environmental drivers that control C, N, and P cycling in crop production in agricultural fields. Adapted from Li et al. (2006), Smith et al. (2020), and Gilhespy et al. (2014).

Three groups of data are required to parameterize DNDC. The first group includes the soil characteristics such as soil texture, bulk density, clay content, hydraulic conductivity, organic C concentration, initial $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ concentrations, field capacity, wilting point, and porosity. The second group includes daily climate information such as wind speed, relative humidity, maximum and minimum air temperature, solar radiation, and precipitation. The third group includes crop profile and management information, the former including temperature degree-day and water requirements, crop morphology, crop (grain, shoot, and root) biomass yield, C and N concentrations in biomass, and the latter including tillage practices, N application rate and method, crop rotation, planting, and harvest dates, *etc*. The soil, climate, and crop parameters are the ecological drivers used by the soil climate sub-model to simulate the soil environmental factors such as soil temperature, pH, NH_4^+ and NO_3^- concentrations, and redox potential. DNDC simulations produce daily N_2O and CO_2 emissions estimates that can be used for reporting emissions and removals from croplands and grasslands.

Compared to other models, DNDC has numerous advantages that make it stand out as a model for simulating agroecosystem dynamics. A review by Brilli et al. (2017) concluded that the DNDC was the only model that simulates all N processes, CO_2 emissions, and non-CO_2-GHG (N_2O, CH_4, NH_3, NOx, and N_2). The next best models for agroecosystem simulation were DailyDayCent and EPIC. In addition, the DNDC model can be linked to a database of activity data and run in an operational context using easily measurable input data (Brown et al., 2002; Smith et al., 2010). The availability of default parameters for over 60 crop types and a complete suite of commonly simulated agroecosystems outputs gives this model an edge over similar models (Gilhespy et al., 2014). The data required to initialize DNDC's SOC pools are more readily available than the data required by DailyDayCent. The simulated SOC content can be stabilized by running a 10-yr spin-up simulation, unlike in DailyDayCent which demands soil information for each soil layer and an SOC initialization simulation of 1,000 years. However, some weakness of DNDC include: (1) unavailability of source code; (2) the soil-crop-atmospheric processes, especially for the more recent versions, are not well documented in the user's manual (Smith, 2019); (3) microbial diversity, growth and abundance are only represented implicitly (Brilli et al., 2017); (4) it often exhibits inaccuracies in simulating the impacts of certain management practices (e.g. tillage) on GHG fluxes (Uzoma et al., 2015); and (5) it often exhibits inaccuracies in simulating soil water and N flow through the soil profile (Smith et al., 2020).

2.5.2. Using DNDCv.CAN to Simulate Carbon and Nitrogen Cycling from Land-Applied Biosolids

DNDC.vCAN is the version of DNDC95 adapted by several Canadian researchers for national use. It estimates soil and hydrological dynamics up to a depth of 2m under conditions typical of Canadian climate, crops, agricultural management practices, and soil types (Smith et al., 2020). The previous version of the model, DNDC95, was designed for use in a wide variety of agroecosystems (Gilhespy et al., 2014), and these features together with improvements in C and N cycling mechanisms were retained in DNDC.vCAN (Smith et al., 2020). To that effect, it performs reasonably across various Canadian geographic regions (Ehrhardt et al., 2018; Deng et al., 2016; Yadav & Wang, 2017; Smith et al., 2020), farm management practices (e.g. Uzoma et al., 2015), and climate conditions (e.g. Congreves et al., 2016). It was recently adapted to cold weather conditions, long winter periods with snowpack, and soil textures that are typical of Canada (Dutta et al., 2018). Also, the deficiencies in simulating soil water flow have been improved by introducing root density functions for different crops and changing the approach for simulating soil hydrology (Smith et al., 2019). The previous cascade water flow model was based on the assumption of a homogenous 50 cm soil profile, but this was improved by accounting for water flow through a 2 m heterogeneous soil profile (Smith et al., 2020). This improvement enables the characterization of the soil profile as comprising up to 20 different layers based on pH, SOC, texture, porosity, bulk density, and hydraulic conductivity.

DNDC can be parameterized to simulate C and N transformation in different types of biosolids. DNDC has been used in several studies of soils amended with different N sources, such as urea (Dutta et al., 2016), digestate from anaerobic digestors (Terhoeven-Urselmans et al., 2009), and crop residue (Ehrhardt et al., 2018) in several countries. The characterization of organic amendments in DNDC demands the values of C/N, organic C, organic N, NO_3^-, urea or NH_4^+, pH, and dry matter as input parameters. These parameters distinguish the different types of biosolids (Arulrajah et al., 2011) and influence the decomposition, nitrification, and denitrification in agricultural soils that receive biosolids, as well as the magnitude of the resulting GHG emissions (Gilmour & Skinner, 1999; Gilmour et al., 2003; Rigby et al., 2016). These parameters are empirically measurable and are also user specified DNDC inputs. The rigorous work already done in the development and use of DNDC.vCAN makes it a suitable model for implementing the objectives of this research.

2.5.3. Simulation of Carbon Mineralization using DNDC

There are seven SOC pools in DNDC, distributed amongst soil, microbial biomass, and litter as follows: (1) labile soil C, (2) passive humus, (3) labile microbial C, (4) resistant microbial C, (5) very labile litter C, (6) labile litter C, and (7) resistant litter C. Carbon mineralization in the model follows a sequential transformation from the very labile to the resistant C pool. When organic matter (e.g., biosolids) is applied to the soil, the organic C from the biosolids is allocated to either the very labile, labile, or resistant SOC pool depending on the C/N ratio of the biosolids in question. DNDC models the SOM decomposition process using first-order kinetics, whereby the decomposition rates of the labile and resistant pools of organic carbon depend on the C/N ratio, soil moisture, and temperature (the moisture and temperature factor) (Eq. 2.5). The decomposition process occurs independently and simultaneously in all SOC pools at different rates. The DNDC model quantifies the daily amounts of SOC, heterotrophic CO_2 production, and root respiration. The equations used to estimate the rate of SOC decomposition have been documented by the Institute for the Study of Earth, Oceans, and Space (2017).

$$\frac{dC}{dt} = CNR \times \mu \times (S \times k_1 + (1 - S) \times k_r) \times [C] \qquad \text{Eq. 2.5}$$

$\frac{dC}{dt}$ is the rate of decomposition of the organic C pool (kg-C ha^{-1} d^{-1}); t is time (day); CNR is the C/N ratio reduction factor; μ is the temperature and moisture factor; S is the labile fraction of organic C compounds; k_1 is the specific decomposition rate of the labile fraction (day^{-1}); $(1 - S)$ is the resistant fraction of organic C compounds; k_r is the specific decomposition rate of the resistant fraction (day^{-1}); and $[C]$ is the organic C content (kg-C ha^{-1}).

During the microbial decomposition of SOC, a fraction of the produced dissolved organic carbon (DOC) serves as an energy source for the microbes and another fraction for microbial biomass growth. Microbial decomposition of SOC leads to CO_2 production and emission from each soil layer, depending on its initial C content. The quantity and quality of C in the biosolids determine the growth rate of decomposers, the CO_2 production rate during decomposition, the mineralization rate of available N compounds, and the quantity of C in the resistant and passive C pools that are available to sustain microbial activity over time. This mechanism assumes that other substrates (e.g., plant micronutrients) are not limiting.

2.5.4. Simulating Nitrification and Denitrification Processes using DNDC

In DNDC, the nitrification and denitrification of N applied to the soil in the form of synthetic fertilizers, crop residue, manure, or biosolids are simulated using the “anaerobic balloon” concept (Li et al., 2000). Here, soil is conceptually divided into an anaerobic volumetric fraction (within the anaerobic balloon) which represents anaerobic microsites in the soil, and the remaining aerobic volumetric fraction (outside the anaerobic balloon) which represents the aerobic microsites in the soil. The proportion of aerobic to anaerobic fractions determine the proportion of substrates (DOC, $\mathrm{NO_3^-}$, $\mathrm{NH_4^+}$, etc.) allocated to each portion. Substrates within the anaerobic volumetric fraction take part in reduction reactions (e.g., denitrification), while substrates allocated outside the anaerobic volumetric fraction (soil aerobic microsites) take part in oxidation reactions (e.g., nitrification). The Nernst equation (Eq. 2.6) describes either nitrification or denitrification, depending on the estimated soil redox potential (Eh) due to concentrations of the existing oxidants and reductants in the soil liquid phase. The equations used in DNDC to estimate Eh, as well as those used to estimate N_2O production through nitrification and denitrification, have been documented by the Institute for the Study of Earth, Oceans, and Space (2017).

$$Eh = E_o + \frac{RT}{nF} \times \ln\left(\frac{[oxidant]}{[reductant]}\right) \qquad \text{Eq. 2.6}$$

Eh is the redox potential of the oxidation-reduction system (V); E_0 is the standard electromotive force (V); *R* is the universal gas constant (8.314 J $\mathrm{mol^{-1}\ K^{-1}}$); *T* is the absolute temperature (K); n is the number of electrons transferred during the redox reaction, *F* is the Faraday constant (96,485 Coulombs $\mathrm{mol^{-1}}$); [*oxidant*] is the concentration (mol $\mathrm{L^{-1}}$) of the dominant oxidant in the system; and [*reductant*] is the concentration (mol $\mathrm{L^{-1}}$) of the dominant reductant in the system.

The concentration of each oxidant (O_2, $\mathrm{NO_3^-}$, $\mathrm{Mn_4^+}$, $\mathrm{Fe_3^+}$, $\mathrm{SO_4^{2-}}$ and CO_2) in the soil is allocated (conceptually) to a unique anaerobic balloon. In descending order of Gibb's free energy from O_2 to CO_2, each oxidant becomes dominant at its suitable range of soil Eh, following the depletion of the preceding oxidant by microbial activity. Once an oxidant becomes active, microbes begin to deplete that specific oxidant, causing a swelling of its anaerobic balloon. The anaerobic balloon bursts as soon as the oxidant is depleted, leading to a decrease in soil Eh, which then activates the use of the next oxidant. This process is sequential and continues repetitively depending on the availability of substrates. The consumption rates of oxidants are described using the dual-nutrient Michaelis-Menten equation (Eq. 2.7), while the reaction rate depends on concentration of the dominant oxidant and available C.

$$F_{[oxidant]} = a\left[\frac{DOC}{b+DOC}\right] \times \left[\frac{oxidant}{c+oxidant}\right] \quad \text{Eq. 2.7}$$

$F_{[oxidant]}$ is the fraction of oxidant reduced during each time step, *DOC* is the dissolved organic carbon content (kg-C ha^{-1}), *oxidant* is the concentration of the dominant oxidant in the oxidation-reduction system, a is the maximum rate of reaction, and *b* and *c* are half-saturation constants for substrates DOC and oxidants, respectively. The constants (*b* and *c*) and a were taken from a laboratory study by Leffelaar and Wessel (1998).

2.5.4.1. Nitrous Oxide Production through Nitrification

In DNDC, N_2O production due to nitrification occurs when soil is aerated, i.e., in the aerobic volumetric fraction of the anaerobic balloon. In this state, O_2 is the dominant oxidant, and the water-filled pore space (WFPS) must be greater than 0.05 for nitrification to occur. The process is modelled after the nitrification reactions shown in Eq. 2.8 and Eq. 2.9.

$$NH_4^+ + O_2 \rightarrow NO_2^- + 4H^+ + 2e^- \quad \text{Eq. 2.8}$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \quad \text{Eq. 2.9}$$

Soil temperature, pH, moisture, DOC concentration, and nitrifying bacteria activity together influence the nitrification rate as shown in Eq. 2.10 to Eq. 2.16. The rate of nitrification is optimum when temperature is 35℃.

Nitrification rate depends on the activity of nitrifying bacteria, soil pH, and the availability of NH_4^+. The effect of soil pH on the nitrification rate is represented by Eq. 2.10, with optimum nitrification occurring at a soil pH of 7.5 to 8.0.

$$RN = k_{35} * [NH_4^+] \times Nitrifier \times pH \qquad \text{Eq. 2.10}$$

RN is the nitrification rate (kg-N ha^{-1} d^{-1}), k_{35} is the nitrification rate (25 mg kg^{-1} manure d^{-1}) at 35 °C, $[NH_4^+]$ is the concentration of ammonium (kg-N kg-soil^{-1}), *Nitrifier* is the biomass of nitrifying bacteria (kg-C ha^{-1}), and *pH* is the soil pH.

The N_2O produced by nitrification is computed as a fraction of the nitrification rate shown in Eq. 2.11.

$$N_2O_N = 0.006 \times RN \times F_t \times WFPS \qquad \text{Eq. 2.11}$$

N_2O_N is N_2O-N production through nitrification (kg-N ha^{-1} d^{-1}), *Ft* is the soil temperature factor, and *WFPS* is water-filled pore space.

Nitrifier activity (growth and death rates) depends on DOC, soil temperature, and soil moisture as represented by Equations 2.12, 2.13 and 2.14.

$$\frac{dNitrifier}{dt} = \left(\frac{dG}{dt} - \frac{dD}{dt}\right) \times Nitrifier \times Ft \times Fm \qquad \text{Eq. 2.12}$$

$$\frac{dG}{dt} = \mu_{max} \times \left(\frac{[DOC]}{1.0 + [DOC]} + \frac{Fm}{1.0 + Fm}\right) \qquad \text{Eq. 2.13}$$

$$\frac{dD}{dt} = a_{max} \times Nitrifier \times \frac{\frac{1.0}{1.0 + [DOC]}}{1.0 + F_m} \qquad \text{Eq. 2.14}$$

$\frac{dNitrifier}{dt}$ is the net change of nitrifying bacteria biomass (kg-C ha^{-1} d^{-1}), $\frac{dG}{dt}$ is the relative growth and $\frac{dD}{dt}$ is the relative death rate of the nitrifying bacteria (d^{-1}), *Fm* is the soil moisture factor, μ_{max} is the maximum growth rate of nitrifiers (4.87 d^{-1}), and a_{max} is the maximum death rate for nitrifiers (1.44 d^{-1}).

The effect of soil moisture on nitrification is shown in Eq. 2.15, with the water-filled pore space (WFPS) limiting the nitrification rate when the soil becomes too dry.

$$F_m = \begin{cases} 0.8 + 0.21 \times (1.0 - WFPS); \; WFPS > 0.05 \\ 0.0; \; WFPS \leq 0.05 \end{cases} \qquad \text{Eq. 2.15}$$

The temperature function is used to calculate the effect of temperature on the nitrifying bacteria growth rate shown in Eq. 2.16.

$$Ft = 3.503^{\left(\frac{60-T}{25.78}\right)} \times \exp^{3.503 \times \left(\frac{T-34.22}{25.78}\right)}. \qquad \text{Eq. 2.16}$$

T is the soil temperature (°C).

2.5.4.2. Nitrous Oxide Production through Denitrification

DNDC models the reduction reaction following Eq. 2.17, representing the reduction of nitrate to diatomic nitrogen and the production of N_2O and NO as intermediate products.

$$NO_3^- + 2e^- \rightarrow NO_2^- + e^- \rightarrow NO + e^- \rightarrow N_2O + 2e^- \rightarrow N_2 \qquad \text{Eq. 2.17}$$

Denitrification begins when Eh = 500 mV or lower due to soil O_2 depletion, therefore sequentially activating NO_3^- and other oxidizers as the electron acceptors. The denitrifying bacteria consume the oxides of N and grow at a rate proportional to their respective biomasses and the available concentrations of DOC and N oxides. The growth of denitrifying bacteria is estimated using the Michaelis-Menten equation that describes growth kinetics based on multiple nutrients (Eq. 2.18). The growth rates of denitrifying bacteria in the different reactions are independent and all compete for the available soluble C substrate.

$$u_{NOx} = u_{NOx,max} \times \left(\frac{[DOC]}{K_c + [DOC]}\right) \times \left(\frac{[NO_x]}{K_N + [NO_x]}\right) \qquad \text{Eq. 2.18}$$

u_{NOx} is the relative growth rate of $\mathrm{NO_3^-}, \mathrm{NO_2^-}, \mathrm{NO}$, or $\mathrm{N_2O}$ denitrifying bacteria (h^{-1}),$u_{NOx,max}$ is the maximum growth rate (0.67 h^{-1}) for $\mathrm{NO_3^-}, \mathrm{NO_2^-}$ denitrifiers, and 0.34 h^{-1} for NO and $\mathrm{N_2O}$ denitrifiers (h^{-1}); [DOC] is the soluble C concentration (kg-C cm^{-3}), *NOx* is the concentration of N oxides or N_2O in soil water (kg-N cm^{-3}); K_C is the half-saturation value of soluble C in the Monod model (kg-C m^{-3} soil water); and K_N is the half saturation value of the N oxides or N_2O in the Monod model (kg-N m^{-3} soil water).

The denitrification reaction is influenced by soil pH (Equations 2.19, 2.29 to 2.31). Denitrification rates increase with increasing pH, having an optimum pH range of 7.0–8.0, while at pH values less than 5.0 denitrification is limited to N_2O production. The growth and death rates of denitrifying bacteria are estimated using Equations 2.19, 2.20, and 2.21.

$$u_{DN} = F_T \times \left(u_{NO3} \times F_{pH-NO3} + u_{NO2} \times F_{pH-NO2} + u_{NO} \times F_{pH-NO} + u_{N2O} \times F_{pH-N2O}\right) \qquad \text{Eq. 2.19}$$

u_{DN} is the relative growth rate of NOx and N_2O denitrifying bacteria (h^{-1}); F_T is the temperature factor; and $F_{PH\text{-}NO3}$, $F_{PH\text{-}NO2}$, $F_{PH\text{-}NO}$, and $F_{PH\text{-}N2O}$ are all soil pH factors for the compound indicated in the subscript.

$$\left(\frac{dDenitrifier}{dt}\right)_g = u_{DN} \times Denitrifier \qquad \text{Eq. 2.20}$$

$\left(\frac{dDenitrifier}{dt}\right)_g$ is the potential growth rate of denitrifier biomass (kg C ha^{-1} d^{-1}),*Denitrifier* is the biomass of denitrifying bacteria (kg-C ha^{-1}).

$$\left(\frac{dDenitrifier}{dt}\right)_d = M_C \times Y_C \times Denitrifier \qquad \text{Eq. 2.21}$$

$\left(\frac{dDenitrifier}{dt}\right)_d$ is the denitrifier death rate, M_C is maintenance coefficient on C (0.0076 kg-N kg h^{-1}), and Y_C is maximum growth yield on soluble carbon (0.503 kg-C kg-C^{-1})

Consumption of DOC and CO2 production through denitrification is shown in Eq. 2.22 and 2.23, respectively.

$$\frac{dC_{con}}{dt} = \left(\frac{\mu_{DN}}{Y_c} + M_c\right) \times Denitrifier \qquad \text{Eq. 2.22}$$

$$\frac{dCO_2}{dt} = \frac{dC_{con}}{dt} - \frac{dDenitrifier}{dt} \qquad \text{Eq. 2.23}$$

$\frac{dC_{con}}{dt}$ is the hourly rate of change of C concentration (kg-C ha^{-1} h^{-1}) and $\frac{dCO_2}{dt}$ is the hourly rate of CO_2 production (kg-C ha^{-1} h^{-1}).

Equations 2.24 to 2.27 are used to calculate the rate of N oxides consumption.

$$\frac{d(NO_3)}{dt} = \left(\frac{u_{NO3}}{Y_{NO3}} + M_{NO3} \times \frac{[NO_3]}{[N]}\right) \times Denitrifier \times F_{pH-NO3} \times F_T$$ Eq. 2.24

$$\frac{d(NO_2)}{dt} = \left(\frac{u_{NO2}}{Y_{NO2}} + M_{NO2} \times \frac{[NO_2]}{[N]}\right) \times Denitrifier \times F_{pH-NO2} \times F_T$$ Eq. 2.25

$$\frac{d(NO)}{dt} = \left(\frac{u_{NO}}{Y_{NO}} + M_{NO2} \times \frac{[NO]}{[N]}\right) \times Denitrifier \times F_{pH-NO} \times F_T$$ Eq. 2.26

$$\frac{d(N_2O)}{dt} = \left(\frac{u_{N2O}}{Y_{N2O}} + M_{N2O} \times \frac{[N_2O]}{[N]}\right) \times Denitrifier \times F_{pH-N2O} \times F_T$$ Eq. 2.27

N is the total nitrogen as the sum of $\mathrm{NO_3^-}, \mathrm{NO_2^-}, \mathrm{NO}$, or $\mathrm{N_2O}$ (kg-N ha^{-1}); and Y_{NO3}, Y_{NO2}, Y_{NO}, and Y_{N2O} are the maximum growth yield on $\mathrm{NO_3^-}, \mathrm{NO_2^-}, \mathrm{NO}$, or $\mathrm{N_2O}$ (kg-C Kg-N^{-1}), respectively.

The effects of temperature on denitrification is estimated using Equation 2.28 and applied to equations 2.24 and 2.27.

$$F_T = \begin{cases} 2.0^{\frac{T-22.5}{10.0}}\,;\ T \leq 60.0 \\ 0.0;\ T > 60.0 \end{cases}$$ Eq. 2.28

DNDC estimates the effect of pH on denitrification using Equations 2.29 to 2.31.

$$F_{pH-NO3} = 1 - \left(\frac{1}{1+\exp^{\frac{pH-4.25}{0.5}}.}\right)$$ Eq. 2.29

$$F_{pH-NO2} = 1 - \left(\frac{1}{1+\exp^{\frac{pH-5.25}{1.0}}.}\right)$$ Eq. 2.30

$$F_{pH-NO3} = 1 - \left(\frac{1}{1+\exp^{\frac{pH-6.25}{1.5}}.}\right) \qquad \text{Eq. 2.31}$$

Under aerated soil conditions in DNDC, SOC decomposition, N nitrification, and NO_3^- denitrification processes release CO_2, N_2O, NOx, and NH_3, and provide mineral N for plant uptake. The soil organic N, having increased by application of biosolids, mineralizes to NH_4^+, which is maintained in equilibrium with NH_3. NH_4^+ is a substrate for denitrification into NO_3^- and can be taken up directly by plants. The quantity of nitrogen in the biosolids determines the amount of NH_4^+ and NO_3^- available for plant uptake and microbial growth, as well as loss through NO_3^- leaching, NH_3 volatilization, and N_2O emissions.

2.5.5. Calibration and Evaluation of DNDC

The complex interactions of variables in DNDC require parameter optimization to properly represent the transformation of C and N and their exchange between soil, crop, and atmosphere in the target system. As a rule, soil temperature, soil moisture, crop N, crop C, crop biomass, SOC, as well as NH_3, N_2O, NO_3^-, NH_4^+ and CO_2 measurements are compared as benchmarks with simulated values from DNDC to assess DNDC's performance (Li, 2013; Li et al., 2014; Li et al., 2017a; Myrgiotis et al., 2018).

Calibration and evaluation ensure confidence in DNDC simulations prior to deployment as a predictive tool. For good calibration to be achieved, multi-parameter optimization is typically done using manual iterations, generic algorithms, machine learning, and Bayesian methods (Kercher & Chambers, 2001; Ratto et al., 2001; Li, 2013; Muehleisen & Bergerson, 2016). Disparities between measured and simulated values occur mostly due to Type 1 and 2 errors in field measurements, the parameterization and structure of DNDC, or combinations of these three (Lamers et al., 2007; Hastings et al., 2010). Poor performance of DNDC is often associated with poor parameterization of soil hydrology and the nitrifying and denitrifying bacteria functions (Li et al., 2006, 2012). For C and N cycling processes to be properly calibrated in DNDC, SOC together with soil temperature, moisture, $\mathrm{NO_3^-}$, and $\mathrm{NH_4^+}$ values should be simulated within acceptable ranges of the mean and standard error values of each of the observed variables (Smith & Smith, 2007). Also, the simulation of the background and episodic N_2O emissions should be monitored concurrently with the simulated crop N and crop water uptake (Li et al., 2013). This is done to achieve optimum DNDC parameter values that produce the least discrepancies between the measured and simulated soil GHG emissions and crop yield values. Some statistical metrics used to determine a model's performance in simulating the measured variables include relative error (E), mean difference (M), Pearson's correlation coefficient (r), root-mean-square error (RMSE), index of agreement (d), paired T-tests, lack-of-fit (LOFIT), and coefficient of determination (R^2) (Smith & Smith, 2007). These metrics quantify the total difference (e.g. RMSE), degree of bias (e.g. M and E), and degree of association (e.g. r and R^2) between the simulated and measured values (Smith & Smith, 2007). The difference between the measured and simulated values minus the errors due to measurement variations can be determined using LOFIT (Smith & Smith, 2007).

Generally, DNDC calibration is necessary to improve the simulation of GHG fluxes under different soil and crop management systems, climates, and agroecosystems (Rafique et al., 2011; Li et al., 2017; Myrgiotis et al., 2018; Zimmermann et al., 2018). Calibrating the model against measured field values ensure the selection of optimum model parameter values to simulate daily moisture, temperature, $\mathrm{NH_4^+}$, and $\mathrm{NO_3^-}$ dynamics in soils, as well as for crop growth processes

(Foltz et al., 2019; Sleutel et al., 2006; Smith et al., 2019). Some DNDC modelling studies of eastern Canadian agroecosystems showed that with minimal adjustments to DNDC parameters, the measured field values where generally well-represented within acceptable error values (e.g. low RMSE values) (Smith et al., 2008; Sansoulet et al., 2014; Guest et al., 2017). In a study by Li et al. (2017), adjusting only the thermal degree days for crop maturity and the root: shoot ratio improved the simulation of daily soil CO_2 fluxes and temporal offset in the soil CO_2 fluxes for soybean under both monoculture and rotation. Meanwhile, in some other cases, particularly when testing DNDC for novel scenarios, e.g. on sites fertilized with mineral N in combination with either nitrification inhibitor or urease inhibitor, detailed representation of the soil water and thermal dynamics and the soil-plant-atmosphere C and N exchange is needed to calibrate DNDC (Smith et al., 2002; Zimmermann et al. 2018; Smith et al., 2020). One major challenge in using DNDC is that the water and N dynamics in soils are complex and cannot be estimated with great certainty (Li et al., 2017). Therefore, to minimize systematic errors, untested scenarios in DNDC (e.g. C and N dynamics when biosolids are land-applied) require site-specific calibration and subsequent validation using independent empirical data sets to ensure the model's consistency in simulating agroecosystem dynamics (Smith et al., 2008).

2.5.6. Validation of DNDC for Estimation of Seasonal and Inter-Annual GHG Emissions from Soils Amended with Biosolids in Canada

Validating DNDC for simulating GHG fluxes from soils amended with biosolids under various Canadian soils and climatic zones is an important step towards generating representative emission factors for the national GHG inventory. Validating process-based models for use in simulating biogeochemical processes is challenging due to the many variables and non-linear interactions between the fitted parameters (Hastings et al., 2010). Across the world, many researchers have validated DNDC for simulating spatio-temporal dynamics of C and N in various agroecosystems, such as those fertilized with animal manure or mineral fertilizer (Beheydt et al., 2007); animal waste (Brown et al., 2002); and urea with or without nitrification inhibitors (Cui et al., 2014). In Canada, some researchers have also validated DNDC under different management practices across different agroecosystems. For instance, He et al. (2018) validated DNDC on a winter wheat-maize-soybean rotation under conventional tillage and no tillage practices at Woodslee, ON, prior to using DNDC to predict the effects of various climate change scenarios of crop yields and N_2O emissions. Also, a study by Smith et al. (2002) validated DNDC on crop fields in eastern (Ontario) and western (Saskatchewan) Canada amended with cattle manure and either mineral fertilizer or no fertilizer, respectively. However, using a model in a novel scenario requires model validation for building user confidence in model predictions (Shaffer et al., 2001). Model validation is particularly important when simulating multi-year C and N dynamics of agroecosystems across Canada, which are amended with vastly heterogenous types of organic materials, such as biosolids.

Model validation over extended time scales minimizes under- and over-estimation of response variables and model inconsistencies. For instance, Qin et al. (2013) reported better simulation of seasonal GHG emissions over longer time scales as compared to shorter ones, indicating that the sensitivities of simulated soil GHG emissions to some important parameters were time-dependent. DNDC does not simulate the effect of long-term tillage practices on soil bulk density and its resulting effect on N_2O emissions as would be expected in a typical agricultural soil under conventional tillage over so many years (Uzoma et al., 2015; Maharjan et al., 2018). In addition to multi-year simulations, when developing national GHG inventories, multiple site-based model validation reduces inconsistencies in the simulation of spatial variations in water, C, and N dynamics in nitrogen-fertilized soils. For example, Brown et al. (2002) reported that, when DNDC was parameterized with site-specific data, the discrepancies between measured and simulated historical N_2O emissions from several UK test sites were reduced. In another study, Beheydt et al. (2007) reported significant under- or over-estimates when similar simulations were done across several Belgian test sites using default data for water-filled pore space. However, these discrepancies in estimating N_2O emissions were reduced across all test sites after water-filled pore space at both wilting point and field capacity were adjusted to reflect the soil conditions on the test sites. In some cases, even with measured site-specific input parameters, validation studies have reported underestimation by DNDC of GHG fluxes and soil moisture in relatively dry years. According to Smith et al. (2018), poor estimation by DNDC of soil water content during the growing season occurs mainly due to two reasons. First, older versions of the model cannot simulate water uptake from the water table through soil capillary rise or direct uptake by roots. Second, older versions of the model did not include root density functions to represent higher density of roots near the soil surface, leading to the underestimation of soil water content in the deeper profile and overestimates at the soil surface. These shortcomings are common in previous versions of DNDC, but the revised version DNDCv.CAN features improvements in the hydrology sub-routine which could improve estimates of GHG emissions and C and N cycling in general (Smith et al., 2018).

2.5.7. Sensitivity and Uncertainty Analysis in GHG Emissions using DNDC

The high temporal and spatial variability of ecological drivers together with the non-linear relationships between them make biogeochemical processes challenging to quantify (Li, 2000;

Bouwman et al., 2002). According to Shaffer et al. (2001), the efficacy of process-based models in estimating GHG emissions, particularly N_2O, is limited by the temporal and spatial resolution of experimental data, lack of definite information for partitioning the C and N pools and determining their different transformation rates, and scant knowledge about parameter uncertainty. These limitations, coupled with field measurement errors, systematic error during GHG analysis, inherent randomness, and subjective judgement make simulations using process-based models vulnerable to error propagation (Uusitalo et al., 2015). This concern becomes even more consequential when a model is being tested for novel scenarios or is used for simulations at large temporal and spatial scales (Chen et al., 2008). An approach to minimize such simulation errors is to quantify the sensitivity of the model to changes in the values of critical parameters (Shaffer et al., 2001). Uncertainty analysis is used in DNDC simulation studies to estimate the distribution and confidence intervals of simulated values, and to develop plans to further reduce uncertainties.

Sensitivity and uncertainty analysis in previous studies show that spatial heterogeneity (e.g., of soil properties) is one key factor influencing GHG emissions from arable soils (Li et al., 2004; Fitton et al., 2017). Mathematical approaches such as the most sensitive factor (MSF), Monte Carlo, Sobol, and Morris methods have been used to estimate the uncertainty arising from the variation of multiple parameters (Qin et al. 2013). For reporting GHG emissions on a national scale, uncertainties are generally quantified on annual time steps for each spatial unit prior to aggregation (IPCC, 2019). However, due to limitations in computing resources and time, full Monte Carlo simulations may not be feasible or sensible to apply to every spatial unit in a country.

Uncertainties introduced in DNDC simulations by spatial heterogeneity may be addressed by using the MSF approach, while those introduced by temporal variation can be addressed using time-intensive, long-term empirical data collection (Qin et al., 2013). Using the MSF approach, a set of maximum and minimum values of the most sensitive soil and environmental factors of a spatial unit are each used in two simulation runs to produce an emissions range representative of the variations in the given soil properties and environmental variables (Li et al., 2004). The MSF approach was also used by Li et al. (1996) for nationwide estimation of N_2O emissions from all US states and found fertilizer inputs and tillage to be the most sensitive factors affecting N_2O emissions at the national scale. On the other hand, initial SOC, tillage, and soil temperature were found to be the factors that most affected CO_2 emissions (Hastings et al., 2010; Abdalla et al., 2011). Temporal variability may also have significant influence, as single-year sensitivity analysis may fall short of representing the long-term effect of parameter uncertainty on model prediction (Qin et al., 2013). Also, uncertainty in the input data and model structure are other sources of uncertainty in model simulation (Uusitalo et al., 2015).

Uncertainty analysis is important for determining the likely contributions of management, climate, and soil to GHG emissions under Canadian conditions given the size and number of ecozones in Canada. DNDC has built-in functions for both the MSF and Monte Carlo methods of uncertainty analysis. The Monte Carlo simulation involves multiple runs of a model using different, randomly chosen sets of parameter values. Li et al. (2000) found that the results from DNDC uncertainty analysis using MSF approach and Monte Carlo approach coincided 60–90% of the time. Due to the computational requirements of a full Monte Carlo simulation, model input uncertainty can be evaluated using the MSF, Morris, Sobol, or MSF+Morris approach to provide a range of uncertainty based on input variance (Qin et al., 2013). Then, structural uncertainty can be evaluated by comparing DNDC-simulated values to good quality empirical observations or through inter-model comparisons (IPCC, 2019).

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Connecting text to Chapter 3

Chapter 2 provided a review of the approaches for estimating greenhouse gas (GHG) emission factors (EF) associated with agricultural land application of biosolids in Canada to be used in the national GHG inventory. A review was done of the Intergovernmental Panel on Climate Change (IPCC) protocols, including process-based modelling approaches, specifically the DeNitrification and DeComposition (DNDC) model. Simulation of decomposition, nitrification, and denitrification processes by DNDC were discussed and a review of calibration, validation, sensitivity analysis, and uncertainty analysis were included.

In Chapter 3, we describe a 92-day incubation study of soil organic carbon degradation and nitrogen mineralization in loam soil amended with mesophilic anaerobically digested, composted, or alkaline-stabilized biosolids under two different moisture conditions. We determine the fractions of C left at the end of the experiment and use that information to choose the equations and coefficient values to describe the kinetics of C and N transformation under both moisture conditions for all three biosolids. The knowledge from this study will be useful for parameterizing DNDC to improve the simulation of C and N cycling in Canadian agroecosystems amended with biosolids.

The following manuscript reporting Chapter 3 results has been submitted for review: Obi-Njoku, Gonzalez-Pavia, A., Boh, M. Y., Price, G.W., and Clark, O. G. (***under review***). Carbon and nitrogen mineralization kinetics of three different types of biosolids. Soil Science Society of America Journal.

Chapter 3. Carbon and Nitrogen Mineralization Kinetics of Different Types of Biosolids Applied to Agricultural Soil

Okenna Obi-Njoku, Michael Yongha Boh, Andrea Gonzalez-Pavia, G.W. Price, and O. Grant Clark

Abstract

A controlled environment study was conducted to assess how differently processed sewage solids, also referred to as biosolids, would impact the rate of carbon and nitrogen mineralization under varying soil moisture conditions. The study aimed to estimate parameter values for modelling the degradation of three biosolids in soil. A soil was amended with either composted, mesophilic anaerobically digested (digested), or alkaline-stabilized biosolids, under soil moisture of 29% water-filled pore space (WFPS) and 49% WFPS. Gas and soil samples were collected and analysed for changes in concentrations of carbon dioxide (CO_2) and nitrous oxide (N_2O) emissions, as well as soil nitrate (NO_3^-) and ammonium (NH_4^+). Then, four different first-order models were fitted to the measured cumulative CO_2-C and N_2O-N emissions resulting in a coefficient of determination (R^2) > 0.98, while soil NO_3^- and NH_4^+ concentrations were $R^2 > 0.65$ and $R^2 > 0.93$, respectively. C mineralization was higher under 49% than 29% WFPS soil moisture conditions. Under soil moisture of 49% WFPS, 79% of the digested biosolids carbon degraded in the soils compared to 52 and 8% for alkaline-stabilized and composted biosolids, respectively. This study shows how C and N mineralization rates may differ between humid and semi-arid regions, as well as during wet and dry cycles of the growing season. It also shows that either of the four first-order models are capable of simulating degradation of different types of biosolids in this agricultural soil, as well as provide useful coefficients for parameterizing mechanistic models.

Keywords: Sewage solids treatment, Biosolids, Carbon and nitrogen mineralization, First-order models

Abbreviations: CEC, cation exchange capacity; CMC, complementary mineralization coefficient; DM, dry matter; DNDC, denitrification and decomposition model; EC, electrical conductivity; GHG, greenhouse gas; NMC, net mineralization coefficient; OM, organic matter; SOC, soil organic carbon; SOM, soil organic matter; TC, total carbon; TN, total nitrogen; WFPS, water-filled pore space

3.1. Introduction

Returning organic C and plant nutrients in municipal biosolids to agriculture soils is one way of improving the health and sustainability of our food production system. Once applied, biosolids decompose and release CO_2 and N_2O into the atmosphere, as well as NO_3^- and NH_4^+ ions into the soil that are available for plant uptake (Lal, 2013; Gougoulias *et al.*, 2014). Biosolids application also builds soil organic carbon content and, in some cases, ameliorate soil pH for increased soil microbial activity. Each year, Canadian farmers apply about 50% of the 780,000 dry tonnes of municipal biosolids generated (Cheminfo Services Inc., 2018). As a signatory to the Copenhagen Accord of the United Nations Framework Convention on Climate Change (UNFCCC), Canada is committed to reporting its greenhouse gas (GHG) emissions from all sources. To date, emissions from land application of biosolids have not been included in the National Inventory Reports due to a lack of empirical data (Environment and Climate Change Canada, 2018).

Biosolids in Canada are typically processed by digestion (aerobic and anaerobic), alkaline stabilization, and composting (Christie *et al.*, 2001; Rubio-Loza & Noyola, 2010; Ippolito *et al.*, 2010; Dentel & Qi, 2013) which makes them different in their biological stability, pH, carbon-to-nitrogen ratio (C/N), morphology, and forms of C (Jamal *et al.*, 2011; Li *et al.*, 2013; Rigby *et al.*, 2016; Cheminfo Services Inc., 2017). Due to these differences, the impact of applying each biosolids type to agricultural soils on GHG emissions could differ across climatic zones (Rochette *et al.*, 2018).

Soil moisture content and biosolids characteristics are known to affect the decomposition kinetics of biosolids C and N (Gilmour *et al.*, 1996; Baral *et al.*, 2016; Charles *et al.*, 2017). The rate of organic matter (OM) degradation in the soil can be measured by tracking the rate of soil respiration (Knapp *et al.*, 1983) or comparing the fraction of OM remaining to that at the start of the process (Gregorich *et al.*, 2017; Pei *et al.*, 2019). In addition, single or multiple exponential decomposition functions can be used to model the dynamics involved in OM degradation (Borgen *et al.*, 2011). To account for the heterogeneous nature of biosolids C, a suitable modelling approach is to use a multiple-pool equation with a specific decomposition rate for the different types of OM (Gillis & Price, 2011). This approach has been used to model C mineralization for different types of biosolids in soils with a percentage moisture content between 11 to 52% (Gilmour *et al.*, 2003). They suggested that using different types of biosolids under soil moisture regimes may have different implications on GHG emissions under agricultural field conditions.

Running long-term field experiments to determine the contribution of agricultural use of biosolids to GHG emissions across Canada is both expensive and time-consuming. To bypass these challenges, researchers have used mechanistic models (e.g. Denitrification and Decomposition (DNDC) model (Li *et al.*, 1992) and DayCent (Parton *et al.*, 1998)) to assess the effect of using manure, compost, and other organics on C degradation rates, soil chemical properties (e.g., mineral N concentration and pH) and GHG emissions in soils (Brilli et al., 2017). However, there is scant evidence in the scientific literature of any mechanistic models parameterized to simulate C and N dynamics in soils amended with biosolids, globally. During preliminary investigations (unpublished), we found that the default parameters in DNDC used to simulate C and N dynamics in soils fertilized with urea and different livestock manures overestimated CO_2 and N_2O emissions when used for biosolids applied on soil near Montreal, Canada.

To accurately estimate GHG emissions from biosolids amended soils in Canada, it is necessary to understand the kinetics of organic C decomposition and N mineralization under distinct soil moisture regimes that reflect those in most Canadian agrizones. The DNDC model is an attractive tool for this due to its ability to account for the different forms of carbon found in organic materials (Fernández *et al.*, 2007). The model requires the input of decomposition rate coefficients for different types of biosolids which can be derived from empirical experimental data (Zacháry *et al.*, 2018). Gilmour *et al.* (1996) identified fast and slow rates of decomposition corresponding to the labile (e.g., cellulose, hemicellulose, and proteins) and recalcitrant (e.g., lignin, waxes, resins, and tannins) carbon fractions in biosolids, respectively. For this double-pool model, the rates of decomposition of the labile and recalcitrant carbon fractions were 0.025 d^{-1} and 0.00287 d^{-1}, respectively, assuming both organic carbon pools decomposed simultaneously. When the labile and recalcitrant organic carbon fractions were assumed to decompose sequentially, the decomposition rates were 0.154 d^{-1} and 0.00297 d^{-1}, respectively. Some biosolids exhibited only one decomposition phase, perhaps due to a slow overall rate of decomposition (Gilmour *et al.*, 2003). This ambiguity demonstrates that simple models are often inadequate to represent the degradation kinetics of biosolids.

The main objectives of this study were to 1.) assess the ability of simple mathematical models to predict biosolids C and N mineralization under simulated field conditions; 2) investigate the effect of soil moisture content and biosolids type on OM degradation (i.e., C and N mineralization) kinetics; and 3) asses the changes in soil pH and electrical conductivity during SOM degradation and how they correlate with soil nitrate and ammonium concentrations. The data generated will provide insights on how to calibrate mechanistic models to simulate the decomposition of these biosolids and improve the predictive capacity of such models under Canadian conditions.

3.2. Materials and Methods

An incubation experiment was conducted under a controlled environment to determine the rate of C and N mineralization for three types of biosolids used in Canada as influenced by soil moisture conditions.

3.2.1. Biosolids and Soil

Three types of commonly used biosolids in Canadian agriculture were used for this experiment, namely (1) mesophilic anaerobically digested biosolids collected from a municipal biomethanization centre (St. Hyacinthe, Quebec) (henceforth, called digested biosolids); (2) alkaline-stabilized biosolids, obtained from N-Viro®, Walker Environmental, Goffs, Nova Scotia which was produced using admixtures that increase the pH to levels >12 (Christie et al., 2001); and (3) composted biosolids obtained from Gaudreau Compost, Victoriaville, Quebec. Composted biosolids were produced by co-composting municipal sewage sludge with wood chips (>40% wet mass). After collection, all three types of biosolids were stored at -18°C for three weeks and then defrosted by placing them in a refrigerator at 4˚C for two days before adding them to the soil.

The soil used for this experiment was collected from the surface layer (15 cm depth) of a field at the Emile A. Lods Agronomy Research Centre, McGill University, Ste-Anne-de-Bellevue, Quebec (45º25′38″ N, 73º55′45″ W). The soils here are classified as Gleysolic (loam) with 190 g kg^{-1} clay, 490 g kg^{-1} sand, 320 g kg^{-1} silt, 1.21 g cm^{-3} bulk density, and 0.24 cm cm^{-3} volumetric field capacity. No fertilizers or biosolids had been applied to the field from where these soil samples were collected for at least 3 years. The chemical characteristics of the biosolids and soil used in the experiment are shown in Table 3.1.

Table 3.1. Chemical characteristics of soil and biosolids used in the experiment as reported by the suppliers.†

Parameter	Soil	Digested biosolids	Alkaline-stabilized biosolids	Composted biosolids
Organic matter (%)	1.5 ± 0.1	67.0 ± 0.2	20.0 ± n/a	75.2 ± n/a
pH (H_2O)	5.8 ± 0.0	8.2 ± n/a	10.8 ± 0.0	7.6 ± n/a
Dry matter (%)	1.5 ± 0.0	19.0 ± 0.2	62.0 ± 0.0	38.1 ± n/a
Electrical conductivity (µS cm^{-1})	403.0 ± 2.0	n/a	n/a	n/a
Cation exchange capacity (cmol kg^{-1})	7.2 ± 0.1	n/a	n/a	n/a
Total carbon (mg g^{-1})	13.4 ± 0.7	333.7 ± n/a	164.0 ± n/a	367.5 ± n/a
Total nitrogen (mg g^{-1})	1.1 ± 0.1	71.0 ± 0.5	10.0 ± 0.2	24.5 ± 0.1
Ammonium (NH_4^+) (µg g^{-1})	1.5 ± 0.4	1.1 ± 0.0	0.2 ± 0.0	0.4 ± n/a
Nitrate (NO_3^-) (µg g^{-1})	9.0 ± 1.3	n/a	n/a	n/a
Total phosphorus (%DM)	n/a	3.3 ± 0.0	n/a	0.9 ± n/a
Phosphate (P_2O_5) (µg g^{-1})	n/a	7.5 ± 0.0	0.0 ± n/a	2.1 ± n/a
Potassium K (%DM)	n/a	0.6 ± 0.0	n/a	0.4 ± n/a
Potash (K_2O) (µg g^{-1})	n/a	0.7 ± 0.0	0.1 ± n/a	0.5 ± n/a
C/N	11.8 ± 0.2	4.7 ± 0.3	16.4 ± 2.0	15.0 ± 0.4

† Values in this table are mean (± standard error); n/a = not available; and C/N = C to N ratio.

3.2.2. Incubation Experiment

The incubation experiment was conducted in the Soil Ecology Laboratory at McGill University. Soil samples from the field were air-dried, sieved through a 2-mm mesh, and mixed to obtain a homogenous sample. A hundred grams of the homogenized soil was placed into each of 1-L Mason jar used, rewetted to 29% WFPS, and incubated in a dark room at 20°C for two weeks. After that, 240 mg of digested biosolids, 380 mg of alkaline-stabilized biosolids, and 780 mg of composted biosolids were added to the respective jars according to the treatment. To ensure that N was not a limiting factor to C mineralization, about 15 mg of urea was added to alkaline-stabilized and composted biosolids. This decision was informed by preliminary data (unpublished) from the research site at Emile A. Lods Agronomy Research Centre which suggested that with equal N application rates, CO_2 and N_2O emissions from digested biosolids treatments were higher than those from composted biosolids and alkaline-stabilized biosolids. After biosolids were added to the jars, deionized water was added and adjusted to achieve the target WFPS for each treatment combination. The 29% and 49% WFPS moisture conditions chosen in this study cover the range of soil moisture conditions that favour soil microbial activity suggested by Schaufler *et al.* (2010). To ensure that moisture content remained the same through out the experiment, Mason jars were weighed weekly. The calculated total C and N contents in each treatment combination are shown in Table 3.2.

The experimental factors were four fertilized treatments (i.e., digested biosolids, alkaline-stabilized biosolids plus urea, composted biosolids plus urea, and a treatment receiving only urea as a control) and two soil moisture regimes (i.e., 29 and 49% water-filled pore space [WFPS] representing dry and wet conditions, respectively. The 4 × 2 factorial experiment (i.e., 8 experimental units) was replicated 4 times in a randomized complete block design (RCBD) for non-destructive gas sampling. A second experiment with the same treatment factors was conducted for destructive soil sampling. It consisted of 228 experimental units (i.e., 8 treatments × 4 replicates

× 7 sampling times). Both experiments were run simultaneously under the same controlled conditions for 92-days.

Table 3.2. Estimated field equivalent amounts of C and N applied as biosolids and/or urea.

Amendment	**Nitrogen** (kg N ha^{-1})			**Carbon** (kg C ha^{-1})			**C/N**
	Biosolids	Urea	Total	Biosolids	Urea	Total	
Digested biosolids	58.8	0	58.8	276.2	0	276.2	4.7
alkaline-stabilized biosolids + urea	42.2	85.6	127.8	692.1	37.2	729.3	5.7
Composted biosolids + urea	132.2	82.4	214.6	1982.2	35.8	2018.1	9.4
Urea	0	120.0	120.0	0	52.2	52.2	0.4

3.2.3. Soil Sampling and Analysis

Soil samples were collected from 4 replicates of each treatment without replacement on days 1, 3, 5, 15, 35, 56, and 72 to analyze for NO_3^-, NH_4^+, pH, and electrical conductivity (EC). After every sampling event, soils were stored in sealed impermeable plastic bags at -5°C before analysis. pH and EC in the soil samples were measured from a 1:2 soil-water extract (Bado *et al.*, 2016) using a pH meter (Accumet® AR 10, Fisher Scientific, Toronto, Canada) and a conductivity meter (CDM 83, Radiometer A/S, Copenhagen, Denmark), respectively. Inorganic nitrogen (NH_4^+ and NO_3^-) was extracted from the soil samples in a 0.5 M K_2SO_4 solution and analyzed on a microplate spectrophotometer (µQuant^{TM}, Bio-Tek Instruments Inc., Burlington, VT, USA) as per Maynard & Kalra (1993). To determine the NO_3^- content, NO_3^- and nitrite (NO_2^-) in the remaining subsample were reduced to NH_4^+ using Devarda's alloy and incubated for 3 h at 35°C. The difference in NH_4^+ content between the two subsamples was assumed to correspond to the NO_3^- fraction in the soil, considering that NO_2^- content was negligible (Sheppard & Bittman, 2013). Soil samples collected at the start of the experiment were analyzed for total carbon (TC) and total nitrogen (TN) in a CN analyzer (Thermo Finnigan Flash EA 1112 Series, Thermo Fisher Scientific Inc, MA, USA) following the procedure described by Skjemstad & Baldock 2006 and Rutherford *et al.* 2006, respectively.

3.2.4. Gas Sampling and Analysis

Gas samples were collected 18 times from four replicates of each experimental treatment on days 0, 1, 3, 5, 7, 10, 12, 15, 21, 28, 35, 42, 49, 56, 63, 70, 77, and 91. During sampling, 20 mL of gas was drawn from the headspace of each jar using a syringe, injected into pre-evacuated 12-mL Labco Exetainer^{TM} vials (Labco Ltd., High Wycombe, UK) and stored in the lab until analysis. After every sampling event, the lids of the jars were removed for 10 to 15 min to dissipate the remaining gas in the headspace. On each day of sampling, ambient air was also sampled from the headspace in the centre of the incubation chamber housing the experimental units. In the laboratory, the concentrations of CO_2 and N_2O were analyzed by gas chromatography (Bruker 450-GC, Bruker Daltonik GmbH, Bremen, Germany). The mass concentrations of CO_2-C and N_2O-N in the headspace were calculated using the Ideal Gas Law and converted to emissions per gram of dry soil using Equation 3.1 (Hogg et al., 1992):

$$F = \left[\frac{Cs - Ca}{M}\right] \times V \qquad \text{Eq. 3.1}$$

F is gas flux (μg g^{-1} dry soil), *V* is the effective volume of the headspace (L), C_s is the sample mass concentrations of CO_2-C (or N_2O-N), C_a is the ambient mass concentrations of CO_2-C (or N_2O-N) in the sampling environment (μg L^{-1}) and *M* is the total mass of dry soil in the jar (g).

3.2.5. Carbon and Nitrogen Mineralization Models

Following a general first-order equation for OM degradation (Jenkinson, 1990; Gilmour *et al.*, 1996), four nonlinear models (**Table 3**) were fitted to the cumulative quantities of CO_2-C and N_2O-N measured during the experiment. The *single-pool first-order exponential* model represents C and N substrate decomposition in biosolids and soil as a single pool with a single mineralization rate throughout the incubation period. The *first-order + zero-order* model is a hybrid model with a labile and resistant pool for C and N. The coefficient X_1 (mg g^{-1} of dry soil) represents the mass of the small pool of short-lived, labile carbon which mineralizes during the early stages of incubation. Meanwhile, the second pool, k_3t (mg g^{-1}) represents the large pool of resistant C or N that mineralizes slowly at a constant rate during the middle and later stages of incubation. The *special first-order double-pool* (Special first-order) model represents the quick C or N flush and the labile C or N as two distinct pools. Finally, the *double-pool simultaneous decomposition* (*double-pool first-order)* model represents the mineralization of C and N substrates as first-order exponential decay of labile and resistant pools occurring simultaneously at specific rates. The concentrations of NO_3^- and NH_4^+ measured during the experiment were fitted to Equations 3.2 and 3.3 below.

$$NH_4^+(t) \ = \ N_0 \times exp^{-k_4 t} \qquad \text{Eq. 3.2}$$

$$NO_3^-(t) \ = \ N_1 \times (1 - exp^{-k_5 t}) \qquad \text{Eq. 3.3}$$

$NH_4^+(t)$ and $NO_3^-(t)$ represent the cumulative net mineralization and nitrification at time t (days), respectively; N_0 and N_1 represent the size of the extractable pools of NH_4^+ and NO_3^-, respectively; and k_4 and k_5 correspond to the mineralization and nitrification rates per day (d^{-1}), respectively.

The model parameters were estimated using the *fitModel* function of the R mosaic package (v1.8.3; Pruim, 2021) and the coefficient of determination (R^2) was used to assess the models' goodness-of-fit.

Table 3.3. Models describing cumulative CO_2 or N_2O emissions from soil.

Model	**Form**	**Parameter description (units)**
Single-pool first-order	$X(t) = X_0(1 - exp^{-k_0 t})$	$X(t)$ = cumulative C or N emitted (mg g^{-1}) at time t (d) X_0 = potentially mineralizable C or N (mg g^{-1}) k_0 = first-order rate constant (d^{-1})
Double-pool first-order	$X(t) = X_1 exp^{-k_1 t} + X_2 exp^{-k_2 t}$	X_1 = size of the labile pool (mg g^{-1}) X_2 = size of the recalcitrant pool (mg g^{-1}) k_1 = labile pool rate constant (d^{-1}) k_2 = recalcitrant pool rate constant (d^{-1})
First-order + zero-order	$X(t) = X_1\left(1 - e^{-k_1 t}\right) + k_3 t$	$k_3 t$ = size of recalcitrant linear C or N pool (mg g^{-1}) k_3 = recalcitrant linear pool rate constant (mg g^{-1} d^{-1})
Special first-order	$X(t) = X_1\left(1 - exp^{-k_1 t}\right) + X_f$	X_f = size of quick flush pool (mg g^{-1})

3.2.6. Mineralization Parameters

The mineralization capacity of biosolids amended soil was estimated by calculating the percentage of initial OM that had degraded at the end of the experiment. This term is called the net mineralization coefficient (NMC; Eq. 3.4). Complementary mineralization coefficient (CMC) is the mineralizable portion of C in biosolids which was estimated at the end of the experiment using Eq. 3.5. NMC and CMC were calculated after accounting for the estimated cumulative CO_2 emissions resulting from C applied through urea in the corresponding treatments. It was assumed that urea hydrolysis released 98% of the C urea in the form of CO_2 within the first eight days of urea application (Tierling, 2016; Souza *et al.*, 2017; Wang *et al.*, 2020). The CMC values for N were not calculated as we did not control for the effect of complementary N addition to either the alkaline-stabilized or composted biosolids on soil N mineralization in this study.

$$NMC(\%) = \left(\frac{R_{te}}{R_{ta} + R_{ts}}\right) \times 100 \qquad \text{Eq. 3.4}$$

$$CMC(\%) = \left(\frac{R_{te} - R_{tes}}{R_{ta}}\right) \times 100 \qquad \text{Eq. 3.5}$$

R_{te} (mg g^{-1}) is the total C or N released as CO_2 and N_2O, respectively; R_{ta} (mg g^{-1}) is the total organic C or N added with the biosolids; R_{ts} (mg g^{-1}) is the total organic C or N in the soil before application of biosolids; R_{tes} (mg g^{-1} of dry soil) is the C evolved as CO_2 from the control treatment (i.e., the urea treatments under the corresponding soil moisture conditions for each treatment).

3.2.7. Statistical Analysis

The data generated from the incubation experiments were analyzed and fitted to models using the open-source statistical software package R (version 3.6.1; R Core Team, 2020). Before subjecting datasets to statistical further statistical analysis, they were checked for homogeneity of variance and normality using the Shapiro-Wilks test. The datasets of CMC and NMC for both carbon and nitrogen, together with the dataset of cumulative N_2O were normalized by log transformation as $p < 0.05$ following the Shapiro-Wilks test. Thereafter, a two-way ANOVA ($\alpha = 5\%$) was performed to examine the effects of biosolids, soil moisture regime, and their interactions on cumulative CO_2 and N_2O emissions, NMC and CMC after 92 days and, soil pH, and EC on days 3 and 72 of the experiment. Days 3 and 72 correspond respectively with the earliest and latest days for which soil samples were collected after biosolids and moisture treatments were applied. Also, a three-way repeated measures ANOVA ($\alpha = 5\%$) was performed to examine the effects of biosolids, soil moisture regime, sampling days (time), and their interactions on soil $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ concentrations. Tukey's pairwise comparison of treatment means was performed using the *LSmeans* function. The *cov* function was then used to find the Pearson coefficient of correlation between all pairs of measured variables (Watier *et al.*, 2016).

3.2.8. Applying Kinetic Parameters Derived from the Incubation Study to Simulate N_2O and CO_2 Emissions using DNDC

3.2.8.1. Description of the Revised DNDC Model

The DNDC model was originally developed to simulate N_2O, CH_4, and CO_2 emissions from agricultural soils in USA on a daily time-step (Li et al., 1992, 1994). The Canadian version of DNDC (DNDC.vCAN) was developed to better represent Canadian climate, soils, and management conditions (Banger et al., 2020; He et al., 2020). DNDC has six sub-models for simulating soil climate, decomposition, nitrification, denitrification, fermentation, and crop growth. The decomposition sub-model of DNDC simulates SOC decomposition across the full 200 cm heterogenous soil profile in ~1cm increments (Jiang et al., 2020; Smith et al., 2020). Manure (including biosolids) decomposition dynamics are controlled by incoming manure C:N which determines the fractional allocation of manure C to the major soil C pools (litter, microbial, humads, and humus). Decomposition of each C pool occurs independently using first-order kinetics and is regulated by soil temperature and moisture conditions (see Equation 3.6).

$$\frac{dC}{dt} = \mathrm{CNR} * \mu * (S * k_l + (1-S) * k_r) * [C] \qquad \text{Eq. 3.6}$$

[C] is the decomposed organic C (kg C kg^{-1} manure per day), CNR is the C:N ratio reduction factor, t is time (day), S is the labile fraction of organic C compounds in the pool, (1 - S) is the resistant fraction of organic C compounds, k_l is the specific decomposition rate (SDR) of labile fraction (day^{-1}), k_r is the SDR of the resistant fraction (day^{-1}), and μ is the temperature and moisture reduction factor. SDR = 0.074, 0.074, 0.02, 0.33, 0.04, 0.16 and 0.006 (day^{-1}) for very labile litter, labile litter, resistant litter, labile microbes, resistant microbes, labile humads, and resistant humads, respectively.

The C:N ratio reduction factor is computed by DNDC using Equation 3.7. Details of the DNDC model's schematic for simulating manure/biosolids C decomposition is shown in Appendix D of Chapter 4 (Section 4.8.4).

$$\text{CNR} = 0.2 + 7.2 * \left(\frac{NP}{CP}\right) \qquad \text{Eq. 3.7}$$

CP is the C produced by potential residue decomposition per day (without CNR reduction factor) (kg C ha^{-1}), *NP* is the N produced by potential residue decomposition per day plus free NH_4 and NO_3^- in soil (kg N ha^{-1}).

The model framework simulates N_2O emissions based on the ‘‘anaerobic balloon” concept (Li et al., 2000), and allows the user control of trace gas parameters that are difficult to measure but can have significant impacts on N cycling. Such parameters include the release of denitrifier substrates during freeze-thaw conditions, overall rates of denitrifier and nitrifier growth, and rainfall intensity impacts, to better calibrate site-specific nitrification and denitrification rates as driven by moisture, nitrogen, and microbial dynamics in soils (Smith et al., 2020). The anaerobic balloon (regulated by soil Eh via the Nernst equation (see Section 4.8.4) cycles the mineralized organic N/ammoniacal N from manure/biosolid application into the nitrification and denitrification pathways to evolve trace gas emissions (N_2O, NO, N_2). The NH_4:NH_3 equilibrium framework derives the partitioning of N that may be subject to NH_3 volatilization (see Congreves et al., 2016).

In previous versions of DNDC.vCAN, the sizes of the major soil C pools could be adjusted by the user, while the turnover rates of the soil C pools were based on DNDC's default specific decomposition rates. The revised version of the model allows user-defined manure labile organic C pool size relative to the total manure C pool size. In addition, it allows changes to the decomposition rates and disaggregates the simulation of decomposition of initial soil C pool independent of the manure C pool.

3.2.8.2. Datasets

CO_2 and N_2O emissions datasets were collected from four selected treatments of a replicated (n = 4) field experiment in Ste-Anne-de-Bellevue, QC (described in detail in Chapter 4) growing corn (*Zea mays* L.) with biosolids, urea, or biosolids and urea applied at a targeted N rate of 120 kg N ha^{-1} of available nitrogen. The selected treatments were full-rate urea, digested biosolids, alkaline-stabilized biosolids, and composted biosolids surface spread on the soil surface as those used in this incubation study. Measured CO_2 and N_2O emissions in 2019, out of the three-year (2017 – 2019) data, was selected to compare DNDC's simulated CO_2 and N_2O emissions in 2019 for the four selected treatments.

3.2.8.3. DNDC Simulations

Two simulations were run for each selected treatment using either DNDC's default manure C decomposition parameter values or those derived from the incubation study. Figure A.3.9 shows a scheme describing the simulation process. The initialization, calibration, and validation of DNDC to simulate CO_2 and N_2O emissions for the treatments are explained in detail in Chapter 4 (Section 4.2.3). Also, the input files for the simulations are the same as those described in Chapter

4. For the simulation run using the empirically-derived biosolids C decomposition parameter values, only two changes were made in the input files used in Chapter 4 prior to the simulation runs: (1) the fraction of labile biosolids C pools for each of the biosolids were changed according to the CMC values derived in the incubation experiment, and (2) the decomposition rates were changed according to the values of k_1 (labile pool rate constant) derived per fertilizer type (biosolids and/or urea) when the *double pool first-order model* was fitted to the measured cumulative CO_2 data. The CMC and k_1 values respectively used for the biosolids were 0.79 and 0.325 d^{-1} for digested biosolids, 0.52 and 0.135 d^{-1} for alkaline-stabilized biosolids, and 0.08 and 0.747 d^{-1} for composted biosolids. The site of the field experiment is located in the humid Eastern Canada, as such the biosolids C decomposition parameter values applied in the DNDC simulation were for treatments under 49% WFPS condition. Biosolids C decomposition parameter values remained unchanged for the default simulation and urea treatment runs. The Pearson's correlation coefficient (r) was used to compare the association between the measured GHG emissions against the simulated emissions for each of the treatments using either the default or adjusted parameters

3.3. Results

3.3.1. Carbon Mineralization and Cumulative Carbon Dioxide Emissions

In this study, oxidative losses of C during microbial degradation of soil organic matter (SOM) were estimated after 92 days via cumulative CO_2-C emissions and CMC (Table 3.4). It was found that soil moisture and biosolids type (fertilizer) influenced cumulative CO_2-C emissions (Table A.3.1) at $p < 0.05$. Cumulative CO_2-C emissions were consistently higher under the 49% than under the 29% WFPS soil moisture condition and were in the range of 0.19 to 0.41 mg CO_2-C g^{-1} and 0.15 to 0.36 mg CO_2-C g^{-1}, respectively (Table 3.4). Cumulative CO_2-C emissions were also higher in soils amended with biosolids than in the control treatment which received urea alone regardless of moisture conditions (Table 3.4). It was further observed that CO_2-C emissions from alkaline-stabilized biosolids were significantly higher than emissions from composted biosolids under both soil moisture conditions. Meanwhile, cumulative CO_2-C emissions from digested biosolids were statistically the same as those of the other types of biosolids regardless of soil moisture conditions.

Soil moisture and biosolids type influenced the soil carbon mineralization capacity (NMC-C; Table A.3.2) at $p < 0.05$. Based on the experimental conditions, the NMC of carbon was in the range of 1.2% and 2.9% and decreased by experimental treatment in the following order: alkaline-stabilized biosolids > digested biosolids > composted biosolids > urea. The NMC of carbon in the soil was significantly higher under 49% than the 29% WFPS soil moisture condition. Also, the NMC of carbon in treatments receiving composted biosolids was not different from the urea treatment while being significantly less than those of alkaline-stabilized biosolids.

Table 3.4. Cumulative CO_2-C emissions, and Net Mineralization Coefficient (NMC) and Complementary Mineralization Coefficient (CMC) of carbon from biosolids-amended soils at the end of the experiment.

Treatment[†]		**CO_2-C**[††]	**NMC-C**[††]	**CMC-C**[††]
Fertilizer	**Moisture**	**mg g^{-1}**	**%**	**%**
Composted biosolids	49% WFPS	0.3 ± 0.05^{de}	2.2 ± 0.31^{cd}	8.3 ± 3.08^{a}
Digested biosolids		0.3 ± 0.06^{ef}	2.4 ± 0.44^{de}	78.8 ± 27.32^{b}
Alkaline-stabilized biosolids		0.4 ± 0.02^{f}	2.85 ± 0.06^{e}	51.93 ± 15.92^{b}
Urea		0.2 ± 0.04^{bc}	1.59 ± 0.17^{bc}	-

Composted biosolids	29% WFPS	0.2 ± 0.02 ^{b}	1.4 ± 0.09 ^{ab}	4.5 ± 0.75 ^{a}
Digested biosolids		0.2 ± 0.06^{bcd}	1.8 ± 0.43 ^{bc}	61.5 ± 42.80 ^{b}
Alkaline-stabilized biosolids		0.3 ± 0.06 ^{cde}	2.15 ± 0.36 ^{cd}	45.87 ± 20.85 ^{b}
Urea		0.2 ± 0.01 ^{a}	1.21 ± 0.08 ^{a}	-

[††] *Different letters within a column represent significant differences at $p < 0.05$ based on Tukey's test for pairwise comparison. Value are means ± standard deviation (n = 4).*

The mineralization of biosolids carbon depended only on the biosolids type as seen the values of CMC for carbon (CMC-C; Table A.3.3). According to the CMC values, the fraction of mineralized carbon was higher in digested than in alkaline-stabilized and composted biosolids (Table 3.4). However, the proportion of carbonaceous compounds that was mineralizable in the digested biosolids was highly variable judging from the high standard deviation of CMC. Even though soil moisture conditions did not significantly affect organic C mineralization across the biosolids types, the rate of organic C mineralization between both soil moisture conditions was about 17 percentage points in digested, 6 percentage points in alkaline-stabilized, and 3 percentage points higher in composted biosolids. Under the 49% WFPS soil moisture condition, the percentage of organic C that degraded over the 92-day period was 79% for digested, 52% for alkaline-stabilized, and 8% for composted biosolids. Under the 29% WFPS soil moisture condition, these were 62%, 46%, and 5% for digested, alkaline-stabilized, and composted biosolids, respectively.

3.3.2. Carbon Mineralization Curves and Model Fitting

Soil organic C (initial SOC + applied biosolids carbon) degradation occurred in two phases. The first phase was marked by a fast rate of degradation at the start of incubation depicted by the steep and short-lived CO_2 gradient curve (Figure 3.1). For instance, on Day 6 in the treatment receiving alkaline-stabilized biosolids under 49% WFPS moisture conditions, about 27% of the measured CO_2-C had been released. The observed rate of biosolids degradation at the later stages of the incubation decreased as seen by the decrease in CO_2 emissions. The second phase was characterized by a slower rate of degradation as seen in Figure 3.1.

Cumulative CO_2 emission curves showed an exponential pattern across all treatments (Figure 3.1 and Table 3.5) with a high degree of association ($R^2 > 0.99$) between the observed data and the four exponential models. Also, the biosolids degradation rate constants for single (k_0) and double (k_1) pool models and the sizes of the mineralized C pools (X_0, $X_1 + X_2$, $X_1 + k_3t$, and $X_1 + X_f$) were of similar magnitudes for all four models.

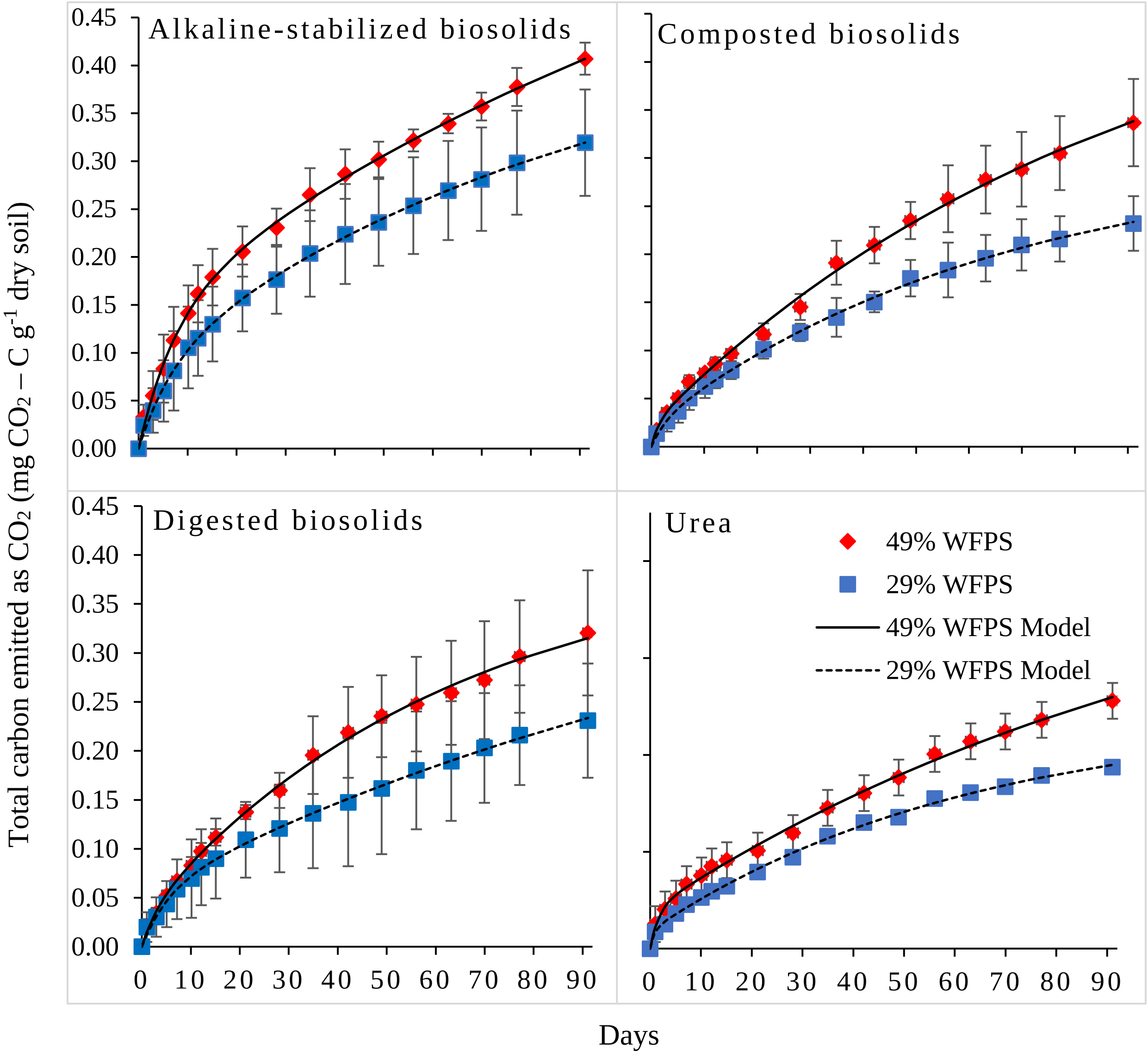

Figure 3.1. Cumulative CO_2 emissions from soils amended with different types of biosolids under 29% WFPS and 49% WFPS soil moisture conditions. *Red diamonds and blue square are means (n = 4) with standard deviation bars. A double-pool first-order model was fitted to the observed data ($R^2 > 0.99$).*

Amongst the four kinetic models, the double pool first-order model provided the best estimate of biosolids degradation across all treatments. In this model, the kinetics of microbial decomposition of biosolids carbon was captured independently as labile and resistant organic C pools, irrespective of soil moisture condition. The double pool first-order model estimated larger sizes of mineralizable C pools (X_1 + X_2) in the 49% than in the 29% WFPS soil moisture treatments, except for digested biosolids treatments. Except for alkaline-stabilized biosolids where approximately 20% of C was within the rapid mineralization phase (X_1), only 10% of the C belonged to this category for all the biosolids types.

Table 3.5. Fitted model parameters and coefficients of determination (R^2) for measured cumulative CO_2 fluxes from incubated loam soil amended with three types of biosolids under 49% and 29% WFPS soil moisture conditions.

Model	**Parameter**	**Treatment**							
		Urea		**Digested biosolids**		**Alkaline-stabilized biosolids**		**Composted biosolids**	
		29% WFPS moisture	*49% WFPS moisture*	*29% WFPS moisture*	*49% WFPS moisture*	*29% WFPS moisture*	*49% WFPS moisture*	*29% WFPS moisture*	*49% WFPS moisture*
First order single-pool	**X_0**	0.204	0.275	0.233	0.340	0.314	0.385	0.256	0.417
	k_0	0.025	0.024	0.028	0.025	0.033	0.037	0.023	0.017
	R^2	0.996	0.990	0.992	0.997	0.995	0.992	0.997	0.997
Double pool first-order	**X_1**	0.018	0.040	0.055	0.031	0.083	0.138	0.022	0.023
	X_2	0.224	0.406	0.390	0.371	0.378	0.583	0.283	0.491
	k_1	1.293	0.624	0.187	0.325	0.147	0.135	0.379	0.747
	k_2	0.016	0.009	0.007	0.016	0.011	0.007	0.015	0.011
	R^2	0.999	0.999	0.999	0.999	1.000	1.000	0.999	0.999
First-order + zero-order	**X_1**	0.074	0.060	0.075	0.136	0.136	0.174	0.096	0.121
	k_1	0.073	0.259	0.128	0.062	0.090	0.107	0.062	0.051
	k_2	0.001	0.002	0.002	0.002	0.002	0.003	0.002	0.002
	R^2	0.996	0.997	0.999	0.999	0.999	0.999	0.998	0.997

Special first order	**X_1**	0.214	0.317	0.246	0.351	0.316	0.382	0.254	0.455
	X_f	0.012	0.024	0.018	0.014	0.019	0.028	0.011	0.014
	k_1	0.019	0.014	0.020	0.020	0.026	0.029	0.019	0.013
	R^2	0.997	0.994	0.994	0.998	0.996	0.994	0.998	0.998

3.3.3. Cumulative Nitrous Oxide Emissions

Cumulative N_2O emissions at the end of the study were generally below 0.6μg N_2O-N g^{-1} of dry soil and were influenced significantly by soil moisture and fertilization ($p < 0.05$; Table A.3.4). Cumulative N_2O emissions were 6 to 10 times higher under the 49% than the 29% WFPS condition, irrespective of the fertilization applied (Tables A.3.5, A.3.6, and A.3.8). The cumulative N_2O emissions did not differ between the treatments receiving alkaline-stabilized, composted, or urea (control) as seen in Table A.3.7. However, under the 49% and 29% WFPS soil moisture conditions, respectively, N_2O emissions were significantly higher in the alkaline-stabilized (0.45 ± 0.25 and 0.05 ± 0.02 μg N_2O-N per g of dry soil) than the digested biosolids treatments (0.18 ± 0.21 and 0.01 ± 0.01 μg N_2O-N per g of dry soil) as seen in Table A.3.8 and Figure 3.2. It is noteworthy to state that digested biosolids received lower N than other biosolids. Also, the variation in the measured N_2O emissions were generally high across all treatments. As such, the NMC values served as the absolute criteria to compare the fraction of N_2O-N emissions relative to initial soil N between the treatments.

The NMC values for N were < 0.04% across all treatments and were higher under 49% than 29% WFPS soil moisture conditions (Tables A.3.9 and A.3.10). The NMC values were not statistically different for the different N fertilization treatments. The CMC of nitrogen was not calculated as there was no unfertilized control treatment to serve as the reference.

3.3.4. Cumulative Nitrous Oxide Emissions Curves and Model Fitting

Nitrous oxide emission rates were nonlinear, starting with an exponential rise, then plateauing over time (Figure 3.2). This pattern was observed for all treatments although the exponential rise in N_2O emission rate was sustained longer in alkaline-stabilized and control treatments.

Except for the control treatment under the 29% WFPS soil moisture condition, cumulative N_2O fluxes were well-represented by the four models ($R^2 > 0.98$) for all treatments (Table 3.6). The single-pool model and special first-order model estimated similar initial N pool sizes and rate constants for all treatments. Meanwhile, the *first-order + zero-order* model estimated larger initial N pools than the *first-order single-pool* and *special first-order* models. The *double-pool first-order* model estimated cumulative N_2O emissions from the control treatment under 29% WFPS moisture conditions with $R^2 = 0.23$.

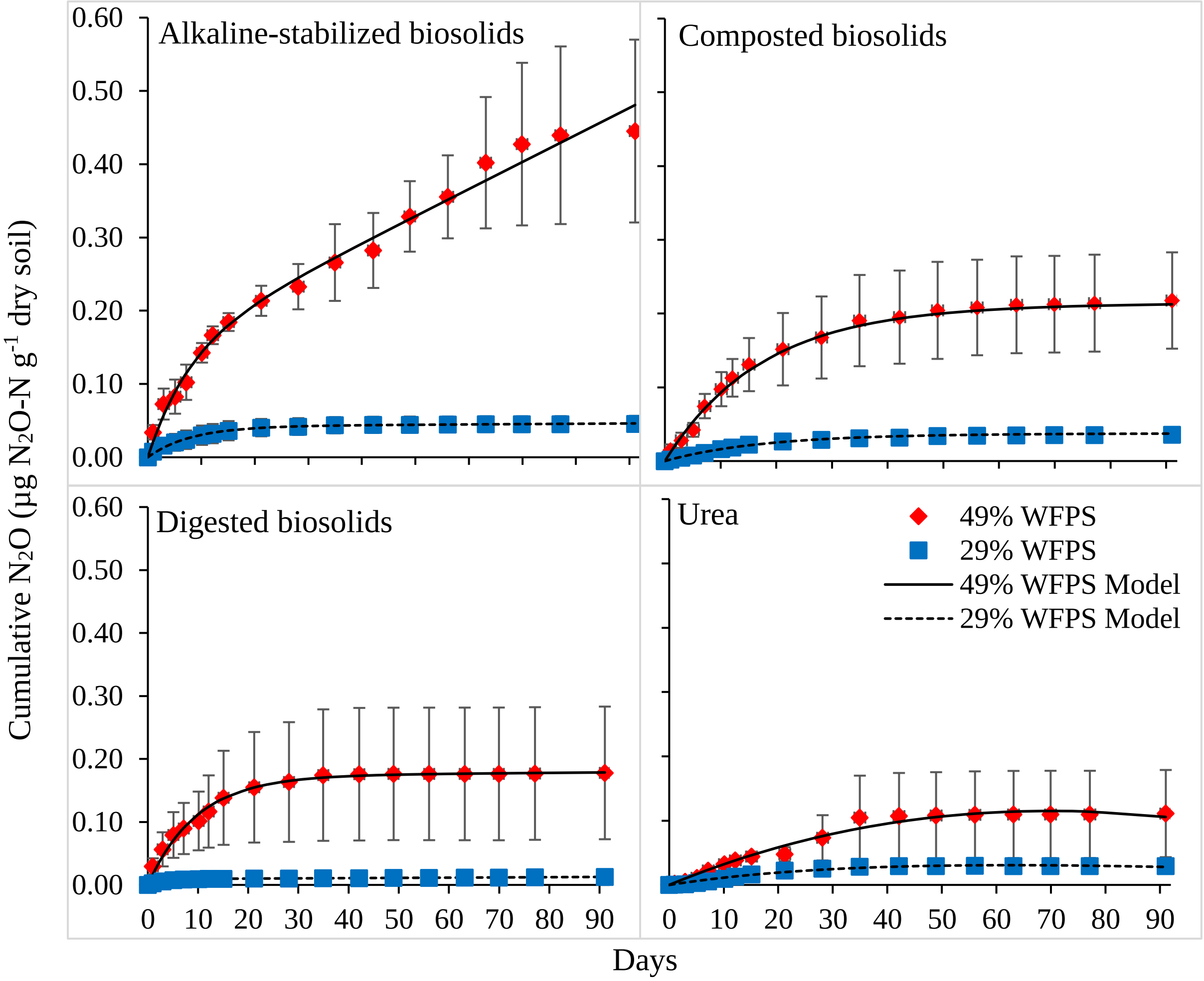

Figure 3.2. Measured and modelled cumulative N_2O emissions from soils amended with different types of biosolids under 29% and 49% WFPS soil moisture conditions. *Red diamonds and blue squares are means (n = 4) with standard deviation bars. A double-pool first-order model (black lines) was fitted to the observed data (*$R^2 > 0.98$*).*

Table 3.6. Fitted model parameters and coefficients of determination (R^2) for measured cumulative N_2O fluxes from incubated loam soil amended with three types of biosolids under 49% and 29% WFPS soil moisture levels.

Model	**Parameters**	**Treatment**							
		Urea		**Digested biosolids**		**Alkaline-stabilized biosolids**		**Composted biosolids**	
		29% WFPS moisture	*49% WFPS moisture*	*29% WFPS moisture*	*49% WFPS moisture*	*29% WFPS moisture*	*49% WFPS moisture*	*29% WFPS moisture*	*49% WFPS moisture*
First-order Single-pool	**X_1**	0.032	0.125	0.011	0.177	0.045	0.479	0.036	0.217
	k_0	0.047	0.033	0.178	0.099	0.113	0.027	0.059	0.057
	R^2	0.989	0.985	0.970	0.996	0.997	0.990	0.999	0.999
Double-pool first-order	**X_1**	0.173	-0.055	0.006	0.136	0.036	0.086	0.040	0.195
	X_2	-0.126	0.161	-0.114	-0.230	-0.105	0.641	0.012	0.218
	k_1	-0.075	0.095	0.370	0.133	0.147	0.253	0.038	0.061
	k_2	1.603	-0.065	0.001	0.001	0.001	-0.010	0.001	-0.001
	R^2	0.231	0.979	0.959	0.992	0.996	0.996	0.988	0.998
First-order + zero-order	**X_1**	0.064	2.428	0.009	0.173	0.042	0.145	0.037	0.214
	k_1	0.026	0.005	0.315	0.103	0.125	0.131	0.058	0.058
	k_2	0.000	0.008	0.000	0.000	0.000	-0.004	0.000	0.000
	R^2	0.992	0.990	0.980	0.996	0.998	0.995	0.999	0.999
	X_1	0.034	0.129	0.010	0.168	0.043	0.507	0.036	0.219

Special first-order	**X_f**	-0.003	-0.007	0.002	0.010	0.002	0.035	-0.001	-0.002
	k_1	0.055	0.037	0.135	0.091	0.105	0.019	0.061	0.058
	R^2	0.990	0.986	0.975	0.997	0.998	0.992	0.999	0.999

3.3.5. Nitrogen Mineralization and Nitrification Dynamics

The concentrations of $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ in the soil changed significantly over time in all cases, but the magnitude of these changes depended on the type of fertilization received ($p < 0.05$; Tables A.3.11 and A.3.12). Meanwhile, soil moisture conditions and biosolids type alone did not have any significant effect on $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ concentrations despite the different amounts of total N at the beginning of the experiment. After Day 3 of the experiment, $\mathrm{NH_4^+}$ concentration peaked followed by an exponential decrease until the end of the experiment. Simultaneously, a non-linear increase in $\mathrm{NO_3^-}$ concentrations was observed (Figure 3.3).

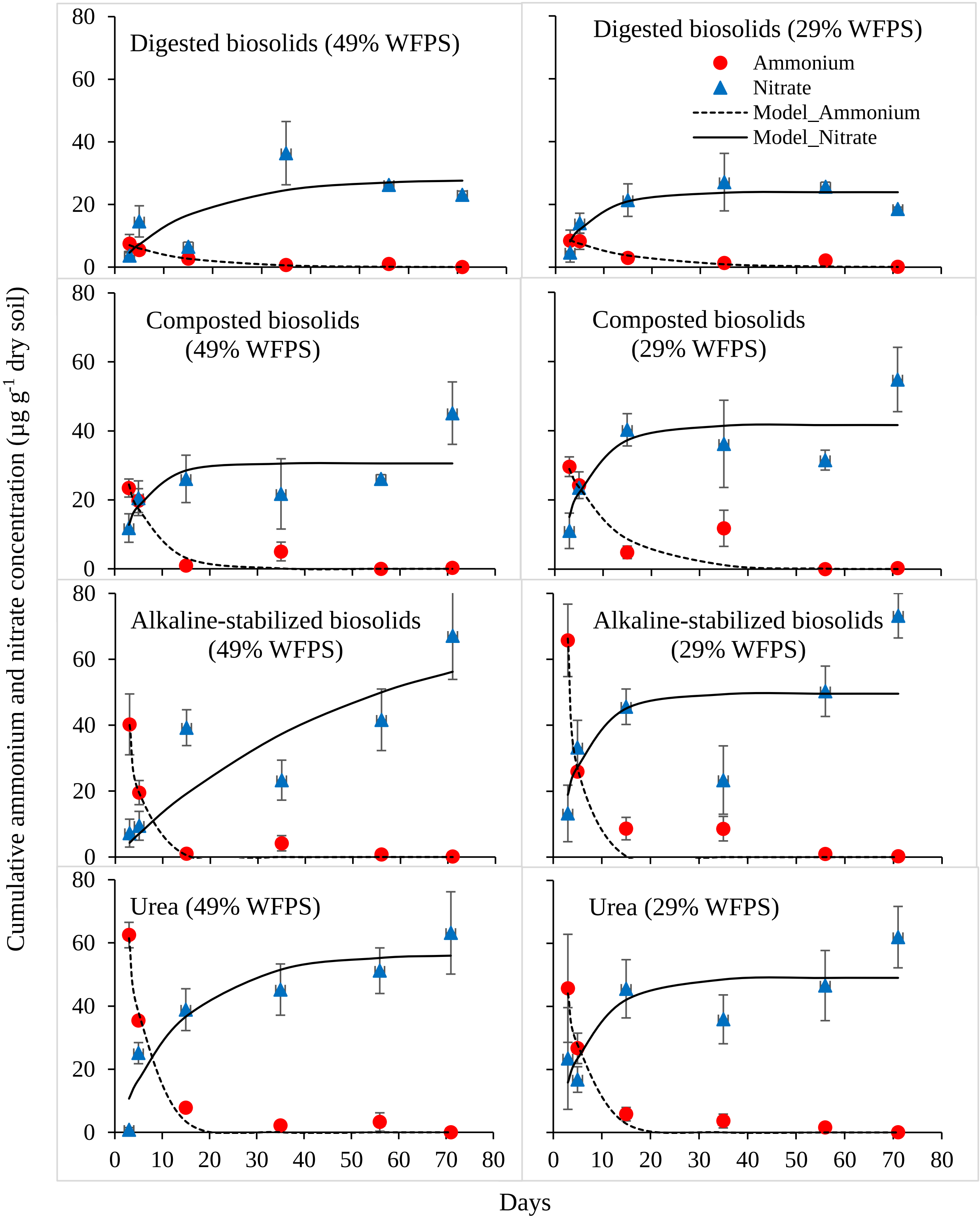

Figure 3.3. Ammonium and nitrate concentrations in soils amended with biosolids under 29% WFPS and 49% WFPS soil moisture conditions. *Red circles and blue triangles are means (n = 4)*

with standard deviation bars. A first-order model was fitted to the observed ammonium ($R^2 > 0.93$) and nitrate ($R^2 > 0.65$) data.

3.3.6. Nitrogen Transformation Kinetics and Model Fitting

The single-pool exponential decay model was fitted to the net N mineralization data for all the treatments, with $R^2 \geq 0.93$ for all treatments as shown in Table 3.7. The net N mineralization rates (k_0) ranged from 0.07 to 0.45 d^{-1} in the order: digested biosolids < composted biosolids < urea < alkaline-stabilized biosolids under 29% WFPS soil moisture conditions. The single-pool exponential model was fitted to the derived net N nitrification values for all the treatments with a resulting $R^2 \geq 0.65$ for all treatments as shown in Table 3.7. The net N nitrification rates ranged from 0.02 to 0.18 d^{-1}.

Table 3.7. Model parameters for cumulative NO_3^- and NH_4^+ concentrations in soil amended with three types of biosolids under soil moisture regimes.

Model	**Parameter**	**Treatment**							
		Urea		**Digested biosolids**		**Alkaline-stabilized biosolids**		**Composted biosolids**	
		29% WFPS	49% WFPS	29% WFPS	49% WFPS	29% WFPS	49% WFPS	29% WFPS	49% WFPS
Ammonium: $N(t) = N_0 \times exp^{-kt}$	N_0	126.2	88.0	10.6	8.9	255.7	118.0	39.1	40.7
	k	0.24	0.23	0.07	0.08	0.45	0.36	0.10	0.17
	R^2	1.00	1.00	0.97	0.99	0.99	1.00	0.93	0.97
Nitrate: $N(t) = N_0 \times (1 - exp^{-kt})$	N_0	56.3	49.1	23.9	28.0	49.6	74.6	41.6	30.6
	k	0.07	0.13	0.14	0.06	0.16	0.02	0.15	0.18
	R^2	0.94	0.82	0.91	0.77	0.65	0.85	0.84	0.69

3.3.7. Changes in Soil pH and Electrical Conductivity

In general, soil pH decreased significantly with time, but the magnitudes of these changes depended on type of fertilization and moisture content (Table A.3.13 and Figure 3.4). Before adding biosolids to the soil, the average soil pH was 5.82 ± 0.02, however, the pH of soils that received alkaline-stabilized biosolids increased temporarily by 0.34 to 0.55 units on average under each moisture condition at Day 3. Afterward, soil pH declined continuously until Day 92.

As seen in Table 3.8, the average soil pH was higher in alkaline-stabilized biosolids treatments than in other treatments throughout the experiment. On Day 3 (at the start of the experiment), under the 49% WFPS moisture condition, the pH of alkaline-stabilized biosolids was

0.21 units higher compared to the 29% WFPS moisture condition. This difference was no longer significant by the end of the experiment.

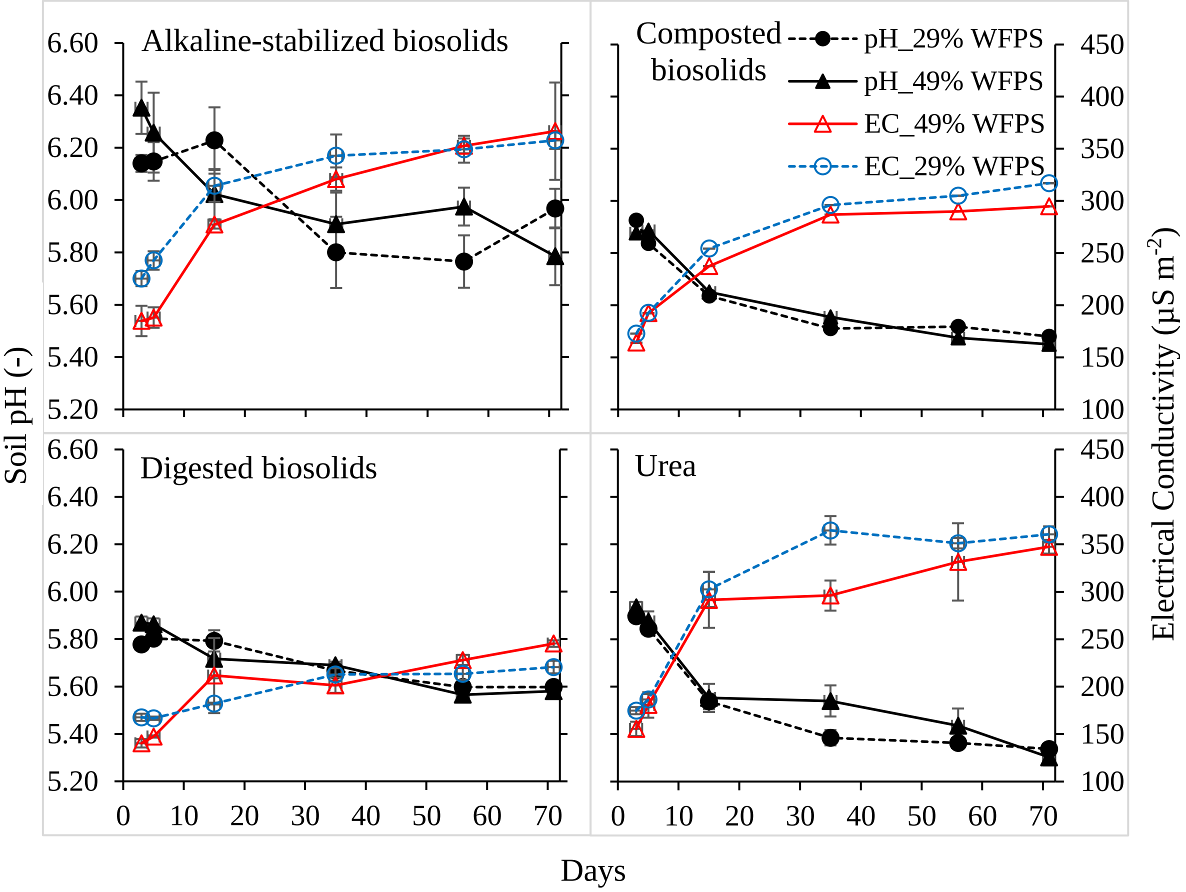

Figure 3.4. Electrical conductivity (EC) and pH of soils amended with biosolids under 29% WFPS and 49% WFPS soil moisture conditions. *Circles and triangles are means (n = 4) with standard deviation bars.*

In general, soil EC increased significantly with time, but the magnitudes differed at each sampling time depended on the type of fertilization (Table A.13). Soil EC values of treatments receiving alkaline-stabilized biosolids were significantly higher ($p < 0.05$) than those of other treatments at the first and last soil sampling events during the experiment (**Table 8**). Compared to digested biosolids treatment, the EC of urea treatment was significantly higher by the end of the experiment.

Table 3.8. Average values of soil pH and EC near the start (Day 3) and end (Day 72) of the experiment from all treatments.

Fertilizer	**Moisture**	**pH**		**EC**	
		Day 3[†]	Day 72[†]	Day 3[†]	Day 72[†]
Alkaline-stabilized biosolids	29% WFPS	6.35^{c}	5.91^{d}	217^{f}	362^{d}
Composted biosolids		5.92^{a}	5.50^{abc}	180^{ce}	306^{bd}
Digested biosolids		5.87^{a}	5.62^{c}	166^{bcde}	233^{ac}
Urea		5.93^{a}	5.35^{ab}	177^{de}	354^{d}
Alkaline-stabilized biosolids	49% WFPS	6.14^{b}	5.84^{d}	193^{e}	361^{d}
Composted biosolids		5.88^{a}	5.43^{abc}	156^{abd}	306^{cd}
Digested biosolids		5.78^{a}	5.56^{bc}	142^{a}	233^{ab}
Urea		5.90^{a}	5.29^{a}	153^{abc}	354^{d}

[†] *Different letters within a column represent significant differences at $p < 0.05$ based on Tukey's test for pairwise comparison. Value are means (n = 4).*

3.3.8. Correlation between Greenhouse Gas Emissions and Measured Soil Variables

The values of Pearson's correlation coefficient shown in Figure 3.5 indicate varying degrees of linear correlation between variables related to N mineralization and nitrification. Positive correlation was observed between pH and NH_4^+ (r = 0.5), but negative correlation between EC and NH_4^+ (r = -0.4). Also, NO_3^- had strong positive correlation with EC (r = 0.7) and time (r = 0.5), but weak negative correlation with pH (r = -0.3) at $p < 0.05$. For all treatments receiving biosolids, mineralization peaked at the early stages of the experiment as seen in Figure 3.3, coinciding with the slight increase in soil pH seen in Figure 3.4. Then, a strong positive linear correlation was observed between inorganic N and NO_3^- (r = 0.7), while a weak positive correlation was observed between inorganic N and NH_4^+. Also NO_3^- and NH_4^+ were negatively correlated (r = - 0.5), perhaps due to the depletion of NH_4^+ as a substrate for NO_3^- formation.

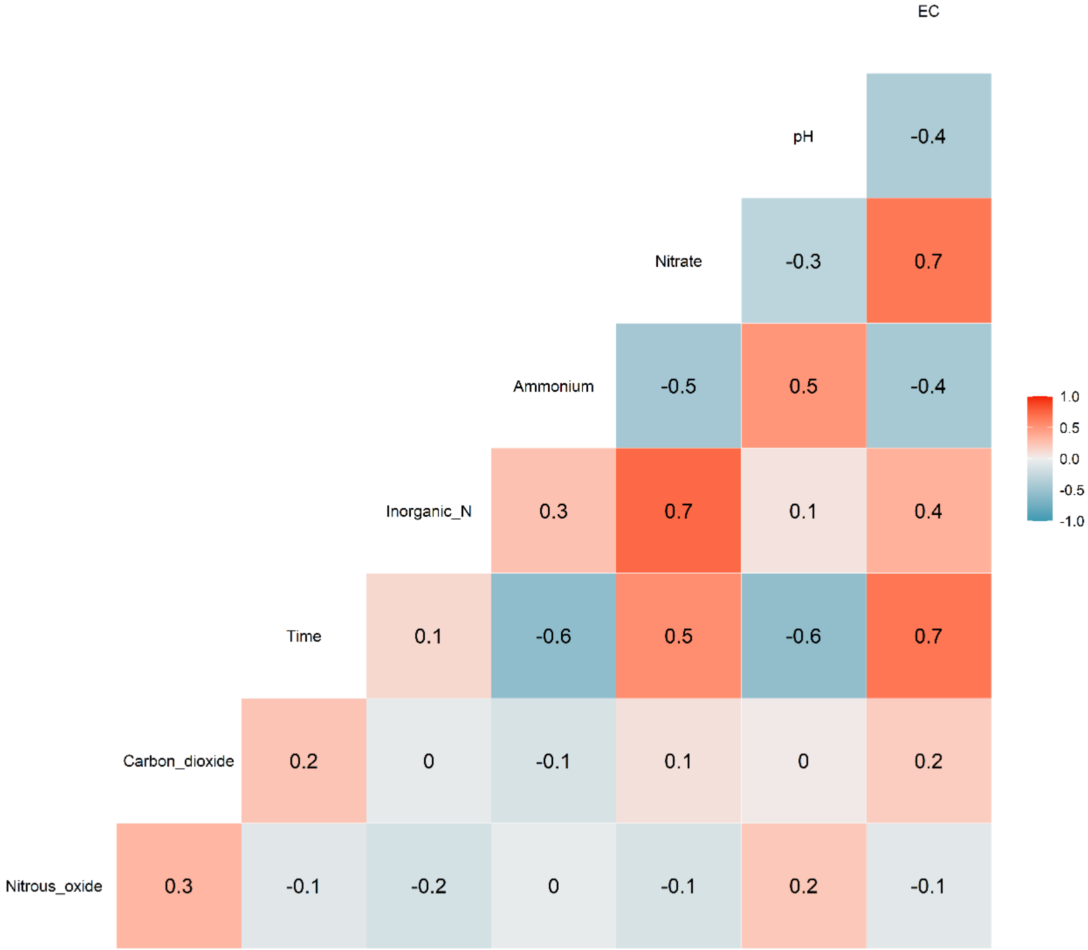

Figure 3.5. Matrix of Pearson's correlation coefficients (α = 0.05) between EC, pH, NH_4^+, NO_3^-, inorganic N, cumulative CO_2 and N_2O emissions, and time of measurement from soils amended with alkaline-stabilized biosolids, composted biosolids, mesophilic anaerobically digested biosolids (digested biosolids), and urea during the incubation experiment.

3.3.9. Simulating N_2O Emissions

Figure 3.6 shows a generally poor simulation of the measured daily N_2O emissions by DNDC given the < 0.6 correlation coefficients, despite the use of empirically derived biosolids C decomposition parameters. However, there was a slight improvement in *r* in the daily trends and magnitudes of N_2O simulations using the empirically derived biosolids C decomposition parameter values over the default manure values, especially for digested and alkaline-stabilized biosolids treatments (see Table 3.9). The r values for urea treatments remained the same because it did not receive biosolids or any organic amendments that would been simulated by the manure/biosolids C pool subroutine.

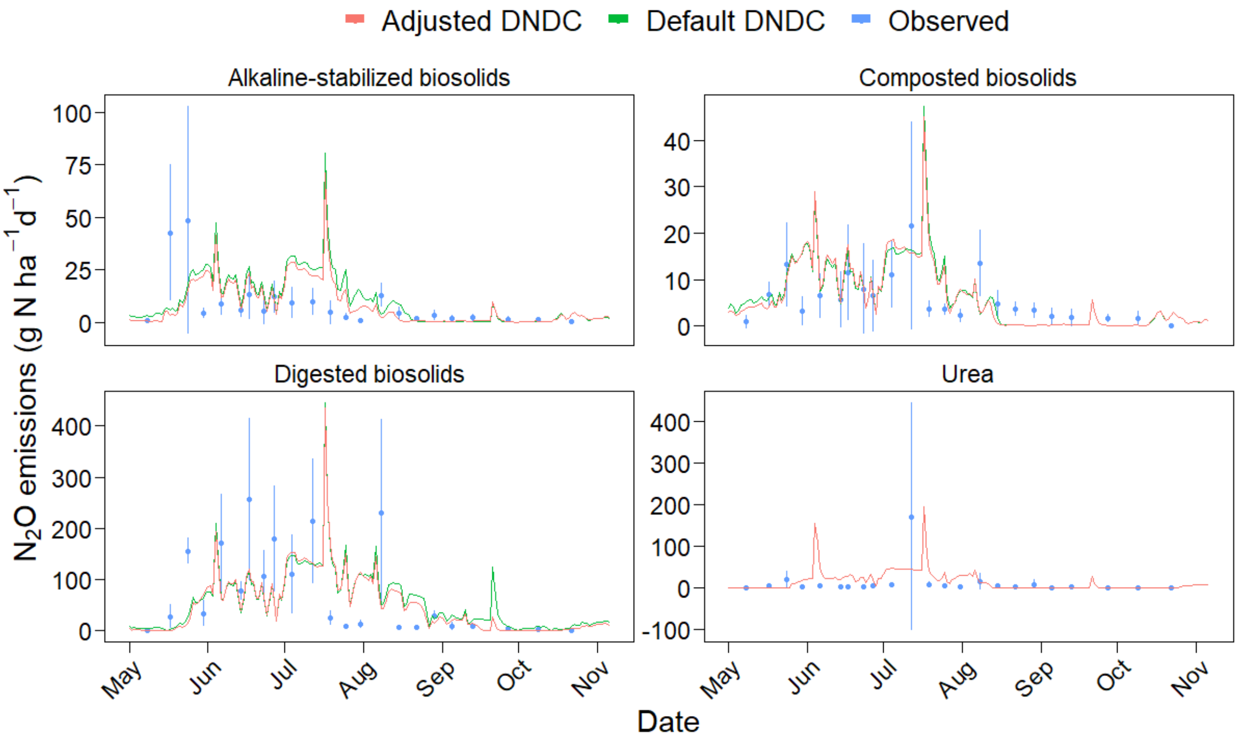

Figure 3.6. comparison of the measured daily N_2O emissions against DNDC simulations using either the default manure (default DNDC) or empirically derived biosolids (adjusted DNDC) carbon decomposition parameters.

3.3.10. Simulating CO_2 Emissions

Figure 3.7 shows that using either set of kinetic parameters (default or biosolids) failed to noticeably improve DNDC's estimates of the measured daily CO_2 emissions. However, there was slight improvement in *r* using the empirically derived values over the default values for the digested and alkaline-stabilized biosolids treatments but not the composted biosolids treatments (see Table 3.9).

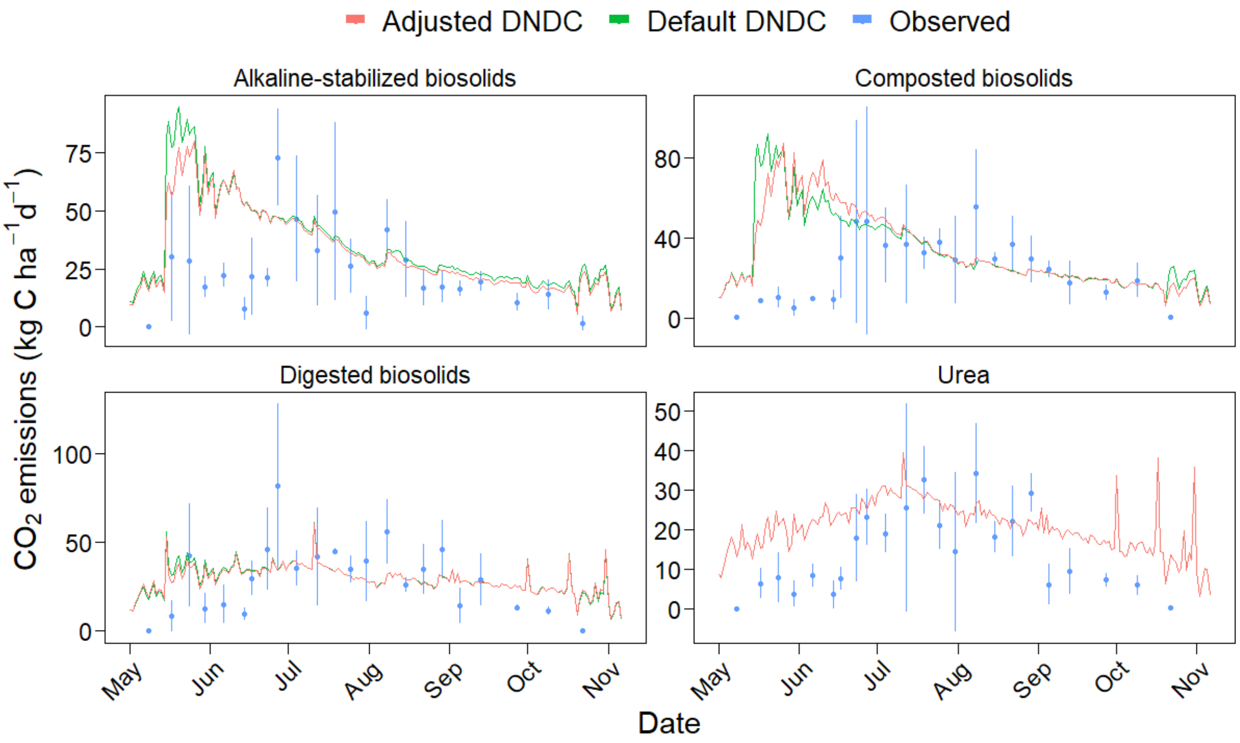

Figure 3.7. comparison of the measured daily CO_2 emissions against DNDC simulations using either the default manure (default DNDC) or empirically derived biosolids (adjusted DNDC) carbon decomposition parameters.

Table 3.9. Values of Pearson's correlation coefficients (*r*) between measured and simulated CO_2 and N_2O emissions using either DNDC default (Default) manure decomposition or empirically derived biosolids (Adjusted) decomposition parameters.

Amendment	CO_2		N_2O	
	Default	Adjusted	Default	Adjusted
Alkaline-stabilized biosolids	0.30	0.32	0.17	0.18
Composted biosolids	-0.18	-0.05	0.48	0.51
Digested biosolids	0.47	0.53	0.25	0.29
Urea	0.72	0.72	0.35	0.35

3.4. Discussion

3.4.1. Carbon Mineralization and Cumulative Carbon Dioxide Emissions

The relatively higher degradation rate of SOM in the 49% than the 29% WFPS soil moisture condition is consistent with findings from other studies. For instance, Wang et al. (2016) found that SOM decomposition and cumulative CO_2-C emissions under unsaturated conditions increased linearly as soil moisture content was raised from 30% to 90%. This was expected given that water is required for OM hydrolysis which in turn determines the availability of dissolved organic compounds necessary for microbial activity (Liao et al., 2016).

Judging from the higher CO_2 emissions in the biosolids treatments relative to the control treatment, adding OM (e.g., biosolids) to soil improves soil microbial activity; thus, improving the soil quality. As also reported by Fernández et al. (2007), the low percentage of mineralized carbon relative to the total soil carbon indicates the fraction of easily degradable OM content of the soil, which mostly consists of newly applied OM; in this case, biosolids.

The low percentage of organic carbon mineralization as seen in the composted biosolids treatment was due to the high lignin content in the 40% woody biomass to 60% municipal sludge used to produce the compost (Coors et al., 2016). From visual inspection, composted biosolids was expected to be more resistant to degradation than digested biosolids and alkaline-stabilized biosolids due to the visible presence of woody particles.

However, the magnitude of the differences in the rate of degradation of biosolids carbon cannot be explained by soil moisture content alone. Carbon mineralization rates of 16% have been reported for composted sewage sludge by Huang & Chen (2009) but their incubation experiment lasted 112 days and composition of the compost feedstock was different. In another incubation study lasting 60 days, Gilmour et al. (2003) recorded C mineralization in the range of 7-35% for digested and alkaline-stabilized biosolids which is lower than in this study. Another study by Gillis & Price (2011) found that C mineralization in alkaline-stabilized biosolids can be as high as 78% in gley and fragic Humo-ferric Podzol soils. The reported differences in the mineralization rates in these studies suggest that incubation temperature, duration of study, biosolids type, and stage of biosolids degradation before land application, as well as the characteristics of receiving soils are critical determinants of the biosolids mineralization which should be taken into consideration when comparing studies (Rigby et al., 2016).

While organic C content is important, the proportion of mineralizable C to total biosolid C is a more important indicator of mineralization rate during the growing season as seen in the CMC values of the biosolids. At the beginning of this experiment, organic C content was 7 times less in digested biosolids compared to composted biosolids, however, both biosolids had similar cumulative CO_2-C emissions at the end of the experiment. This suggests that slow degrading biosolids like composted biosolids have a relatively higher potential to sequester carbon in soils to improve quality. This slow rate of degradation also implies a slow release of mineral N vis-à-vis slow rate of N_2O emissions. This mechanism is in contrast with the rate of degradation for digested biosolids, suggesting a higher cumulative CO_2 and N_2O emissions if applied at the same rate as the composted and alkaline-stabilized biosolids.

3.4.2. Carbon Mineralization Curves and Model Fitting

The early-stage rapid decomposition seen in Figure 1 is typically influenced by the form of C present in the biosolids, initial soil moisture, and temperature (Gillis & Price, 2011). After the easily degradable fraction of biosolids C has been microbially metabolized, the remainder is usually more recalcitrant and can only degrade slowly. Additionally, increasing the concentration of inorganic soil N due to the degradation of nitrogenous compounds limit the activity of oxidative enzymes as reported by Saggar et al. (2013). Nitrogen release after land application of biosolids corresponded with the fast and slow phases observed with CO_2 release (Pei et al., 2019). The kinetics of these two phases support the hypothesis that the type of biosolid vis-à-vis the form of organic carbon and C/N of biosolids influence its carbon sequestration and N_2O emissions potential (Figure 3.1).

The high degree of association ($R^2 > 0.99$) between the observed data and the four exponential models, especially the double-pool first-order model, were similar to the observation in an earlier study (Gillis & Price, 2011). The degradation coefficients deduced from the double pool first-order model were in the range of 0.007 to 1.293 per day and compared to the default values between 0.074 and 0.02 per day used for litter degradation in DNDC (University of New Hampshire, 2012). These coefficients can be used to initialize mechanistic models like DNDC to better simulate SOC degradation when soil is amended with biosolids.

3.4.3. Cumulative Nitrous Oxide Emissions

Under relatively high soil moisture conditions in well-aerated soils, ammonia (NH_3) or NH_4^+ is rapidly oxidized to NO_2^- and/or NO_3^- by *Nitrosomonas* and *Nitrobacter* which leads to the production of nitric oxide (NO) and N_2O as intermediate products of N_2 production (Norton & Stark, 2011; Xing et al. 2011). Moisture-limited conditions impact microbial activities; thus, adversely affecting *Nitrosomonas* and *Nitrobacters* ability to oxidize NH_3 or NH_4^+ to N_2O. Since N_2O is an intermediate product of nitrification and denitrification, majority of N will be found in the form of organic N and other forms of N such as NH_3 or NH_4^+, NO_2^-, NO_3^-, and NO.

Alkaline-stabilized biosolids emitted more N_2O than the digested biosolids treatment due to its relatively higher total N content (in the form of both organic N and urea enrichment) than other treatments. The unique physicochemical characteristics (e.g., pH > 7 and Ca content) of alkaline-stabilized biosolids also ameliorates pH of low-pH soils thereby enhancing soil microbial activity. However, there is scant evidence in this study to suggest that biosolids pH had a significant on soil microbial activity.

3.4.4. Cumulative Nitrous Oxide Emissions Curves and Model Fitting

The tested models provide simplified methods and coefficients that indicate the potential magnitude and rates of N_2O emissions. The initial N pools are indicative of the potential N_2O emissions, while the rate constants quantify the rate of emissions under any of the assumed N kinetics. In most cases, the initial N pools were larger for the 49% than the 29% WFPS conditions, and this effect of soil moisture on N_2O emissions is described in mechanistic models such as DNDC using a parameter called the soil moisture factor. The soil moisture factor interacts with the soil temperature factor in DNDC in DNDC is influenced by soil hydraulic parameters such as bulk density, porosity, field capacity, permanent wilting point, hydraulic conductivity, and clay fraction (Li et al., 1992). As seen in a few cases where the model coefficients (see Table 3.6) indicate negative values of the N pools, the size of the N pool and the rate of N_2O emissions alone are not enough parameters to describe the complex physical and biological processes that drive N_2O emissions. Modelling the variation in nitrous oxide emissions does not only depend on soil physical parameters, but also on the rates of organic N mineralization and nitrification vis-à-vis the microbial dynamics.

3.4.5. Nitrogen Mineralization and Nitrification Dynamics

According to Wang & Cai (2008), the temporal pattern of soil NH_4^+ is influenced by N mineralization and nitrification, while the temporal pattern observed for NO_3^- is due to the net effect of NO_3^- production from nitrification and its denitrification to N_2O and N_2. As seen in the early stage of this study, the immediate fixation of NH_4^+ and its subsequent conversion to NO_3^- by nitrifiers indicate a rapid rate of nitrification (Bateman & Baggs, 2005). Though these changes were first observed after Day 3 of our experiments, other studies have shown that this can occur within a couple of hours after soil incubation (Xing et al., 2011). Given that the first day of soil sampling was on Day 3, perhaps, our sampling frequency may have failed to capture the actual N dynamics at the early stages of the experiment. The lack of intensive early-stage measurement of NH_4^+ and NH_3 dynamics in such closed systems may have limited our understanding of N balance between the treatments to model N dynamics in agricultural soils amended with biosolids. For instance, the surface application of urea on wet soil could have led to urea N volatilization and eventual NH_3 loss due to intensive gas sampling and repeated aeration of the jars during the early stages of the experiment.

Nitrification is usually the dominant process compared to denitrification in well-aerated soils (Vilain et al., 2014). There seems to be a direct relationship between low moisture conditions and low N_2O production as observed under 29% WFPS soil moisture conditions. Westphal *et al.* (2018), have suggested that the quantity of mineralized N in the soil at any given time is a function of available water, temperature, rate of oxygen replenishment, pH, amount and nature of organic amendment, and levels of other nutrients. Between the two common microbial pathways for N_2O production, i.e. nitrification via hydroxylamine and through nitrifier denitrification, the former is the major source of N_2O production (Vilain et al., 2014). In this experiment pH, moisture, amount of OM amendment and temperature were measured assuming that the effects of other factors were negligible due to the controlled conditions under which the experiment was run.

The relatively low mineral N concentration and low NH_4^+ peaks in digested biosolids treatments were perhaps due to no urea enrichment in the digested biosolids compared to other treatments. Urea will typically hydrolyse between a few hours to few days after application, to sequentially produce ammonium carbonate and NH_3 (Wang et al., 2020). This accounts for the high NH_4^+ peaks and overall high levels of mineral N for urea-enriched biosolids treatments. However, this was not the case with composted biosolids, which had a relatively low soil mineral N despite having the highest total N amongst all the treatments. This was likely due to the slow rate of composted biosolids degradation and organic N release (Abbasi & Khaliq, 2016). Adjusting for the effects of urea enrichment, digested biosolids supplied about 1.5 and 3 times the amount of mineral N than alkaline-stabilized biosolids and composted biosolids, respectively at peak periods. These results suggest that more mineral N could be supplied to crops from digested biosolids despite applying a lower total N relative to other treatments. This insight offers a possibility of cutting down N losses when land applying digested biosolids.

3.4.6. Nitrogen Transformation Kinetics and Model Fitting

The coefficients derived from fitting the single-pool exponential decay model to the measured soil NH_4^+ and NO_3^- data offer a means to quantify mineral N dynamics in soils and inform farm practices.

3.4.7. Changes in Soil pH and Electrical Conductivity

The temporary increase in soil pH after biosolids application occurs due to the mineralization of nitrogenous compounds to NH_4^+ with the release of hydroxyl ions (OH^-) (Kunhikrishnan et al., 2016; McCauley et al., 2017). The subsequent decline in soil pH was due to the release of hydrogen ions (H^+) through dissociation of carboxylic acids which is enhanced by the degradation of SOM, as well as the mineralization and oxidation of organic N causing this decrease in soil pH (Kunhikrishnan et al., 2016). This effect was more pronounced in treatments receiving alkaline-stabilized biosolids due to the addition of alkaline materials during stabilization of the biosolids using N-Viro® method.

The results of this study suggests that in low-pH soils, microbial activity could be enhanced by adding alkaline-stabilized biosolids; thus, reinforcing the science behind its use as a soil pH buffer. Based on the findings of Price et al. (2015) who sourced alkaline-stabilized biosolids from the same company, the increase in soil pH could be attributed to the presence of base-forming cations in the form of calcium carbonate contained in the biosolids.

The EC value at the end of the experiment reflects the number of cations (e.g. Ca^{2+} and Na^+) that were released into the soil solution by the degradation of biosolids and initial SOM (Niu et al., 2015). The higher soil EC in alkaline-stabilized biosolids treatments relative to other treatments was due to the matrix of alkaline materials, including CaO, mixed with the alkaline-stabilized biosolids during the N-Viro® process (Sloan & Basta, 1995).

3.4.8. Correlation between Greenhouse Gas Emissions and Measured Soil Variables

NH_4^+ is the dominant form of soil mineral-N in the early weeks after N fertilizer application and is influenced by nitrifier activity, which is sensitive to soil pH (Blagodatsky et al., 2011; Abbasi & Khaliq, 2016). The slightly acidic soil pH (~5.8) at the start of the experiment may have affected the build-up of nitrifier populations due to initial soil pre-incubation. Only the treatment receiving urea decreased in soil pH without any prior increase. In soils receiving inorganic fertilizers, such as urea, H^+ accumulates through nitrification in the absence of leaching (Kunhikrishnan et al., 2016). The accumulation of H^+ results in soil acidification and decreased OM degradation (Ge et al., 2013). Perhaps the concurrent degradation of biosolids and NH_4^+ nitrification leading to H^+ accumulation explains the negative correlation between CO_2 emissions and NO_3^-. The observed correlations between the variables are indicative of the relationships between variables in the soil biochemical processes that drive C and N dynamics as observed in a closed system without vegetation. Such relationships can be extrapolated beyond the current scientific context to inform further scientific research, quantify the effects of these variables, and improve predictive models.

3.4.9. Simulation of CO_2 and N_2O Emissions

The result of the simulation trial only demonstrates the possibility of improving the simulation of biosolids degradation in soils using empirically derived kinetic parameters. Given that the quantity of biosolids organic carbon applied to the soil constitutes < 3% of the total soil organic carbon, the effect of changing the degradation rate of biosolids were miniscule. While there was only a slight increase in correlation coefficients between the measured and simulated emissions when empirically derived kinetic parameter values were used over default DNDC values, DNDC parameters could be further adjusted to improve the simulated emissions. DNDC parameters which are difficult to measure such as the nitrification adjustment factor, rainfall intensity index, fraction of soil humads, and denitrifier growth rates could further be adjusted to improve simulations of organic carbon mineralization in soils. Also, incubation experiments are conducted in controlled environments, as such they differ from field conditions in the number of biotic and abiotic factors that interact to influence soil C mineralization.

3.5. Conclusion

Our findings suggest that the rate of biosolids degradation is affected by the type of biosolids and soil moisture condition. The differences in the degradation kinetics of the three types of biosolids were perhaps due to the forms of organic C inherent in the biosolids, which influenced the rates of soil respiration, N_2O production, and NH_4^+ and NO_3^- dynamics after biosolids application. While about 79 and 62% of digested biosolids C, 52 and 46% of alkaline-stabilized biosolids C degraded during the experiment under 49% and 29% WFPS moisture conditions respectively, only 8 and 5% of composted biosolids C was degraded. N mineralization occurred within three days after biosolids application, with NH_4^+ and NO_3^- dominating the initial and later stages of the experiment, respectively. Biosolids degradation in soils occurs in two phases: an initial rapid release of C and N, followed by a slower rate of C and N release in the later stages of the incubation experiment.

The four first-order models were well-fitted to the C and N mineralization curves ($R^2 > 0.65$), to estimate the kinetic parameters of C and N mineralization. The kinetics of biosolids degradation and the associated cumulative CO_2 and N_2O emissions over time can be best described using a double-pool simultaneous decomposition first-order model and a special first-order model, respectively. Meanwhile, the kinetics of N mineralization and nitrification can be best described using single-pool first-order models. From these results, the estimated values of the mineralizable C and N for biosolids, as well as their degradation rate constants were found to be akin to those of manures and other biological materials under similar soil moisture and temperature conditions, in most cases.

We further conclude that land-application of composted biosolids offer the best option for sequestering soil C and minimizing N losses due to its slower rate of degradation than alkaline-stabilized biosolids and digested biosolids. Meanwhile, alkaline-stabilized biosolids offer the best option for adjusting the pH of acidic soils. Applying 1.5 and 3 times the amount of alkaline-stabilized biosolids and composted biosolids, respectively, supplies about the same amount of mineral N as digested biosolids, under the given experimental conditions. The results of this study are useful for biosolids regulators, policymakers, and farmers who consider using biosolids as a soils amendment to improve C sequestration, mitigate N_2O emissions, reduce soil acidity, and potentially improve N use efficiency based on location-specific moisture regimes. These results may also be used to improve mechanistic models like DNDC to better simulate the degradation of biosolids, and the C and N dynamics in soils amended with biosolids.

As this study only aims to demonstrate the effect of simulating GHG emissions using empirically derived kinetic parameter values of the biosolids C pools, the range of conditions considered in the incubation study do not represent the typical field conditions. As such, parameter values derived from incubation studies alone are not sufficient for improving mechanistic models.

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3.7. Appendix

3.7.1. Appendix A: Statistical Analysis Tables

Table A.3.1. Two-way ANOVA table for the effects of fertilizer, soil moisture, and their interaction (fertilizer × moisture) on cumulative CO_2 emissions.

Effect	Sum of Square	DF	F value	Pr(>F)	Significance
Fertilizer	0.078752	3	16.6445	4.62E-06	***
Moisture	0.065139	1	41.3023	1.21E-06	***
Fertilizer:Moisture	0.002697	3	0.5701	0.6401	
Residuals	0.037851	24			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the *p* value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.3.2. Two-way ANOVA table for the effects of fertilizer and moisture on net mineralization coefficient (NMC) of carbon due to fertilizer, soil moisture, and their interaction (fertilizer × moisture).

Effect	Sum of Square	DF	F value	Pr(>F)	Significance
Fertilizer	1.1517	3	16.201	3.20E-06	***
Moisture	0.84002	1	35.449	2.39E-06	***
Fertilizer:Moisture	0.001714	3	0.31	8.18E-01	
Residuals	0.63981	24			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the *p* value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.3.3. Two-way ANOVA table for the effects of fertilizer and moisture on the complementary mineralization coefficient (CMC) of carbon due to fertilizer, soil moisture, and their interaction (fertilizer × moisture).

Effect	Sum of Square	DF	F value	Pr(>F)	Significance
Fertilizer	25.3631	2	48.1591	5.95E-08	***
Moisture	0.9558	1	3.6297	0.07286	.
Fertilizer:Moisture	0.1496	2	0.2841	0.75603	
Residuals	4.7399	18			

Note: *p* < 0.001 (***), *p* < 0.01 (**), *p* < 0.05 (*), *p* < 0.1 (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the *p* value in the brackets. *p* < 0.05 (*) was the tested significance level for the main and interaction effects in this study.

Table A.3.4. Two-way ANOVA table for the effects of fertilizer, soil moisture, and their interaction (fertilizer × moisture) on cumulative N_2O emissions.

Effect	Sum of Square	DF	F value	Pr(>F)	Significance
Fertilizer	10.512	3	5.1704	0.00673	**
Moisture	25.4107	1	37.4958	2.52E-06	***
Fertilizer:Moisture	2.3844	3	1.1728	0.34078	
Residuals	16.2647	24			

Note: *p* < 0.001 (***), *p* < 0.01 (**), *p* < 0.05 (*), *p* < 0.1 (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the *p* value in the brackets. *p* < 0.05 (*) was the tested significance level for the main and interaction effects in this study.

Table A.3.5. Tukey HSD pairwise comparison of means of cumulative nitrous oxide emissions due to fertilizer and soil moisture level.

Fertilizer	Moisture	LSmean	SE	df	Lower CL	Upper CL	[††]group
Digested biosolids	29% WFPS	-2.66	0.329	27	-3.34	-1.988	bcd
Urea	29% WFPS	-2.21	0.329	27	-2.89	-1.537	cde
Composted biosolids	29% WFPS	-1.64	0.329	27	-2.31	-0.964	de
Alkaline-stabilized biosolids	29% WFPS	-1.15	0.329	27	-1.82	-0.472	e
Urea	49% WFPS	-4.44	0.329	27	-5.12	-3.771	a
Digested biosolids	49% WFPS	-3.99	0.329	27	-4.67	-3.319	ab
Composted biosolids	49% WFPS	-3.42	0.329	27	-4.09	-2.747	abc
Alkaline-stabilized biosolids	49% WFPS	-2.93	0.329	27	-3.6	-2.254	bcd

[††] Different letters within the "group" column represent significant differences at alpha = 0.05 based on Tukey's test for pairwise comparison of a family of 8 estimates. LSmean = least squared means, DF = degrees of freedom, CL = confidence limit, and WFPS = water-filled pore space. **Note:** Results are given on the log (not the response) scale. Confidence level used: 0.95.

Table A.3.6. Tukey HSD pairwise comparison of means of cumulative nitrous oxide emissions due to soil moisture level.

Moisture	LSmean	SE	DF	lower.CL	upper.CL	[††]group
29% WFPS	-3.7	0.206	24	-4.12	-3.27	a
49% WFPS	-1.91	0.206	24	-2.34	-1.49	b

Results are averaged over the levels of: Fertilizer; Results are given on the log (not the response) scale. Confidence level used: 0.95; significance level used: alpha = 0.05. LSmean = least squared means, DF = degrees of freedom, CL = confidence limit, and WFPS = water-filled pore space.

Table A.3.7. Tukey HSD pairwise comparison of means of cumulative nitrous oxide emissions due to fertilizer type.

Fertilizer	LSmean	SE	df	lower.CL	upper.CL	††group
Digested	-3.55	0.294	27	-4.16	-2.95	a
Urea	-3.1	0.294	27	-3.71	-2.5	ab
Composted	-2.53	0.294	27	-3.13	-1.93	ab
Alkaline-stabilized	-2.04	0.294	27	-2.64	-1.43	b

Results are averaged over the levels of: Moisture; Results are given on the log (not the response) scale. Confidence level used: 0.95; P value adjustment based on Tukey method for comparing a family of 4 estimates; significance level used: alpha = 0.05. LSmean = least squared means, DF = degrees of freedom, CL = confidence limit, and WFPS = water-filled pore space.

Table A.3.8. Measured mean and standard deviations (n=4) of cumulative N_2O emissions from the treatments during the incubation experiment

Fertilizer	Moisture	Mean ($\mu g\ N_2O\text{-}N\ g^{-1}$)	SD ($\mu g\ N_2O\text{-}N\ g^{-1}$)
Alkaline-stabilized biosolids	29% WFPS	0.046	0.021
Composted biosolids		0.036	0.015
Urea		0.030	0.010
Digested biosolids		0.013	0.009
Alkaline-stabilized biosolids	49% WFPS	0.445	0.250
Composted biosolids		0.218	0.131
Digested biosolids		0.178	0.211
Urea		0.111	0.136

Table A.3.9. Two-way ANOVA table for the effects of fertilizer and moisture on net mineralization coefficient of nitrogen due to fertilizer, soil moisture, and their interaction (fertilizer × moisture).

Effect	Sum of Square	DF	F value	Pr(>F)	Significance
Fertilizer	5.1712	3	1.5571	0.25088	
Moisture	19.5413	1	17.6525	0.00123	**
Fertilizer:Moisture	0.086	2	0.0389	0.96201	
Residuals	13.284	12			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the *p* value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.3.10. Tukey HSD pairwise comparison of means of net mineralization coefficient of nitrogen (minus urea treatment) due to soil moisture level.

Moisture	LSmean	SE	DF	Lower CL	Upper CL	††group
49% WFPS	-4.38	0.282	14	-4.99	-3.78	b
29% WFPS	-6.71	0.431	14	-7.64	-5.79	a

†† Different letters within the “group” column represent significant differences at alpha = 0.05 based on Tukey’s test for pairwise comparison of a family of 2 estimates. LSmean = least squared means, DF = degrees of freedom, CL = confidence limit, and WFPS = water-filled pore space.
Note: Results are averaged over the levels of fertilizer and are given on the log (not the response) scale. Confidence level used: 0.95.

Table A.3.11. Three-way repeated measures ANOVA for soil nitrate concentration during the incubation experiment

Effect	DF	Sum of Squares	Mean Square	F value	Pr(>F)	Significance
Time	1	26835	26835	101.263	< 2e-16	***
Fertilizer	3	296	99	0.372	0.77307	
Moisture	1	97	97	0.367	0.54556	
Time:Fertilizer	3	3667	1222	4.612	0.00397	**
Time:Moisture	1	2	2	0.007	0.9318	
Fertilizer:Moisture	3	355	118	0.446	0.72048	
Time:Fertilizer:Moisture	3	517	172	0.651	0.58344	
Residuals	168	44521	265			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the p value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.3.12. Three-way repeated measures ANOVA for soil ammonium concentration during the incubation experiment

Effect	DF	Sum of Squares	Mean Squares	F value	Pr(>F)	Significance
Time	1	18980	18980	118.973	< 2e-16	***
Fertilizer	3	203	68	0.423	0.7366	
Moisture	1	7	7	0.047	0.8291	
Time:Fertilizer	3	4643	1548	9.702	6.12E-06	***
Time:Moisture	1	526	526	3.299	0.0711	.
Fertilizer:Moisture	3	138	46	0.287	0.8344	
Time:Fertilizer:Moisture	3	241	80	0.503	0.6808	
Residuals	168	26801	160			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the *p* value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.3.13. Three-way repeated measures ANOVA for soil pH during the incubation experiment

Effect	DF	Sum of Squares	Mean Squares	F value	Pr(>F)	Significance
Time	5	5.109	1.0218	78.927	<2.0E-16	***
Time:Fertilizer	15	0.574	0.0382	2.954	0.00052	***
Time:Moisture	5	0.186	0.0372	2.87	0.01754	*
Time:Fertilizer:Moisture	15	0.261	0.0174	1.346	0.18609	

Residuals	118	1.528	0.0129			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the *p* value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.3.14. Three-way repeated measures ANOVA for soil electrical conductivity during the incubation experiment

Effect	DF	Sum of Square	Mean Square	F value	Pr(>F)	Significance
Time	5	583945	116789	131.092	<2E-16	***
Time:Fertilizer	15	58358	3891	4.367	1.9E-16	***
Time:Moisture	5	4743	949	1.065	0.383	
Time:Fertilizer:Moisture	15	12589	839	0.942	0.52	
Residuals	118	105126	891			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on the dependent variable at the *p* value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

3.7.2. Appendix B

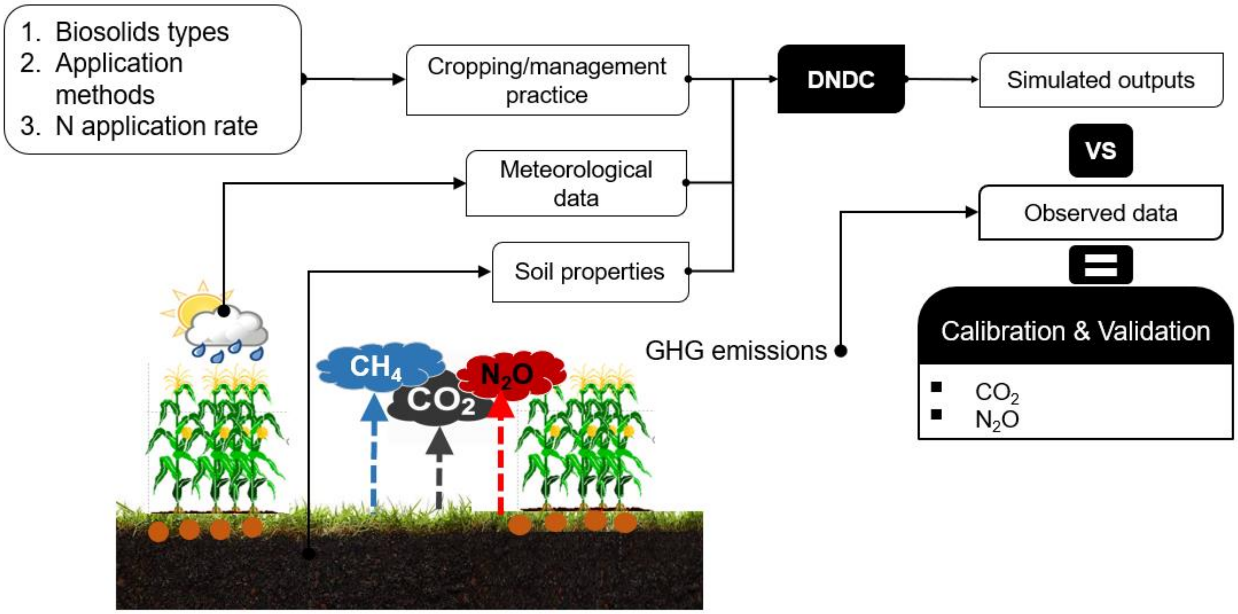

Figure A 3.1. Initializing DNDC using measured soil properties, daily climate variables (e.g., precipitation and temperature), and cropping/management practice data, followed by calibration and validation against measured CO_2 and N_2O emissions from surface spreading of biosolids.

Connecting text to Chapter 4

An important step in estimating C and N dynamics in soils amended with biosolids was done in Chapter 3 whereby the rates of decomposition and mineralization of organic carbon and nitrogen for the biosolids were determined in an incubation experiment. This sets the background for Chapter 4 where DNDC was tested for simulating daily and seasonal CO_2 and N_2O emissions, annual corn yields, and initial and final SOC and total soil N on a Quebec soil amended with three different types of biosolids. The differences in the decomposition rates of the mesophilic anaerobically digested, alkaline-stabilized, and composted biosolids observed in Chapter 3 provided insights for calibrating DNDC to simulate organic C degradation in the soil receiving biosolids. The DNDC model used in Chapter 3 is still under development; hence, it was not used in Chapter 4. Chapter 4 also suggests further improvement in the decomposition mechanism of DNDC to better simulate C and N dynamics in reference to the measured variables.

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Chapter 4. Greenhouse gas emissions following biosolids application to farmland: Estimates from the DeNitrification and DeComposition model

Okenna Obi-Njoku, Ward Smith, Brian Grant, Michael Yongha Boh, G.W. Price, Naseer Hussain, Joann Whalen, and O. Grant Clark

Abstract

Biosolids supply plant nutrients and increase soil organic carbon, but also contribute to the production of greenhouse gases (GHGs: carbon dioxide (CO_2) and nitrous oxide (N_2O)) that must be included in national GHG inventories. In this study, the DeNitrification and DeComposition (DNDC) model was used to simulate the effect of biosolids applications on GHGs in farmlands, towards implementing the model in Canada's GHG inventory. Three years (2017–2019) of data were collected from corn (*Zea mays* L.) plots in a replicated field experiment in Quebec, Canada. The plots received 120 kg of available N ha^{-1} y^{-1} in the form of mesophilic anaerobically digested (digested) biosolids, composted biosolids, alkaline-stabilized biosolids, urea, or combinations of these, while control plots were left unfertilized. Treatments receiving digested biosolids emitted higher N_2O during the growing season than other treatments, while CO_2 emissions were rarely varied between the treatments. After calibration and validation, DNDC estimates were within 95% confidence interval of the measured variables, signifying a good representation of C and N transformations in the soil. Correlation coefficients (r) indicated discrepancies in trends between the estimated and measured values for daily CO_2 and N_2O emissions (r = 0.3). These emissions were generally underestimated in the early and mid-growing season of 2018 and were more variable from plots fertilized with composted or alkaline-stabilized biosolids, as compared with digested biosolids. Annual changes in cumulative N_2O emissions (r = 0.8), crop yields (r = 0.5),

and soil organic carbon (r = 0.4) were modelled with higher accuracy than cumulative CO_2 emissions (r = 0.3) and total soil N (r = 0.1). These findings suggest that DNDC would be most suitable for estimating field-scale N_2O emissions following biosolids application however, estimated CO_2 emissions could be improved by disaggregating the biosolid decomposition from the existing soil organic matter pools.

4.1. Introduction

Disposal of treated municipal wastewater sludge (hereafter referred to as biosolids) in landfills is recognized as an unsustainable practice due to the environmental pollution associated with GHG emissions and nutrient leaching. For instance, of the 44 Gt carbon dioxide equivalent (CO_2e) of global anthropogenic emissions in 2005, landfill emissions represented ~2% (794 Mt CO_2e), and are increasing by 1–2% annually (UN-Habitat, 2008; Drechsel et al., 2015). Landfilling of organic waste has been banned in many countries to reduce GHG emissions and increasing amounts of biosolids are therefore applied to farmland as soil conditioner and fertilizer. Biosolids are a nutrient-rich organic material that is safe for crop production and increases soil fertility by building the soil organic carbon (SOC) and total soil N pools (Vogel, 2006; Barbarick et al., 2010; Price et al., 2015; Coors et al., 2016). However, there is a lack of information about the GHG emissions from agricultural land that receives biosolids. For example, approximately 500,000 t of biosolids are applied annually to farmland in Canada (Cheminfo Services Inc., 2018), but there are scant empirical data on GHG emissions from biosolids-amended land; thus they are not considered in the national GHG inventory (Environment and Climate Change Canada, 2015). The Intergovernmental Panel on Climate Change (IPCC) recommends a three-tier approach for estimating GHG emissions, designated as Tier 1 to Tier 3 in order of increasing accuracy, data requirements, and spatial resolution. The baseline assumption under the IPCC Tier 1 approach is that 1% of the applied N is emitted as N_2O, regardless of the N fertilizer source or site-specific field conditions, although Charles et al. (2017) reported 0.57 ± 0.30% for organic amendments. To implement the Tier 2 method in the national GHG inventory, GHG emissions data specific to biosolids application in Canadian agroecosystems is required.

Since there are few empirical measurements of GHG emissions following biosolids application to farmland, mathematical models that represent biogeochemical processes and crop production in agroecosystems can complement available local measurements to produce more accurate GHG estimates than those of the Tiers 1 and 2 methods. Process-based models (Tier 3 approach) provide a realistic estimate of GHG emissions in agricultural eco-regions when adjusted to reflect local agricultural practices. For example, N_2O emissions were approximately 25% lower when site-specific conditions in US croplands were considered in the DailyDayCent model (Parton et al., 1994) than when the baseline Tier 1 method was used to calculate the N_2O emissions (Del Grosso et al., 2010). The GHG emissions from corn agroecosystems managed according to best management practices were predicted within 2–8% of the measured N_2O and NH_3 values using the DeNitrification and DeComposition (DNDC) model (Li et al., 1992). Also, DNDC has been used to quantify N_2O emissions and estimate Tier 3 emission factors from the application of green compost, slurry, and digestate (Shen et al., 2018; 2019). However, any process-based model like DNDC is only as good as the data used to calibrate and validate its function, due to inherent uncertainties in the model structure and initial parameters. With a novel organic amendment like biosolids, its physico-chemical characteristics and assumptions about its transformations and fate in the soil-plant system (e.g., what proportion of the nutrients are plant-available or partitioned into the SOC and associated pools) must be well defined. Then, the DNDC model can be calibrated with key environmental inputs that influence microbial production of N_2O and CO_2, in the soil (organic matter, texture, pH, Eh), including the temporal and spatial variation in weather (precipitation, temperature, humidity) and vegetation (crop type, residues) (Lugato et al., 2010; Gilmour et al., 2013; Smith, 2017). Finally, the DNDC model should describe realistic agricultural practices, such as fertilizer application methods, that influence crop yield and N_2O emissions

(Webb et al., 2010; VanderZaag et al., 2011; Uzoma et al., 2015). The accuracy of GHG emissions predicted by the DNDC model must then be validated relative to experimental data before the model estimates can be accepted in a Tier 2 method for estimating the GHGs lost from biosolids-amended soils on Canadian farms.

The goal of this study was to calibrate and validate the DNDC model to estimate GHG emissions from biosolids-amended soils in a corn agroecosystem, as part of a broader study with three representative sites in Canada. The DNDC model was validated with daily and cumulative CO_2 and N_2O emissions, crop yield, SOC and total soil N data collected during three growing seasons (2017–2019) from an agricultural field experiment in Ste-Anne-de-Bellevue, Quebec, Canada.

4.2. Materials and Methods

4.2.1. Site Description and Field Experiment

4.2.1.1. Physico-chemical Characteristics of Biosolids

Chemical characteristics of the biosolids are shown in Table 4.1 and Table A.4.1. The mesophilic anaerobically digested biosolids (henceforth referred to as digested biosolids) were collected from a municipal biomethanization centre (St-Hyacinthe, Quebec); composted biosolids were collected from Gaudreau Compost, Victoriaville, Quebec; and alkaline-stabilized biosolids were produced the N-Viro® process by Walker Environmental, Goffs, Nova Scotia.

Table 4.1. Chemical characteristics of biosolids applied consecutively to agricultural soils over the three years (2017–2019) of field experiment in Ste-Anne-de-Bellevue, Quebec, Canada.

Parameter[a]	**2017**			**2018**			**2019**		
	Digested	**Composted**	**alkaline-stabilized**	**Digested**	**Composted**	**alkaline-stabilized**	**Digested**	**Composted**	**alkaline-stabilized**
DM (kg kg^{-1})	0.20	0.38	0.62	0.23	0.42	0.62	0.17	0.45	0.62
pH	8.2	7.6	10.8	8.2	7.4	9.8	8.1	7.0	8.7
TKN (g kg^{-1})	71.0	24.5	n/a	64.3	11.7	11.3	61.7	11.3	7.3
NH_4^+ N (g kg^{-1})	11.0	4.10	n/a	13.4	1.3	0.7	13.3	1.3	1.0
K (g kg^{-1})	0.6	0.4	n/a	n/a	n/a	n/a	8.1	1.6	1.1
P (g kg^{-1})	3.3	0.9	n/a	n/a	n/a	n/a	39.1	6.4	5.9
OM-LOI (g kg^{-1})	670	752	315	567	451	350	547	428	279
OC (g kg^{-1})	390	437	183	330	262	204	274	249	162
C:N (kg kg^{-1})	4.7	15.0	22.3	5.1	22.4	18.1	4.4	22.0	22.2

[a] C:N = carbon to nitrogen ratio; DM = dry matter; NH_4^+ = ammonium; OC = organic carbon; OM = organic matter; TKN = total Kjeldhal nitrogen; n/a = not available.

***Note**: Besides the alkaline-stabilized biosolids, the OM and C:N values of the biosolids in 2017 were reported in the suppliers' data sheet based on monthly sampling of biosolids in 2016 and 2017. The C:N for all biosolids in 2018 and 2019 were calculated by dividing the yearly measured OM contents derived using the loss-on-ignition method by the van Bemmelen factor of 1.72, and subsequently dividing the OC by TKN. For the alkaline-stabilized biosolids, the OM and C:N values in 2017 were the averages of the reported 2018 and 2019 values.*

4.2.1.2. Study Area and Materials

The field experiment was a three-year study (2017–2019) at the Emile A. Lods Agronomy Research Centre, Ste-Anne-de-Bellevue, Quebec, Canada (Latitude 45˚28'N, 73˚45'W). The site has a 30-year mean annual rainfall of 785 mm, mean annual snowfall of 206 cm, and mean annual temperature of 6.5˚C (Environment and Climate Change Canada, 2021). The growing season is from May to October with a mean daily temperature of about 16˚C. The experiment was established on a 0.6 ha area of a moderate to well drained alluvio-lacustrine parent material with <5% slope. The soil is classified as Gleysol under the Canadian Soil Classification System and has a loam soil texture (490 g sand kg^{-1}, 320 g silt kg^{-1} and 190 g clay kg^{-1}) with 2.58% organic matter (OM), bulk density of 1.21 ± 0.15 (g cm^{-3}), and pH of 6.1 ± 0.2 at the start of the field study. The fields were under a corn-soybean-pea rotation from 2007 until 2015, then in 2016, Field 1 (see Figure A.4.1) was cropped with corn, while Field 2 was cropped with spring wheat. In the spring of 2017, both fields where moldboard ploughed (17 cm depth) and harrowed (10 cm depth) prior to seeding.

4.2.1.3. Experimental Design

The field experiment was designed as an unbalanced factorial with three treatment factors: fertilizer type, rate of biosolid application, and method of application. Silage corn was grown with either commercial urea, digested biosolids, alkaline-stabilized biosolids, or composted biosolids, or a combination (1:1 ratio) of one type of biosolids and urea (e.g., digested biosolids + urea). The fertilizers were either surface-spread or soil-incorporated, with an unfertilized treatment serving as the negative control. In total, there were 15 treatments organized within each of 4 blocks, resulting in 60 experimental plots (see Figure A.4.1). Each experimental plot (8 m × 5 m) received

39 kg N ha^{-1} in the form of calcium ammonium nitrate as a starter dose of N at seeding (27% total applied N, including 13.5% as ammonia N and 13.5% as nitrate N). The remaining N was applied to the fertilized treatments as either of the biosolids before seeding and/or commercial urea applied at the six-leaf stage, depending on the treatment, to achieve a targeted 120 kg of applied available N per hectare, annually. For the treatments biosolids without urea, the target was achieved by adding a total of 162 kg N ha^{-1} as biosolids, with 50% assumed to be available to the crop, i.e., 81 kg available N ha^{-1} from biosolids and 39 kg N ha^{-1} from the starter fertilizer. Then for the treatments receiving half N from biosolids, the target was achieved by applying 39 kg N ha^{-1} as starter fertilizer, 21 kg N ha^{-1} as urea, and 60 kg available N ha^{-1} as biosolids (120 kg total N as biosolids but assuming only 50% was available to the plants). There were two control treatments: the positive control which received all N in mineral form (81 kg N ha^{-1} as urea and 39 kg N ha^{-1} as calcium ammonium nitrate), and the negative (unfertilized) control which received only the starter fertilizer. After the biosolids were applied, they were spread uniformly over the experimental plots and either left on the surface until planting or else incorporated using a cultivator to a depth of 15 cm within 24 h. All the plots were seeded with silage corn DKC 35-54 in 2017 and DKC 3378-RIB in 2018 and 2019, at a rate of 76,000 seeds ha^{-1}. Between 10–20% of corn residues were left on the plots after harvest and were incorporated into the soil during post-harvest tillage. The management practices during the planting season are shown in Table A.4.2.

4.2.1.4. Gas Sampling and Analysis

Soil CO_2 and N_2O fluxes were determined in every plot with manual non-steady-state chambers during the growing season (late Apr. to Oct. of 2018 and 2019). The non-steady-state chambers were made of acrylic (50 cm × 50 cm × 15 cm), with collars that were buried to a depth of 10 cm in the centre of each plot in accordance to the quality criteria described in Rochette and Eriksen-Hamel (2008). The top 5 cm of the collar protruded above the ground and served as the base over which an insulated cover (50 cm × 50 cm × 15 cm) was placed during each sampling event (Hung et al., 2021). After covering the chamber, 20 mL of headspace gas was sampled at 15-min intervals from 0 to 60 min and transferred into pre-vacuumed 12-ml glass Exetainers™ (Labco Limited, Lampeter, Wales, UK). Gas sampling was conducted twice weekly immediately after biosolids and urea fertilizer applications, once weekly thereafter, and within 48 h after every rainfall event to capture any spikes in gas flux as a consequence of increased soil moisture (Barton et al., 2015). In some cases, it was impossible to conduct gas sampling after consecutive rainy days due to muddy soil conditions. Gas samples were analyzed for N_2O and CO_2 concentrations using a gas chromatograph (Bruker 450-GC, Bruker Corporation, Billerica, MA, USA) fitted with a flame ionisation detector (FID) for CO_2 analysis, a 63Ni electron capture detector (ECD) for N_2O analysis, and using high-purity helium as a carrier gas.

The concentrations of N_2O and CO_2 were estimated using the Hutchinson-Mosier R (HMR) software package (v1.0.1; Pedersen, 2020) considering the relative molecular mass of C and N, i.e., CO_2 equals 12 g mol^{-1} and N_2O equals 28 g mol^{-1}. During each of the gas sampling events, a Kestrel Drop 3 environmental data logger (Kestrel Meters, Boothwyn, PA, USA) was placed in a chamber to record the air temperature and water vapor pressure. The N_2O and CO_2 fluxes were adjusted for air temperature and water vapor pressure according to the procedure described in Hung et al. (2021). N_2O and CO_2 fluxes measured in 2017 failed to meet the quality criteria as described by Rochette and Eriksen-Hamel (2008), as such were excluded from further analysis. The cumulative flux for the 2018 and 2019 growing seasons were estimated by linear interpolation, assuming that the flux changed linearly between successive sampling dates (De Klein & Harvey, 2012). Soil temperature was measured by inserting a thermometer probe 10 cm into the soil, while soil moisture was measured gravimetrically by collecting about 50 g of soil from the top 10 cm and drying it at 60˚C for 48 h.

4.2.1.5. Soil and Crop Biomass Sampling and Analysis

Sampling and analysis of soil and the above-ground biomass of corn were done as per Halpern et al. (2010). To test DNDC's ability to simulate SOC and total soil N changes across different soil layers, soil samples were collected at 0–10 cm, 10–20 cm, and 20–30 cm depths of each plot at the start (before ploughing in April 2017) and end (after crop harvest in October 2019) of the field experiment. Subsamples of the collected soil were dried and finely ground to pass through a 1-mm-mesh sieve before analysis for total C and N with a Thermo Finnigan Flash EA 1112 CN analyzer (Carbo Erba, Milan, Italy). It was assumed that total C was equivalent to SOC at this site because no carbonates were detected during treatment of the soil with dilute acid (1 mol L^{-1} HCl). Each year, above-ground biomass of the corn plants was harvested at half-milk stage within an area of 1.5 m × 2.5 m at the center of each plot, shredded, homogenized, weighed, and dried in an oven (Type K T/C ST498, JPW Industrial Ovens & Furnaces, PA, USA) at 55℃ to constant dry weight.

4.2.2. The DeNitrification and DeComposition (DNDC) Model

The DNDC model was originally developed to simulate N_2O, CH_4, and CO_2 emissions from agricultural soils in USA on a daily time-step (Li et al., 1992, 1994). Since 2013, a Canadian regionalized version named DNDC.vCAN, has been developed to better represent Canadian climate, soils, and management conditions (Banger et al., 2020; He et al., 2020). The model framework simulates N_2O emissions based on the ‘‘anaerobic balloon” concept (Li et al., 2000), and allows the user control of trace gas parameters that are difficult to measure but can have significant impacts on N cycling. Such parameters include the release of denitrifier substrates during freeze-thaw conditions, overall rates of denitrifier and nitrifier growth, and rainfall intensity impacts to better calibrate site-specific nitrification and denitrification rates as driven by moisture, nitrogen, and microbial dynamics in soils (Smith et al., 2020). The decomposition sub-model estimates SOC decomposition and soil respiration across the full 200 cm heterogenous soil profile in ~1cm increments (Jiang et al., 2020; Smith et al., 2020). Manure (raw/digested slurries, farmyard composted and biosolids) decomposition dynamics are controlled by incoming manure C:N which determines the fractional allocation of manure C to the major soil C pools (litter, microbial, humads, and humus). Potential daily crop growth is regulated using crop specific empirical growth curves (Kröbel et al., 2011) modified by water, temperature and nutrient stresses as influenced by root growth & density algorithms (Smith et al., 2020). The DNDC model’s capability in being able to simultaneously track a mass balance of soil C and N dynamics and losses for a wide-range of fertilizer-manure management options made its selection ideal for use in this study.

4.2.3. Model Calibration, Validation, and Evaluation

4.2.3.1. Model Input and Set Up

The DNDC.vCAN simulation was set up using the following input data: (1) daily climate data from 2007 to 2019 collected from the Ste-Anne-de-Bellevue weather station, located within 50 m of the experimental site. Missing data from this station was supplemented with data from the Montreal/Pierre Elliott Trudeau International Airport weather station (Environment and Climate

Change Canada, 2021) located about 20 km from the experimental site; (2) soil properties were established using measured values (Table A.4.3) with the exception of hydraulic conductivity, field capacity, and wilting point for the loam soil which were estimated using soil water characteristic equations derived by Saxton & Rawls (2006); (3) historical management practices at the field site from 2007 to 2016, as recorded at the Emile A. Lods Agronomy Research Center (M. Samoisette, personal communication, 2018; Tables A.4.4 and A.4.5); and (4) crop management practices and the properties for each type of biosolids (Tables 4.1 and A.4.2). Based on the collected input data, one input file was created for each of the 15 treatments. DNDC simulations were run on site mode for 13 consecutive years from 2007 to 2019 (i.e., a 10-year spin-up was simulated) to reduce the residual effects of initial conditions and previous season's crop residue. The results were then extracted for the study period when the measurements were made from 2017 to 2019.

4.2.3.2. Model Calibration and Validation

Following the procedure described in Li (2013), DNDC was calibrated against measured soil moisture and temperature in the top 10 cm of soil, CO_2 and N_2O emissions, crop yield, and total soil N and SOC at 0–10, 10–20, and 20–30 cm depths. Using the measured values of the soil, crop, and climate parameters (Table A.4.3), five of the 15 treatments were used to calibrate DNDC: i.e., the unfertilized and surface-spread treatments of urea, digested biosolids, alkaline-stabilized biosolids, and composted biosolids. The snow melt factor, denitrifier growth rate, crop N and water demand, and SOC decomposition factor were adjusted manually in an iterative manner until minimum RMSE values between the simulated and measured variables were achieved across all calibration treatments (see parameter values in Table A.4.3 and flowchart in Figure A.4.2). The adjustment factors for decomposition rates of the SOC pools and denitrifier growth rates respectively were set for the following calibration treatments: unfertilized = 1.35, urea = 1.35, composted biosolids = 1.45, digested biosolids = 2.65, and alkaline-stabilized biosolids = 1.65. The adjusted parameters were then fixed for the rest of the treatments for their simulation runs. Only the management practices unique to each treatment were modified during the validation runs. Following the DNDC model user guide (University of New Hampshire, 2012), the simulated biomass yield expressed on an equivalent C basis was converted to dry matter (DM) basis, where 1 kg C is equivalent to 2.5 kg (DM) of silage corn grain, while N_2O and CO_2 emissions were based on equivalent N and C contents, respectively.

4.2.4. Statistical Analysis and Model Evaluation

The data were analysed using R (v3.6.1, R Core Team, 2020) prior to model evaluation. The data were checked for homogeneity of variance and normality using the Shapiro-Wilks test and the N_2O emissions data for the growing season were log-transformed. A three-way ANOVA ($\alpha = 5\%$) was used to examine treatment effects on CO_2 and N_2O emissions and crop yields for the growing seasons. The *HSD.test* function of the Agricolae package was used to perform Tukey's test for pairwise comparison on the analysed datasets (v1.3-5; De Mendiburu, 2021).

Statistical procedures from Smith & Smith (2007) and Giltrap et al. (2020) were employed to estimate the measures of association and confidence of model simulations. The degree of association between the patterns of the DNDC simulation results and the field measurements were evaluated using the Pearson's correlation coefficient r (Eq. A.4.1; see Appendix for all equations) and the significance of association F (Eq. A.4.2) at $p = 0.05$. The difference and bias between observed and simulated values were assessed by calculating the root-mean-squared error (RMSE;

Eq. A.4.3) and relative error (E; Eq. A.4.4), respectively. Meanwhile, the significance of the RMSE and E values were tested by comparing them to the $RMSE_{95\%}$ (Eq. A.4.5) and $E_{95\%}$ (Eq. A.4.6) values, respectively which were based on the standard error of the measurements.

4.3. Results

4.3.1. Temperature and Precipitation during the Growing Season

Daily precipitation was lower and daily temperatures were higher on average during the growing season in 2018, relative to 2017 and 2019. The mean daily precipitation was generally lower in 2018 than in 2019 and 2017, except in July and September. For instance, in May of 2018, when biosolids were applied, the mean daily precipitation was 1.45 mm, while it was 4.0 mm and 2.89 mm in May 2017 and 2019, respectively (see Table A.4.6). The mean daily temperature in 2018 was at least 1.5°C higher than in 2017 and 2019 until August (see Table A.4.6).

4.3.2. Model Calibration and Validation

The total bias and error between the measured and simulated GHG emissions, SOC, total soil N, and corn yields were within the 95% confidence interval of the measurements for both calibration and validation (Table 4.2). DNDC was well-calibrated for soil moisture (r = 0.55) and soil temperature (r = 0.90). The method of biosolids application was found to have no significant effect on the measured variables (Tables A.4.7, A.4.9, and A.4.10), so the application method was removed as a treatment effect during data analysis.

Table 4.2. Statistical analyses of the model performance in simulating daily and cumulative carbon dioxide and nitrous oxide emissions during the growing season in 2018 and 2019, crop yields from 2017 to 2019, and soil organic carbon and total soil N at 0–30 cm depth for the calibration and validation stages. Total model error is not significant if RMSE < $RMSE_{95\%}$. Model bias is not significant for E < $E_{95\%}$. Model association ranges from -1 to 1 with increasing association for r values ranging from 0 - 1.

Variable	Calibration					Validation				
	r	**E (%)**	**$E_{95\%}$ (%)**	**RMSE**	**$RMSE_{95\%}$**	**r**	**E (%)**	**$E_{95\%}$ (%)**	**RMSE**	**$RMSE_{95\%}$**
Ave. N_2O	0.2	-2.5	155.2	25.7	45.7	0.3	6.2	155.2	33.2	72.3
Ave. CO_2	0.4	-53.4	85.6	20.2	19.7	0.3	-85.0	92.8	22.7	24.7
Cum. N_2O	0.8	-16.1	84.8	1.2	2.4	0.8	-5.8	80.7	1.0	3.0
Cum. CO_2	0.3	-33.3	66.9	1.1	2.1	0.3	-26	67.5	0.9	2.2
Crop yield	0.7	2.2	19.1	1.4	2.3	0.4	1.1	19.9	1.8	2.5
SOC	0.6	-9.1	19.5	2.4	3.1	0.3	-15.8	21.9	3.1	3.5
Soil N	0.3	7.7	26.9	0.3	0.4	0.0	3.1	28.0	0.3	0.5

[†] Ave. N_2O = average daily nitrogen emission as nitrous oxide (g N ha^{-1} d^{-1}), Ave. CO_2 = average daily carbon emission as carbon dioxide (kg C ha^{-1} d^{-1}), Cum. N_2O = cumulative nitrogen emission as nitrous oxide during the growing season (kg N ha^{-1} y^{-1}), Cum. CO_2 = cumulative carbon emission as carbon dioxide during the growing season (t C ha^{-1} y^{-1}), Crop yield (t DM ha^{-1} y^{-1}), and SOC = soil organic carbon (t C ha^{-1}) at 0–30 cm soil depth; and Soil N = total soil nitrogen (t N ha^{-1}) at 0–30 cm soil depth.

4.3.3. Corn Yields

Measured corn yields were significantly influenced by fertilizer type depending on annual effects (Year; as written in Table A.4.7 and other ANOVA tables) as they generally declined from 2017 to 2019, except for treatments receiving only alkaline-stabilized and digested biosolids, which also had the highest corn yields in each year (see Figure 4.1 and Tables A.4.8, A.4.11 and A.4.12). Across the treatments, the average corn yields ranged from 11.6 to 16.4 t DM ha^{-1} in 2017, 9.4 to 17.5 t DM ha^{-1} in 2018, and 7.5 to 14.8 t DM ha^{-1} in 2019. In 2017 and 2018, there was no marked difference in yield among the biosolids treatments. Meanwhile, in 2019 there were observable differences in yields among the treatments amended with digested and alkaline-stabilized biosolids and the unfertilized control (see Figure 4.1 and Table A.4.8). Also, the effects of method of application and rate of biosolids application on crop yields were not significant.

DNDC underestimated corn yields by 12% and 14% during the model calibration and validation stages, respectively. The RMSE values for crop yield are shown in Table A.4.13. The simulated interannual variation in corn yields were similar to those for the field observations ($r = 0.6$; Figure 4.1), especially for the following treatments: unfertilized ($r = 1.0$), urea + digested biosolids ($r = 0.9$), urea + alkaline-stabilized biosolids ($r = 0.7$), and urea + composted biosolids ($r = 0.9$). However, the trends in simulated and observed yield were dissimilar for the treatments receiving only alkaline-stabilized ($r = -0.5$) or composted ($r = -0.1$) biosolids.

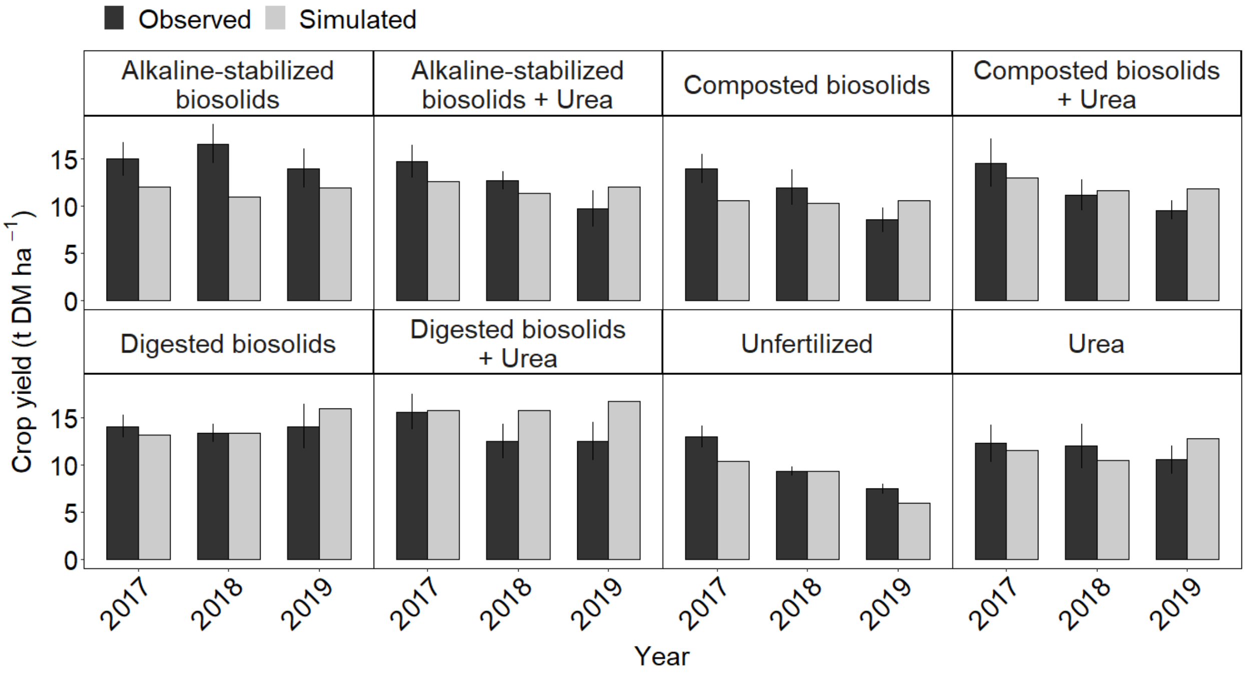

Figure 4.1. Simulated (DNDC) and measured above-ground biomass (dry basis) for all treatments for 2017, 2018, and 2019. Mean values within treatments; n = 8 for fertilized and n = 4 for unfertilized treatments; error bars indicate standard deviation. The method of application had no significant effect on crop yield ($\alpha = 0.05$), so data from surface-spread and soil-incorporated treatments were pooled.

4.3.4. Daily Nitrous Oxide Emissions

There were differences among treatments in the trends, magnitude, and variability of the daily N_2O emissions. The mean daily N_2O emissions from treatments amended with digested biosolids only (27.0–73.9 g N ha^{-1} d^{-1}) were generally higher than those from treatments amended with either composted biosolids (2.6–13.9 g N ha^{-1} d^{-1}) or alkaline-stabilized biosolids (5.6–16.0 g N ha^{-1} d^{-1}; Table A.4.10). The daily N_2O emissions were generally low during the early growing season (< 50 g N ha^{-1} d^{-1}) even after the application of biosolids but peaked in the mid-growing season in both 2018 and 2019. The daily N_2O emissions then declined during late summer and early fall and remained low until the end of the growing season (see Figures 4.2 and 4.3).

The RMSE and E values for N_2O flux were within the 95% confidence limits in 2018 and 2019 for all treatments except for composted biosolids in 2018, where $RMSE > RMSE_{95\%}$. However, in 2018 the simulated fluxes were significantly different from the observed N_2O fluxes for urea, composted biosolids, alkaline-stabilized biosolids + urea, composted biosolids + urea, and the unfertilized control (Figure 4.2 and Table A.4.14). Overall, the model overestimated the mean daily N_2O emissions by 3.3%. In 2018, the correlation between the simulated and measured daily N_2O emissions was low ($r = 0.3$). This was mainly due to the overestimation by the model of N_2O emissions in the early season followed by underestimation of emission peaks in mid-August. However, the correlation coefficients were higher in 2019 (Figure 4.3) than in 2018 (Figure 4.2). In 2019, the r values were 0.4–0.9 for all treatments except the unfertilized control (r = -0.2–0.1; Table A.4.14) and treatments receiving either full or half alkaline-stabilized biosolids (r = 0–0.2). Interestingly, the model captured the major N_2O peaks observed in 2019 across most of the treatments (Figure 4.3).

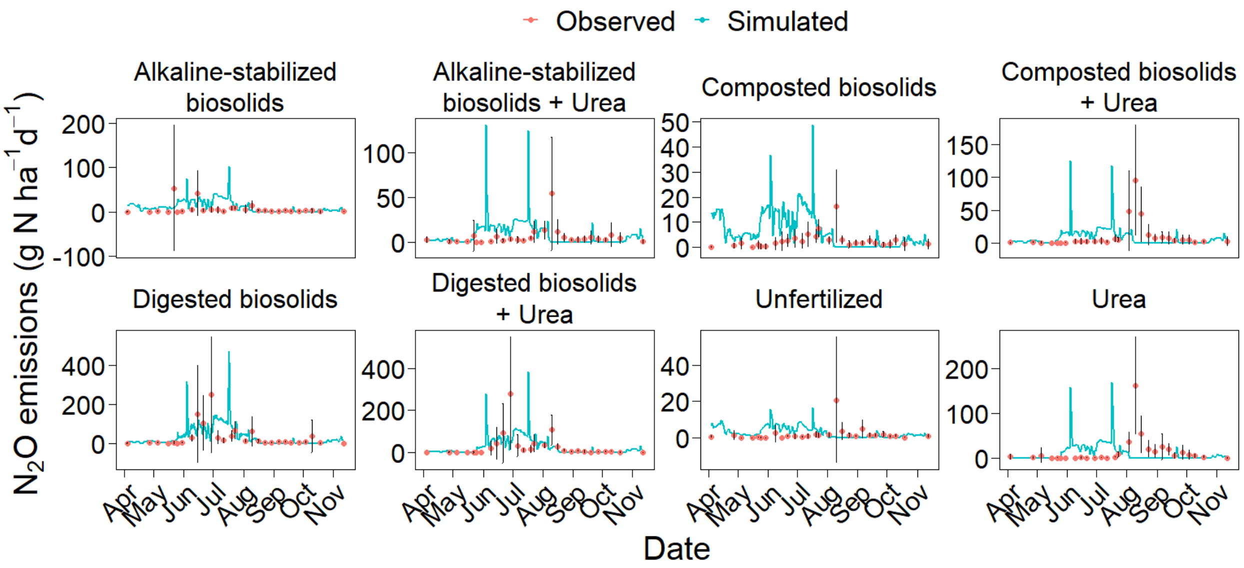

Figure 4.2. Simulated (DNDC) and measured daily nitrous oxide flux for all treatments during the 2018 growing season. Mean values within treatments; n = 8 for fertilized and n = 4 for unfertilized treatments; error bars indicate standard deviation. The method of application had no significant effect on nitrous oxide flux (α = 0.05), so data from surface-spread and soil-incorporated treatments were pooled.

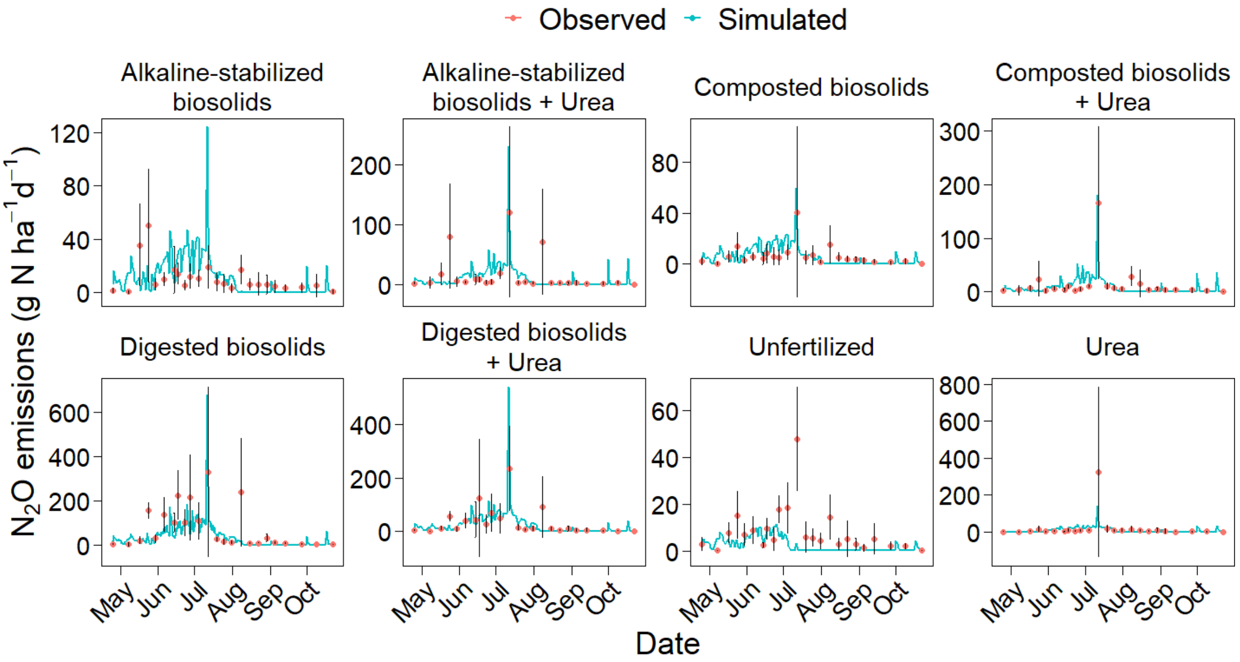

Figure 4.3. Simulated (DNDC) and measured daily nitrous oxide flux for all treatments during the 2019 growing season. Mean values within treatments; n = 8 for fertilized and n = 4 for unfertilized treatments; error bars indicate standard deviation. The method of application had no significant effect on nitrous oxide flux ($\alpha = 0.05$), so data from surface-spread and soil-incorporated treatments were pooled.

4.3.5. Daily Carbon Dioxide Emissions

The mean daily CO_2 emissions during the growing season ranged from 9.9 to 27.3 kg C ha^{-1} d^{-1} and showed similar trends across treatments (Figures 4.4 and 4.5). In 2018, the daily CO_2 emissions were lower from early May until mid-July in relation to the mid-season (Figure 4.4). From mid-July, the daily CO_2 emissions increased to a peak in August, then declined gradually until the end of the season. The pattern of CO_2 emissions was similar in 2019 (Figure 4.5). The CO_2 emissions gradually increased from mid-June to mid-August, then declined until the end of the season. In 2019, however, there was an initial peak in CO_2 emissions in mid-May from treatments receiving alkaline-stabilized biosolids.

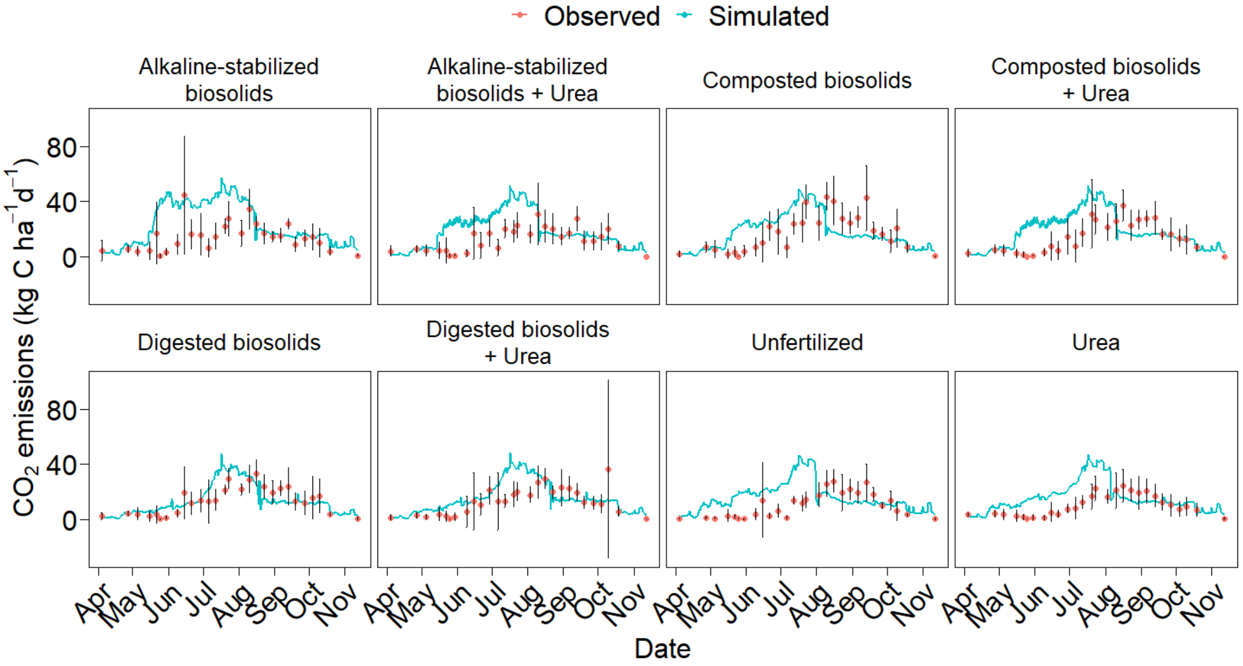

Figure 4.4. Simulated (DNDC) and measured daily carbon dioxide fluxes for all treatments during the 2018 growing season. Mean values within treatments; n = 8 for fertilized and n = 4 for unfertilized treatments; error bars indicate standard deviation. The method of application had no significant effect on carbon dioxide flux (α = 0.05), so data from surface-spread and soil-incorporated treatments were pooled. The y-axis values are the same for all plots.

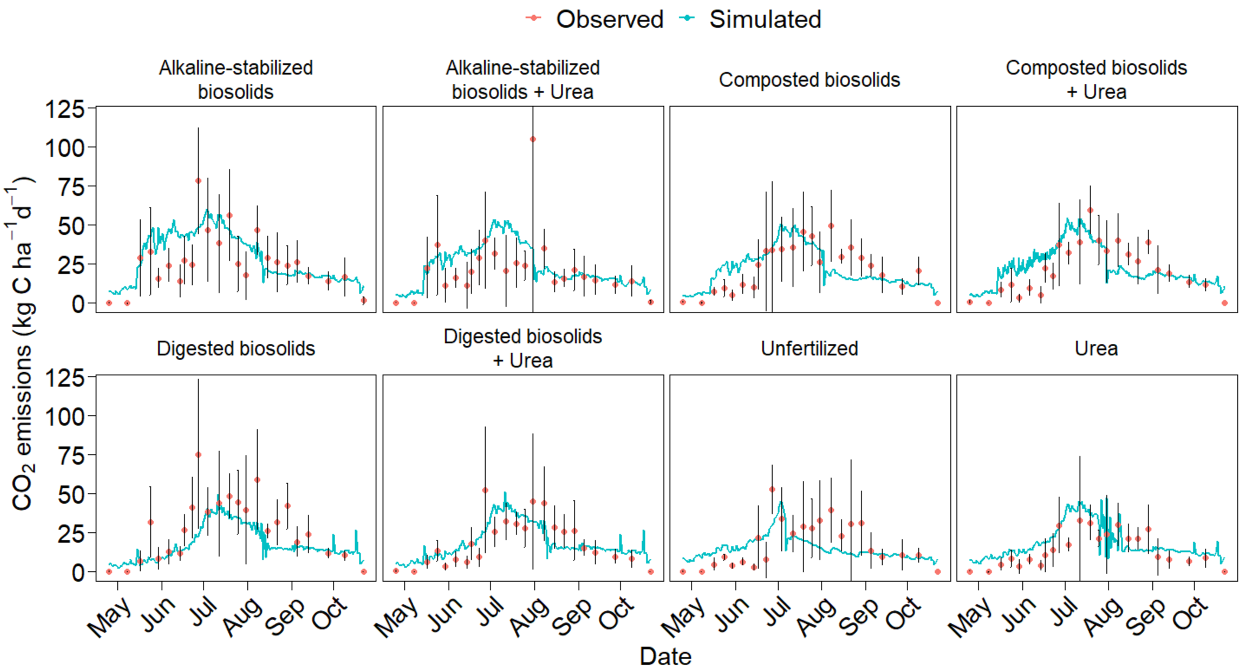

Figure 4.5. Simulated (DNDC) and measured daily carbon dioxide fluxes for all treatments during the 2019 growing season. Mean values within treatments; n = 8 for fertilized and n = 4 for unfertilized treatments; error bars indicate standard deviation. The method of application had no significant effect on carbon dioxide flux (α = 0.05), so data from surface-spread and soil-incorporated treatments were pooled. The y-axis values are the same for all plots.

There was no significant difference between the simulated and observed daily CO_2 fluxes across treatments, and the RMSE and E values were within the 95% confidence limits, except for the unfertilized and urea treatments where RMSE > $RMSE_{95\%}$ (see Table A.4.15). The correlation coefficients between the simulated and measured daily CO_2 fluxes ranged from -0.1 to 0.8. For treatments receiving composted biosolids, the r values were mostly at the lower end of this range (Table A.4.15). During the early growing season in 2018, the mean daily CO_2 emissions were low and were overestimated by DNDC. However, DNDC more accurately reflected the emissions trends later in the season for most treatments. In 2019, both the trends and magnitudes of the measured CO_2 emissions were well represented (r = 0.5) for most treatments.

4.3.6. Seasonal Nitrous Oxide Emissions

Cumulative N_2O emissions during the growing season were influenced by fertilizer and annual effects (see Table A.4.9). Digested biosolids had the highest mean cumulative N_2O emissions during the growing season (Table A.4.11) and the highest variability among all treatments, at 5.93 ± 4.34 kg -N ha^{-1} in 2018 and 11.58 ± 5.12 kg -N ha^{-1} in 2019 (Table 4.3). Soils receiving composted biosolids emitted the least N_2O, at 0.53 kg N_2O-N ha^{-1}, followed by alkaline-stabilized biosolids at 1.09 kg N_2O-N ha^{-1}. The difference in cumulative N_2O emissions between these latter two treatments was statistically significant. Also, the effects of method of application and rate of biosolids application on cumulative N_2O emissions were not significant.

Table 4.3. Measured and simulated cumulative carbon dioxide and nitrous oxide emissions from the experimental site located at Ste-Anne-de-Bellevue, Quebec, during the 2018 and 2019 growing seasons.

Treatment	N_2O (kg N ha^{-1})				CO_2 (t C ha^{-1})			
	2018		2019		2018		2019	
	Obs.†	Sim.	Obs.†	Sim.	Obs.†	Sim.	Obs.†	Sim.
Unfertilized	0.36 (0.35)^{e}	0.6	1.37 (0.44)^{bc}	0.43	1.98 (0.50)^{b}	3.49	3.46 (0.48)^{ab}	3.92
Urea	2.81 (1.64)^{abc}	2.22	3.42 (4.13)^{bc}	1.42	3.02 (1.74)^{b}	2.71	3.86 (0.99)^{b}	3.94
Digested biosolids	5.93 (4.39)^{ab}	6.93	11.58 (5.12)^{a}	6.2	2.04 (0.69)^{ab}	3.39	2.59 (0.69)^{a}	3.38
Alkaline-stabilized biosolids	1.09 (0.75)^{cde}	1.99	1.76 (0.71)^{bc}	1.94	2.44 (1.02)^{ab}	3.3	3.18 (0.98)^{a}	3.38
Composted biosolids	0.53 (0.20)^{de}	1.36	1.09 (0.61)^{c}	1.09	2.68 (0.45)^{a}	2.99	2.53 (0.55)^{ab}	4.09
Digested biosolids + urea	5.39 (2.97)^{a}	5.64	5.52 (3.52)^{ab}	4.39	4.54 (0.86)^{ab}	3.18	3.83 (1.87)^{ab}	4.3
Alkaline-stabilized biosolids + urea	1.13 (0.72)^{cde}	1.73	2.77 (1.72)^{bc}	1.91	2.74 (0.50)^{b}	5.21	2.76 (0.60)^{ab}	4.08
Composted biosolids + urea	2.00 (1.39)^{bcd}	1.66	2.44 (1.33)^{bc}	1.52	4.48 (1.52)^{ab}	5.25	3.75 (0.45)^{ab}	4.16

† Obs. = Mean measured values by treatment (n=4 for the unfertilized treatment and n = 8 for the other treatments) with standard deviations in parentheses; Sim. = Values simulated using DNDC. Different letters within each column of the measured variables represent significant differences at $p < 0.05$ based on Tukey's test for pairwise comparison.

Deducting the background N_2O emissions (i.e., emissions from the unfertilized treatment), the average value of N_2O-N emitted relative to the total N applied was highest in both 2018 and 2019 for treatments receiving only digested biosolids (3.4% and 6.3%), followed by treatments receiving urea (3.0% and 2.5%). More N_2O-N per N applied (less background emission) was emitted from treatments that received alkaline-stabilized biosolids + urea (0.55% and 0.99%) or composted biosolids + urea (1.16% and 0.76%) than from those receiving only alkaline-stabilized biosolids (0.45% and 0.24%) or composted biosolids (0.11% and 0.17%).

Overall, the RMSE and E values of simulated, cumulative N_2O emissions for the growing season were within 95% confidence limits of the measurements, except for treatments of composted biosolids in 2018 and the unfertilized treatment in 2019, for which RMSE ($RMSE_{95\%}$) values were 0.8 (0.2) and 0.9 (0.7), respectively. Overall, DNDC underestimated the mean cumulative N_2O emissions for the growing season by 9.3%. In most cases, the model was able to capture differences in cumulative N_2O emissions between years (r = 0.8) (Table 4.2 and Table A.4.16).

4.3.7. Seasonal Carbon Dioxide Emissions

The mean cumulative CO_2 emissions for the growing season were higher in 2019 than in 2018 across all treatments (Tables 4.3 and A.4.12). Also, the effects of method of application and rate of biosolids application on cumulative CO_2 emissions were not significant. DNDC was generally able to accurately simulate these values, with RMSE and E values mostly within the 95% confidence limits, except in a few cases (Table A.4.17). In 2018, for instance, the RMSE ($RMSE_{95\%}$) values were 1.5 (1.2) for the unfertilized treatment, 1.4 (0.8) for urea, 2.5 (0.6) for alkaline-stabilized biosolids, 1.6 (0.6) for alkaline-stabilized + urea biosolids, and 1.3 (0.7) for composted + urea biosolids. In 2019, RMSE ($RMSE_{95\%}$) values were 0.4 (1.0) for digested biosolids and 0.3 (0.2) for composted biosolids + urea. The model overestimated the cumulative CO_2 emissions by 27.6% overall and poorly (r = 0.3) represented trends during the growing season.

4.3.8. Soil Organic Carbon

SOC generally increased between the start of the field experiment, in April 2017, and the end, in November 2019 (Figure A 4.3). DNDC generally represented the values and trends in SOC well at the three depths, as indicated by Pearson's correlation coefficient (r = 0.4–0.8), except for treatments of urea (r = 0.1) and urea + composted biosolids (r = 0). The RMSE values for most biosolids and biosolids + urea treatments, however, were not within the 95% confidence interval, even though SOC values were overestimated by only about 13% overall (Table A.4.18).

4.3.9. Total Soil Nitrogen

In general, total soil N decreased at the end of the experiment relative to the initial soil N, especially in the top 0–20 cm soil layers (Figure A 4.4). Overall, DNDC underestimated the observed soil N by 4.3% on average (Table A.4.19). The model estimated the total soil N better at the end of the experiment than at the start of the experiment. The model poorly represented the observed trends in total soil N between April 2017 (initial) and November 2019 (final) (r = 0.2).

4.4. Discussion

4.4.1. Crop and Soil Responses

The corn silage yields in this study were generally lower than yields from a typical farm in Quebec, as reported by the Institut de la statistique du Québec (2021). This was likely because we applied only 120 kg of available N per hectare in each growing season compared to the 170–240 kg N typically applied by farmers in Quebec. There was also an overall decline in corn yields in 2018 and 2019 as compared with 2017, likely due to less precipitation and higher temperatures. Among the experimental treatments, difference in the rate of biosolids degradation and the resultant release of mineral N (NO_3^- and NH_4^+) appeared to influence yields. Corn yields are typically influenced by soil mineral N release, especially during the critical stages of plant growth (Kablan et al., 2017). Differences in degradation rates were observed in the incubation experiment (Chapter 3) using similarly sourced biosolids applied to soil samples collected from the same experimental site. Corn yields were higher in treatments that received only digested biosolids and alkaline-stabilized biosolids than in those that received composted biosolids. We presume that this was due to higher rates of organic matter degradation and N mineralization in the digested and alkaline-stabilized biosolids relative to the composted biosolids as observed in the incubation experiment.

DNDC simulated values that were in general agreement with the observed magnitudes and interannual variation in corn yields. Similar results were found in crop yield simulations for similar corn agroecosystem in Ottawa, Canada (Dutta et al., 2016). In DNDC, crop yield simulation is influenced by the simulated SOC (biosolids C + initial soil organic C) and soil N degradation dynamics as well as precipitation-driven soil moisture and soil temperature (Zhang et al., 2017; Zhang et al., 2019). While simulated soil moisture and soil temperature correlated strongly with the observed values, the agreement between the measured and simulated magnitudes and changes in SOC (good; r = 0.4) and organic N (poor; r = 0.1) for the 0–30 cm soil depth varied across the treatments.

While the two measurements taken for SOC and total soil N were not sufficient to describe the detailed dynamics of C and N transformations in the soil, they were typical of Humic Gleysols in the St. Lawrence Lowlands of Quebec where this experiment was conducted (Bedard-Haughn, 2011). Tillage depletes soil C and N in Humic Gleysols while, in contrast, the application of organics increases SOC. In our experiment, SOC increased in the 0–10 cm soil depth over the course of the experiment, likely due to the net accumulation of biosolids and crop residue. Plots that received both biosolids and urea may have experienced a priming effect that accelerated SOC decomposition (Torri et al., 2014; Qiu et al., 2016), but the results from this study cannot provide any insights on this effect. Soil N did not decrease during the experiment, however, likely due to net N losses through crop uptake, N_2O and NH_3 emissions, leaching and runoff.

The discrepancies between the measured and simulated SOC and total soil N seen in this study were similar to those reported in other studies of Canadian agroecosystems (Smith et al., 2012; Cui and Wang, 2019). The accurate simulation of CO_2 and N_2O emissions using DNDC is very sensitive to SOC changes (Li et al., 1994), so more intensive SOC measurements over a longer time period would help to more accurately model the effects of repeated biosolids application on SOC dynamics, especially in the 0–10 cm soil depth. To the best knowledge of the authors, moreover, this is the only study in which DNDC was evaluated for simulating the co-application of biosolids and urea. Therefore, simulation of C and N dynamics resulting from the co-application of biosolids and urea would benefit from further investigation over longer time periods.

4.4.2. Nitrous Oxide Emissions

The N_2O emissions factor is the mean N_2O emissions during the growing season relative to the total applied N. The IPCC (2006) reported an emissions factor of 1% for all biosolids, wastewaters, and animal slurries and Charles et al. (2017) reported a value of 1.21 ± 0.14%. Those values are higher than what we observed in this experiment, except for treatments receiving digested biosolids and/or urea. The digested biosolids differed from the alkaline-stabilized and composted biosolids in terms of C/N, the chemical form of organic C, and in moisture content. The C/N of the digested biosolids ranged from 4.7 to 8.9, while the C/N of the other biosolids ranged from 15 to 22. In addition, more of the organic C in the digested biosolids was labile and the DM was lower (0.17 to 0.23 kg kg^{-1}) than in composted and alkaline-stabilized biosolids, leading to faster mineralization and more N_2O emission during the growing season.

In addition to the differences in the physico-chemical characteristics of the biosolids in this study, variations in soil and weather conditions also contributed to spatial and temporal variations in the N_2O emissions. The amount and variability of N_2O emissions are known to be affected by mineral N availability, soil pH, and soil clay content as well as precipitation and temperature (Oertel et al., 2016; Congreves et al., 2016). High N_2O emissions driven by precipitation during late spring to mid-summer are often observed in Quebec (Almaraz et al., 2009). It is also common to observe early bursts of N_2O within 10 days after the application of urea and biosolids (Case et al., 2016). In our study, however, manual gas sampling immediately after such events was physically challenging and we did not observe such spikes in emissions, possibly due to the sparsity of field measurements. The variations that we observed in N_2O emissions within and between the treatments were consistent with findings from other studies. Several other field experiments showed that N_2O fluxes varied from 56 to 262% of the measured average emissions (Saggar et al., 2007). This spatial heterogeneity in N_2O emissions within the treatments was likely due to differences in soil characteristics and uneven distribution of the biosolids across the plots. In addition, the field measurements using manual chambers were often done weekly or fortnightly, introducing potential error due to insufficient spatial coverage, sampling time and frequency, chamber position, and data censoring, as seen in other studies (Collier et al., 2014; Lee, 2018).

The DNDC estimates were generally close to the observed N_2O emissions, especially in 2019 (E = 26%). DNDC was unable to simulate the observed N_2O emissions peaks in some instances, e.g. in mid-August of 2018, especially for composted biosolids, possibly due to a mismatch between the measured and simulated soil C and N dynamics (Li et al., 2017). Some erroneous model estimates could have resulted from limited experimental data for model calibration (Smith et al., 2002). In addition, discrepancies between observed and simulated N_2O emissions between July and September 2018 may have been due to insufficient local weather data, which were substituted with data from another weather station located ~20 km away from the field.

DNDC does not have the input resolution (and often the measurements are not available) to appropriately characterize biogeochemical processes and their drivers at the temporal resolution necessary to simulate changes at a daily scale for trace gas emissions. For example, climate sensitive inputs such as precipitation & temperature are only input at a daily value, soil microbial heterogeneity is not explicitly defined, soil hydraulic parameterization is simplified across larger soil layers and hydraulic processes are aggregated to the hourly time step. All these input differences contribute to a divergence from the in-field conditions and can result in daily desynchronization between observed and simulated events. The impacts of these input simplifications become less of an issue when modelled comparisons are made at larger temporal timescales (i.e., monthly, seasonal, annual).

4.4.3. Carbon Dioxide Emissions

The CO_2 emissions observed in this study were within the range measured by Almaraz et al. (2009) from a similar Quebec corn agroecosystem. Emissions increased in mid-summer relative to late spring and early autumn, as typically caused by increased soil temperatures driving microbial respiration and SOC decomposition (Riggs and Hobbie, 2016). Increased growth of corn biomass during the growing season was also a driver of CO_2 emissions from the soil during mid-summer, given that root respiration is a function of root biomass (Li et al., 2017). However, the use of manual chambers in fixed positions to measure CO_2 emissions from corn fields is quite limiting. In this study, the manual chambers were placed between corn rows which could have limited the measurement of actual CO_2 emissions due to root respiration.

DNDC estimates of CO_2 emissions from soils amended with biosolids were similar in most instances to the observed magnitudes and temporal trends, as found in other studies (e.g. Yadav and Wang, 2017; Li et al., 2017). Following the application of biosolids in mid-May 2018, the observed CO_2 emissions remained unexpectedly low until mid-June. The decomposition of the biosolids may have been slow due to low precipitation or there may have been shortcomings in the measurements done early in the growing season of 2018. Simulations showed root autotrophic respiration rates that were higher than expected during the vegetative stage, while root maintenance respiration values were lower than expected, resulting in an under-estimation of CO_2 emissions in the late growing season. Coefficients for root growth and maintenance respiration originally were hardcoded in DNDC and were the same for all crop types. Adjustable parameters for root autotrophic and soil heterotrophic respiration were therefore added to DNDC.vCAN, which improved the simulation of temperature-driven CO_2 emissions during the mid-growing season, especially for the treatments receiving digested biosolids. Further improvement is still required, however, to simulate the peaks in daily CO_2 emissions which were observed early in 2018 from the land-application of alkaline-stabilized and composted biosolids.

The simulation of SOC decomposition dynamics and the resulting CO_2 emissions for treatments receiving alkaline-stabilized and composted biosolids were more difficult to calibrate than those for digested biosolids. Prior to this study, DNDC had been used mainly to simulate the land application of N as synthetic fertilizer or as manure, which resembles digested biosolids in terms of C/N and the form of organic C. Alkaline-stabilized and composted biosolids, however, both contain complex organic compounds that are harder to decompose. Most of the readily decomposable substances in these biosolids are degraded during the thermophilic processes involved in their stabilization. The Ca-O-C bonding that results from the addition of $CaCO_3$ or CaO during the alkaline-stabilized stabilization of biosolids retards the hydrolysis of organic compounds (Wang et al., 2007). In addition, wood chips were used in the composted biosolids of this study, resulting in > 40% recalcitrant organic C content. The decomposition module in DNDC aggregates the organic C of soil and biosolids in the same pool, making it impossible to explicitly represent different rates of decomposition for these different materials. Disaggregating the representation of initial SOC and applied organic C pools would allow the modelling of specific decomposition rates and further improve the simulation of trends in CO_2 and N_2O emissions.

4.5. Conclusion

The DNDC model was calibrated and validated using measured weather, crop, field management, and soil data and was able to simulate corn yield and GHG emissions from fields in Quebec receiving three different types of biosolids, generating simulated values that were mostly statistically similar to observed values. In addition, the underlying drivers of C and N cycling in agroecosystems, such as soil moisture, soil temperature, SOC, and total soil N, were also simulated within acceptable ranges of the observed variables, especially in the top 10 cm depth of the soil. Discrepancies between the simulated and observed values in this study were likely due in part to DNDC's inability to represent different rates of decomposition of complex carbon structures in the biosolids, especially composted biosolids and alkaline-stabilized biosolids. Temporal and spatial variability in the biotic and abiotic factors that influence C and N cycling in agroecosystems may also have contributed to inaccuracies in the simulation. Also, DNDC outputs CO_2 and N_2O fluxes on a daily scale using average parameter values, while field measurements were done using manual chambers, often only once weekly, across randomly replicated treatments. Despite these challenges, however, there was general agreement between simulated and observed values.

We conclude, based on our results, that DNDC is a suitable tool for simulating C and N dynamics in farmland in Southwestern Quebec that has been amended with biosolids. DNDC had previously been tested for simulating C and N cycling in agroecosystems receiving manures and synthetic fertilizers. This novel work therefore extends the functionality of DNDC to simulate agroecosystems amended with biosolids. As researchers continue to improve the functionality of DNDC, it may be implemented beyond the field scale to simulate crop yields and GHG emissions on landscape, regional, and national scales, given the availability of high-quality reference datasets for model testing. DNDC may be a useful tool to help researchers answer questions about the optimization of crop production, the regulation of biosolids use, and climate change impacts and mitigation. However, DNDC still needs to be improved to better simulate daily CO_2 emissions during the early growing season and daily N_2O emissions during the mid-season, especially for fields amended with composted or alkaline-stabilized biosolids. We recommend that the representation of C and N decomposition and mineralization kinetics in SOM and organic amendments like biosolids be disaggregated in the decomposition module of DNDC, to improve the simulation of C and N turnover from the biosolids to the soil.

4.6. Acknowledgments

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4.8. Appendix

4.8.1. Appendix A: Supporting Data

Table A.4.1. Macro- and micro-nutrient concentrations in treated municipal wastewater biosolids applied to agricultural soils in 2017 and 2019. No data was available in 2018. The agricultural field experiment was in Ste-Anne-de-Bellevue, QC, Canada.†

Parameter	**2017**			**2019**		
	Digested	**Composted**	**Alkaline-stabilized**	**Digested**	**Composted**	**Alkaline-stabilized**
Ca (g kg^{-1})	23	29	250	38	12	229
Mg (g kg^{-1})	4.8	2.7	n/a	4.5	1.6	1.0
Na (g kg^{-1})	2.5	11.2	n/a	4.2	0.4	0.4
Fe (g kg^{-1})	29.0	6.6	n/a	28.1	6.2	3.4
B (mg kg^{-1})	11	16	n/a	12	12	10
Cu (mg kg^{-1})	350	91	n/a	139	27	72
Zn (mg kg^{-1})	320	266	n/a	281	124	178

†n/a = not available

Table A.4.2. Management practices and timing during the agricultural field experiment in Ste-Anne-de-Bellevue, QC, Canada from 2017–2019.

Management practice	**2017**	**2018**	**2019**
Tillage date	May 15	May 3	May 6
Tillage method	Disc plough (1st pass) and disc harrow (2nd pass)		
Tillage depth	10 cm	10 cm	10 cm
Biosolids application	May 23	May 5	May 5
Biosolids incorporation	May 24	May 16	May 16
Incorporation method	--------- Cultivator at 10–15 cm depth -----------		
Planting/starter N application	June 8	May 17	May 23
Post emergence urea application	July 5	July 19	July 24
Harvest date	October 4	October 18	October 24
Post-harvest tillage	October 11	October 20	October 24
Tool used for termination till	Chisel plough	Chisel plough	Chisel plough

Table A.4.3. List of crop, soil and climate parameters used in DNDC calibration and simulation of C and N cycling on the experimental field in Ste-Anne-de-Bellevue, QC, Canada.

Parameter	**Value**	**Unit**	**Parameter Type**
Land-use type	Upland crop field	-	Soil
Bulk density	1.21	g cm^{-3}	Soil
Soil pH	7.0	-	Soil
Clay fraction	0.19	-	Soil
Porosity	0.45	cm^3 cm^{-3}	Soil
Field capacity (WFPS)[†]	0.46	mL mL^{-1}	Soil
Wilting point (WFPS)[†]	0.20	mL mL^{-1}	Soil
Hydraulic conductivity	0.015	m hr^{-1}	Soil
Top layer SOC to 20 cm depth[†]	0.015	kg C kg^{-1}	Soil
Litter fraction	0.01	-	Soil
Humads fraction	0.19	-	Soil
Humus fraction	0.80	-	Soil
Initial soil nitrate	0.50	mg N kg^{-1}	Soil
Initial soil ammonium	0.05	mg N kg^{-1}	Soil
Crop residue fraction left in field	0.20	-	Soil
Snow melt factor[††]	1.10	-	Soil
Soil evaporation factor[††]	0.80	-	Soil
Run-off snow melt fraction[††]	0.20	-	Soil
N_2O rain intensity factor[††]	0.70	-	Soil

Parameter	**Value**	**Unit**	**Parameter Type**
Litter decomposition factor[††]	0.80	-	Soil
Humads decomposition factor[††]	0.80	-	Soil
Humus decomposition factor[††]	0.80	-	Soil
Denitrifier growth rate[††]	1.35	-	Soil
Grain yield	4,800	kg C ha^{-1} yr^{-1}	Crop
Grain fraction of crop biomass	0.25	-	Crop
Leaf fraction of crop biomass	0.30	-	Crop
Stem fraction of crop biomass	0.30	-	Crop
Root fraction of crop biomass	0.15	-	Crop
TDD[†]	2,600	°C d	Crop
Optimum crop temperature	30	°C	Crop
Crop water requirement	151	g water g^{-1} DM	Crop
N in rainfall	0.19	mg N kg^{-1}	Climate
Air NH_3 concentration	0.15	µg N m^{-3}	Climate
Air_CO_2 concentration	407	Mg CO_2 kg^{-1} air	Climate

[†] SOC = soil organic carbon; TDD = temperature degree days; WFPS = water-filled pore space

[††] Rate of snow melt, soil evaporation, litter decomposition, humads (active humus) decomposition, humus decomposition, and rainfall induced denitrification rate as a fraction of the default values

Table A.4.4. Dates and activities of historical (2007 to 2016) agricultural practices on Field 1 of the Ste-Anne-de-Bellevue site used for the field experiment.

Date	Activity
10-May-16	Fertilizer 0-0-60 at 66 kg ha^{-1},
17-Nov-16	Mouldboard plough 17 cm deep
25-Oct-16	Harvest corn
20-Jun-16	Post emergence fertilization 34-0-0, 418 kg ha^{-1} left on surface
10-May-16	Seeding of corn DKC 39-97RIB 76000 seeds ha^{-1}
10-May-16	Fertilizer banded and incorporated 23-23-0, 168 kg ha^{-1}
30-Oct-15	Mouldboard plough 17 cm deep
27-Oct-15	Limestone applied 3 tons ha^{-1}
25-Aug-15	Harvest of canola
21-May-15	Seeding of canola
20-May-15	Fertilization 0-20-40 in the form of 11-52-0 and 0-0-60
20-May-15	Incorporation of fertilizer using cultivator 7 cm deep
30-Apr-15	Disc harrow 10 cm deep
23-Oct-14	Mouldboard plough 17 cm deep
20-Oct-14	Harvest soybeans
22-May-14	Seed soybeans
20-May-14	Fertilizer 20-0-40 in the form of 27.5-0-0 and 0-0-60
1-May-13	Soybeans
1-May-12	Corn and soybeans
1-May-11	Corn

Date	Activity
1-May-10	Processing beans
1-May-09	Corn
1-May-08	Soybeans
1-May-07	Processing peas

Table A.4.5. Dates and activities of historical (2007 to 2016) agricultural practices on Field 2 of the Ste-Anne-de-Bellevue site used for the field experiment.

Date	Activity
10-Nov-16	Mouldboard plough 17 cm deep
10-Aug-16	Harvest wheat
24-Aug-16	Disc harrow 10 cm deep
26-Aug-16	Seed green manure winter wheat
25-Apr-16	Cultivator 7 cm deep
25-Apr-16	Fertilizer 27.5-0-0 300 kg ha^{-1} + 11-52-0 67 kg ha^{-1} + 0-0-60 75 kg ha^{-1} broadcast
25-Apr-16	Cultivator 7 cm deep to incorporate fertilizer
25-Apr-16	Seeding of spring wheat
30-Oct-15	Mouldboard plough 17 cm deep
27-Oct-15	Limestone applied 3 tons ha^{-1}
25-Aug-15	Harvest of canola
21-May-15	Seeding of canola
20-May-15	Fertilizer 50-30-40 in the form of 27.5-0-0, 11-52-0, and 0-0-60
20-May-15	Incorporation of fertilizer using cultivator 7 cm deep
30-Apr-15	Disc harrow 10 cm deep
23-Oct-14	Mouldboard plough 17 cm deep
20-Oct-14	Harvest soybeans
22-May-14	Seed soybeans
20-May-14	Fertilizer 20-20-40 in the form of 27.5-0-0 + 3-18-36 and 0-0-60
1-May-13	Soybeans

Date	Activity
1-May-12	Corn and soybeans
1-May-11	Corn
1-May-10	Processing beans
1-May-09	Fallow
1-May-08	Soybeans
1-May-07	Processing peas

Table A.4.6. Mean daily temperature and precipitation during months of the growing seasons as recorded at the Ste-Anne-de-Bellevue experimental site from 2017 to 2019.

Month	Mean daily temperature (°C)			Mean daily precipitation (mm)		
	2017	2018	2019	2017	2018	2019
May	13.12	15.04	11.50	4.00	1.45	2.89
Jun	18.66	18.25	17.56	4.51	2.36	2.69
Jul	20.79	23.36	22.76	4.05	2.14	1.25
Aug	19.99	22.03	19.75	2.82	1.69	1.81
Sep	18.39	17.18	15.18	1.79	3.05	3.33
Oct	13.15	6.46	9.49	3.95	2.15	8.37
Average	17.35	17.06	16.04	3.52	2.14	3.39

4.8.2. Appendix B: Statistical Analysis

Table A.4.7. The three-way ANOVA table for the effects of fertilizer N source (Fert), method of application (MA) and annual effects (Year) on crop yield from 2017 to 2019 on the experimental field in Ste-Anne-de-Bellevue, Quebec, Canada at α = 0.05.

Source	DF	Sum of Squares	Mean Square	F value	Pr (>F value)	Significance
Fert	7	375,270,249	53,610,036	18.5538	<2.20E-16	***
MA	1	4,690,849	4,690,849	1.6234	0.2048	
Year	2	307,204,919	153,602,460	53.1599	<2.20E-16	***
Fert:MA	6	20,770,773	3,461,795	1.1981	0.3111	
Fert:Year	14	174,297,005	12,449,786	4.3087	2.82E-06	***
MA:Year	2	10,876,999	5,438,499	1.8822	0.1562	
Fert:MA:Year	12	52,269,647	4,355,804	1.5075	0.1286	
Residuals	135	390,074,656	2,889,442			

Note: *** indicates significant influence of effect (factor or combination of factors) on crop yield at $p = 0.001$.

Table A.4.8. Tukey HSD pairwise comparison of means of crop yield (tonne dry mass of silage corn) during the growing seasons from 2017 to 2019 due to the interaction of fertilizer type and annual effects (year). Mean differences are significant at α = 0.05.

Fertilizer type and year interaction	**Mean**	**SD**	**N**	**groups**
Alkaline-stabilized biosolids:2017	15.03	1.78	8	abc
Alkaline-stabilized biosolids:2018	16.60	2.05	8	a
Alkaline-stabilized biosolids:2019	14.02	2.07	8	abcd

Composted biosolids:2017	14.00	1.51	8	abcd
Composted biosolids:2018	12.00	1.89	8	cdef
Composted biosolids:2019	8.58	1.29	8	g
Control:2017	12.98	1.17	4	bcdef
Control:2018	9.37	0.46	4	fg
Control:2019	7.49	0.50	4	g
Digested biosolids:2017	14.07	1.20	8	abcd
Digested biosolids:2018	13.41	0.94	8	bcde
Digested biosolids:2019	14.09	2.38	8	abcd
Urea:2017	12.30	1.95	8	cdef
Urea:2018	11.99	2.36	8	cdef
Urea:2019	10.57	1.51	8	efg
Alkaline-stabilized biosolids+Urea:2017	14.77	1.75	8	abc
Alkaline-stabilized biosolids+Urea:2018	12.74	1.00	8	bcdef
Alkaline-stabilized biosolids+Urea:2019	9.78	1.92	8	fg
Composted biosolids+Urea:2017	14.59	2.52	8	abc
Composted biosolids+Urea:2018	11.22	1.64	8	defg
Composted biosolids+Urea:2019	9.61	1.04	8	fg
Digested biosolids+Urea:2017	15.64	1.88	8	ab
Digested biosolids+Urea:2018	12.56	1.83	8	bcdef
Digested biosolids+Urea:2019	12.49	2.00	8	bcdef

Different letters within the “groups” column represent significant differences in crop yields at $p < 0.05$ based on Tukey’s test for pairwise comparison. SD = standard deviation.

Table A.4.9. The three-way ANOVA table for the effects of fertilizer N source (Fert), method of application (MA) and year (Year) on N_2O emissions during the growing season in 2018 and 2019 on the experimental field in Ste-Anne-de-Bellevue, Quebec, Canada at $\alpha = 0.05$.

Source	DF	Sum of Squares	Mean Square	F value	Pr (>F value)	Significance
Fert	7	72.484	10.3548	20.334	3.99E-16	***
MA	1	0.196	0.1962	0.3852	0.536383	
Year	1	7.571	7.5714	14.8681	0.000216	***
Fert:MA	6	0.67	0.1116	0.2192	0.969715	
Fert:Year	7	7.09	1.0129	1.9891	0.06516	
MA:Year	1	1.525	1.5247	2.994	0.087	
Fert:MA:Year	6	1.448	0.2414	0.474	0.826023	
Residuals	90	45.831	0.5092			

Note: *** indicates significant influence of effect (factor or combination of factors) on growing season N_2O emission at $p = 0.001$.

Table A.4.10. The three-way ANOVA table for the effects of fertilizer N source (Fert), method of application (MA) and year (Year) on growing season CO_2 emission in 2018 and 2019 on the experimental field in Ste-Anne-de-Bellevue, Quebec, Canada at α = 0.05.

Source	DF	Sum of Squares	Mean Square	F value	Pr(>F value)	Significance
Fert	7	28,889,439	4,127,063	4.8589	0.000111	***
MA	1	1,201,701	1,201,701	1.4148	0.237391	
Year	1	32,390,008	32,390,008	38.1336	1.87E-08	***
Fert:MA	6	7,423,483	1,237,247	1.4566	0.202189	
Fert:Year	7	9,111,184	1,301,598	1.5324	0.166463	
MA:Year	1	234,297	234,297	0.2758	0.60073	
Fert:MA:Year	6	8,563,047	1,427,174	1.6802	0.134917	
Residuals	90	76,444,408	849,382			

Note: *** indicates significant influence of effect (factor or combination of factors) on growing season CO_2 emission at *p* =0.001.

Table A.4.11. Tukey HSD pairwise comparison of means of cumulative N_2O and CO_2 emissions and crop yield across the growing seasons from 2017 to 2019 due to type of fertilizer. Mean differences are significant at α = 0.05.

Year	$N_2O^{††}$ (g N ha^{-1})	$CO_2^{††}$ (t C ha^{-1})	Crop yield†† (t DM ha^{-1})
Alkaline-stabilized biosolids	7.10 ± 0.62^{bc}	3.61 ± 1.42^{a}	15.22 ± 2.18^{a}
Alkaline-stabilized biosolids + Urea	7.31 ± 0.76^{bc}	3.18 ± 1.49^{ab}	12.43 ± 2.59^{bc}
Composted biosolids	6.54 ± 0.57^{c}	3.66 ± 0.78^{a}	11.53 ± 2.74^{cd}

Composted biosolids + Urea	7.46 ± 0.80 ^{b}	3.25 ± 0.72 ^{ab}	11.80 ± 2.75 ^{c}
Unfertilized	6.38 ± 1.06 ^{c}	2.50 ± 1.31 ^{ab}	9.94 ± 2.48 ^{d}
Digested biosolids	8.85 ± 0.76 ^{a}	3.61 ± 1.17 ^{a}	13.86 ± 1.59 ^{ab}
Digested biosolids + Urea	8.47 ± 0.53 ^{a}	2.88 ± 0.87 ^{ab}	13.56 ± 2.36 ^{b}

[††] Different letters within each column of the analysed variables represent significant differences at $p < 0.05$ based on Tukey's test for pairwise comparison. **Note:** N_2O data was log transformed. Also, data for soil C and total soil N were collected at the start (before planting in 2017) and end (after harvest in 2019) of the experiment.

Table A.4.12. Tukey HSD pairwise comparison of means of cumulative N_2O and CO_2 emissions, crop yield, soil organic carbon, and total soil nitrogen across all treatments due to annual effects during the growing seasons from 2017 to 2019. Mean differences are significant at $\alpha = 0.05$.

Year	N_2O[††] (g N ha^{-1})	CO_2[††] (t C ha^{-1})	Crop yield[††] (t DM ha^{-1})
2017	n/a	n/a	14.25±1.98^{a}
2018	7.29±1.09^{b}	2.64±0.68^{b}	12.69±2.42^{b}
2019	7.79±1.00^{a}	3.68±1.33^{a}	11.05±2.77^{c}

[††] Different letters within each column of the analysed variables represent significant differences at $p < 0.05$ based on Tukey's test for pairwise comparison. n/a = not applicable. **Note:** N_2O data was log transformed. Also, data for soil C and total soil N were collected at the start (before planting in 2017) and end (after harvest in 2019) of the experiment.

Table A.4.13. Statistical evaluation of DNDC-simulated crop yield using field experimental data (n = 8 for the fertilized and n = 4 for unfertilized treatments) from the site at Ste-Anne-de-Bellevue, Quebec, Canada. The standard deviation for the simulated crop yield is not included in this Table for the purpose of clarity. Total model error is not significant if RMSE < $RMSE_{95\%}$. Model bias is not significant for E < $E_{95\%}$.

Treatment	Year	Obs (t DM ha^{-1})	Std. Dev. (t DM ha^{-1})	Sim (t DM ha^{-1})	E (%)	$E_{95\%}$ (%)	RMSE (t DM ha^{-1})	$RMSE_{95\%}$ (t DM ha^{-1})
Unfertilized	2017	13.0	1.2	11.6	10.4	14.3	1.3	1.9
Unfertilized	2018	9.4	0.5	9.2	1.8	7.8	0.2	0.7
Unfertilized	2019	7.5	0.5	6.0	20.2	10.6	1.5	0.8
Urea	2017	12.3	1.9	11.6	6.0	17.8	0.7	2.2
Urea	2018	12.0	2.4	10.3	13.8	22.1	1.7	2.7
Urea	2019	10.6	1.5	12.7	-20.5	16.0	2.2	1.7
Digested biosolids	2017	14.1	1.2	12.9	8.2	9.6	1.2	1.4
Digested biosolids	2018	13.4	0.9	13.5	-1.0	7.9	0.1	1.1
Digested biosolids	2019	14.1	2.4	14.9	-5.7	19.0	0.8	2.7
Alkaline-stabilized biosolids	2017	15.0	1.8	11.9	21.1	13.4	3.2	2.0
Alkaline-stabilized biosolids	2018	16.6	2.1	13.0	21.6	13.9	3.6	2.3

Treatment	Year	Obs (t DM ha^{-1})	Std. Dev. (t DM ha^{-1})	Sim (t DM ha^{-1})	E (%)	$E_{95\%}$ (%)	RMSE (t DM ha^{-1})	$RMSE_{95\%}$ (t DM ha^{-1})
Alkaline-stabilized biosolids	2019	14.0	2.1	14.8	-5.3	16.6	0.7	2.3
Composted biosolids	2017	14.0	1.5	10.4	25.8	12.1	3.6	1.7
Composted biosolids	2018	12.0	1.9	10.7	10.6	17.7	1.3	2.1
Composted biosolids	2019	8.6	1.3	12.3	-43.8	17.0	3.8	1.5
Digested biosolids + Urea	2017	15.6	1.9	15.2	2.6	13.5	0.4	2.1
Digested biosolids + Urea	2018	12.6	1.8	13.9	-10.9	16.4	1.4	2.1
Digested biosolids + Urea	2019	12.5	2.0	13.9	-11.6	18.0	1.5	2.3
Alkaline-stabilized biosolids + Urea	2017	14.8	1.7	12.7	14.3	13.3	2.1	2.0
Alkaline-stabilized biosolids + Urea	2018	12.7	1.0	11.0	13.6	8.8	1.7	1.1
Alkaline-stabilized biosolids + Urea	2019	9.8	1.9	11.3	-15.2	22.1	1.5	2.2
Composted biosolids + Urea	2017	14.6	2.5	12.8	12.3	19.4	1.8	2.8
Composted biosolids + Urea	2018	11.2	1.6	11.0	2.3	16.4	0.3	1.8
Composted biosolids + Urea	2019	9.6	1.0	11.0	14.3	12.1	1.4	1.2

Table A.4.14. Statistical evaluation of DNDC-simulated daily N_2O fluxes (g N ha^{-1} d^{-1}) using field experimental data (n = 8 for the fertilized and n = 4 for unfertilized treatments) from the site at Ste-Anne-de-Bellevue, Quebec, Canada. Total model error is not significant if RMSE < $RMSE_{95\%}$. Model bias is not significant for E < $E_{95\%}$.

Treatment	**Year**	**Mean Obs**	**Mean Sim**	**r**	**F**	**Sig.diff?**	**E (%)**	**$E_{95\%}$ (%)**	**RMSE**	**$RMSE_{95\%}$**
Unfertilized	2018	1.8	2.3	-0.2	-6.4	yes	-30.9	220.5	5.1	10.9
Unfertilized	2019	8.1	2.7	0.1	3.1	no	66.9	104.5	11.2	11.2
Urea	2018	14.2	8.2	-0.3	-15.3	yes	42.4	122.1	37.2	39.2
Urea	2019	19.4	8.6	0.7	58.0	no	55.7	198.0	62.6	152.6
Digested biosolids	2018	30.4	30.4	0.4	30.0	no	0.1	186.7	52.2	138.5
Digested biosolids	2019	73.9	39.6	0.7	56.7	no	46.5	115.2	79.2	179.5
Alkaline-stabilized biosolids	2018	6.4	8.3	0.1	3.0	no	-30.7	204.7	17.4	46.1
Alkaline-stabilized biosolids	2019	10.5	12.6	0.2	7.9	no	-20.3	125.0	17.6	21.2
Composted biosolids	2018	2.6	5.7	-0.1	-6.0	yes	-116.0	130.9	7.6	5.8
Composted biosolids	2019	6.4	7.0	0.5	36.1	no	-8.6	160.8	8.1	24.2
Digested biosolids + Urea	2018	27.0	24.1	0.4	23.5	no	10.6	163.8	52.8	106.7

Treatment	**Year**	**Mean Obs**	**Mean Sim**	**r**	**F**	**Sig.diff?**	**E (%)**	**$E_{95\%}$ (%)**	**RMSE**	**$RMSE_{95\%}$**
Digested biosolids + Urea	2019	34.7	28.4	0.8	79.1	no	18.1	132.1	39.2	101.8
Alkaline-stabilized biosolids + Urea	2018	5.6	6.8	-0.2	-9.0	yes	-20.8	183.9	14.0	23.3
Alkaline-stabilized biosolids + Urea	2019	16.0	11.3	0.6	40.9	no	29.3	168.4	25.9	65.0
Composted biosolids + Urea	2018	9.9	6.4	-0.2	-8.5	yes	35.1	162.0	23.1	36.9
Composted biosolids + Urea	2019	13.9	8.4	0.7	52.7	no	39.7	126.2	29.0	46.0

Note: The mean observed and simulated daily N_2O fluxes are not significantly different from each other when $F \geq 1$ (**Sig.diff?)**.

Table A.4.15. Statistical evaluation of DNDC-simulated daily CO_2 fluxes using field experimental data (n = 8 for the fertilized and n = 4 for unfertilized treatments) from the site at Ste-Anne-de-Bellevue, Quebec, Canada. Total model error is not significant if RMSE < $RMSE_{95\%}$. Model bias is not significant for E < $E_{95\%}$.

Treatment	**Year**	**Mean Obs (kg C ha^{-1})**	**Mean Sim (kg C ha^{-1})**	**r**	**F**	**Sig. diff?**	**E (%)**	**$E_{95\%}$ (%)**	**RMSE (kg C ha^{-1})**	**$RMSE_{95\%}$ (kg C ha^{-1})**
Unfertilized	2018	10.0	17.2	0.1	3.9	no	-70.9	88.8	14.0	12.6
Unfertilized	2019	17.8	16.5	0.5	14.8	no	7.6	108.0	12.4	25.5
Urea	2018	9.9	16.3	0.5	32.5	no	-64.6	90.4	11.4	10.9
Urea	2019	14.4	19.3	0.6	47.1	no	-34.7	98.3	11.0	21.0
Digested biosolids	2018	13.4	14.2	0.6	56.9	no	-5.7	81.7	8.8	13.8
Digested biosolids	2019	27.3	17.8	0.7	67.5	no	35.0	80.4	17.2	31.2
Alkaline-stabilized biosolids	2018	13.9	22.7	0.4	25.2	no	-63.0	94.0	15.5	19.2
Alkaline-stabilized biosolids	2019	26.5	26.9	0.6	48.9	no	-1.4	88.6	14.2	30.1
Composted biosolids	2018	17.1	21.1	0.3	20.2	no	-23.5	78.8	15.2	17.1
Composted biosolids	2019	22.6	27.2	0.4	23.4	no	-20.7	92.0	17.0	28.6
Digested biosolids + Urea	2018	12.9	16.3	0.6	47.1	no	-26.3	103.2	10.3	24.5
Digested biosolids + Urea	2019	18.8	19.4	0.7	66.4	no	-3.1	87.2	11.0	24.2

Treatment	**Year**	**Mean Obs (kg C ha^{-1})**	**Mean Sim (kg C ha^{-1})**	**r**	**F**	**Sig. diff?**	**E (%)**	**E$_{95\%}$ (%)**	**RMSE (kg C ha^{-1})**	**RMSE$_{95\%}$ (kg C ha^{-1})**
Alkaline-stabilized biosolids + Urea	2018	12.4	20.8	0.4	26.0	no	-68.1	93.5	14.2	14.7
Alkaline-stabilized biosolids + Urea	2019	22.5	24.8	0.3	17.5	no	-10.1	121.1	26.2	73.1
Composted biosolids + Urea	2018	13.6	18.7	0.5	31.8	no	-37.0	83.9	12.6	15.2
Composted biosolids + Urea	2019	21.9	23.7	0.6	50.7	no	-8.1	71.6	12.5	20.4

Note: The mean observed and simulated daily CO_2 fluxes are not significantly different from each other when $F \geq 1$ (**Sig.diff?)**.

Table A.4.16. Statistical evaluation of DNDC-simulated cumulative N_2O fluxes using field experimental data (n = 8 for the fertilized and n = 4 for unfertilized treatments) from the site at Ste-Anne-de-Bellevue, Quebec, Canada. Total model error is not significant if RMSE < $RMSE_{95\%}$. Model bias is not significant for E < $E_{95\%}$.

Treatment	**Year**	**N**	**Sim (kg N ha^{-1})**	**Obs (kg N ha^{-1})**	**Std. Dev. (kg N ha^{-1})**	**E (%)**	**$E_{95\%}$ (%)**	**RMSE (kg N ha^{-1})**	**$RMSE_{95\%}$ (kg N ha^{-1})**
Unfertilized	2018	4	0.61	0.36	0.35	-69.2	155.1	0.25	0.56
Unfertilized	2019	4	0.43	1.37	0.44	68.6	51.4	0.94	0.70
Urea	2018	8	2.22	2.81	1.64	20.9	65.8	0.59	1.85
Urea	2019	8	1.52	3.42	4.13	55.5	135.7	1.90	4.64
Digested biosolids	2018	8	6.57	5.93	4.39	-10.7	83.3	0.64	4.94
Digested biosolids	2019	8	6.97	11.58	5.12	39.8	49.8	4.61	5.76
Alkaline-stabilized biosolids	2018	8	2.61	1.09	0.75	-139.4	77.2	1.52	0.84
Alkaline-stabilized biosolids	2019	8	1.82	1.76	0.71	-3.6	45.1	0.06	0.79
Composted biosolids	2018	8	1.35	0.53	0.20	-153.0	41.6	0.82	0.22
Composted biosolids	2019	8	0.93	1.09	0.61	14.4	63.1	0.16	0.69
Digested biosolids + Urea	2018	8	6.98	5.39	2.97	-29.5	62.0	1.59	3.34

Treatment	**Year**	**N**	**Sim** (kg N ha^{-1})	**Obs** (kg N ha^{-1})	**Std. Dev.** (kg N ha^{-1})	**E** (%)	**E$_{95\%}$** (%)	**RMSE** (kg N ha^{-1})	**RMSE$_{95\%}$** (kg N ha^{-1})
Digested biosolids + Urea	2019	8	6.17	5.52	3.52	-11.8	71.7	0.65	3.96
Alkaline-stabilized biosolids + Urea	2018	8	1.88	1.13	0.72	-65.5	71.2	0.74	0.81
Alkaline-stabilized biosolids + Urea	2019	8	2.21	2.77	1.72	20.3	70.0	0.56	1.94
Composted biosolids + Urea	2018	8	1.97	2.00	1.39	1.6	78.1	0.03	1.56
Composted biosolids + Urea	2019	8	2.15	2.44	1.33	11.8	61.4	0.29	1.50

Table A.4.17. Statistical evaluation of DNDC-simulated cumulative CO_2 fluxes using field experimental data (n = 8 for the fertilized and n = 4 for unfertilized treatments) from the site at Ste-Anne-de-Bellevue, Quebec, Canada. Total model error is not significant if RMSE < $RMSE_{95\%}$. Model bias is not significant for E < $E_{95\%}$.

Treatment	**Year**	**N**	**Sim** (t C ha^{-1})	**Obs** (t C ha^{-1})	**Std. Dev.** (t C ha^{-1})	**E** (%)	**$E_{95\%}$** (%)	**RMSE** (t C ha^{-1})	**$RMSE_{95\%}$** (t C ha^{-1})
Unfertilized	2018	4	3.49	1.98	0.50	-76.4	40.1	1.51	0.79
Unfertilized	2019	4	2.71	3.02	1.74	10.2	91.9	0.31	2.77
Urea	2018	8	3.39	2.04	0.69	-66.2	38.0	1.35	0.78
Urea	2019	8	3.30	2.44	1.02	-35.2	46.9	0.86	1.14
Digested biosolids	2018	8	2.99	2.68	0.45	-11.7	18.8	0.31	0.51
Digested biosolids	2019	8	3.18	4.54	0.86	30.0	21.2	1.36	0.96
Alkaline-stabilized biosolids	2018	8	5.21	2.74	0.50	-90.2	20.4	2.47	0.56
Alkaline-stabilized biosolids	2019	8	5.25	4.48	1.52	-17.1	38.1	0.77	1.71
Composted biosolids	2018	8	3.92	3.46	0.48	-13.2	15.6	0.46	0.54
Composted biosolids	2019	8	3.94	3.86	0.99	-2.2	28.9	0.09	1.11
Digested biosolids + Urea	2018	8	3.38	2.59	0.69	-30.4	29.9	0.79	0.78

Treatment	**Year**	**N**	**Sim** (t C ha^{-1})	**Obs** (t C ha^{-1})	**Std. Dev.** (t C ha^{-1})	**E** (%)	**E$_{95\%}$** (%)	**RMSE** (t C ha^{-1})	**RMSE$_{95\%}$** (t C ha^{-1})
Digested biosolids + Urea	2019	8	3.38	3.18	0.98	-6.4	34.7	0.20	1.10
Alkaline-stabilized biosolids + Urea	2018	8	4.09	2.53	0.55	-61.3	24.4	1.55	0.62
Alkaline-stabilized biosolids + Urea	2019	8	4.30	3.83	1.87	-12.3	54.9	0.47	2.10
Composted biosolids + Urea	2018	8	4.08	2.76	0.60	-48.1	24.3	1.33	0.67
Composted biosolids + Urea	2019	8	4.16	3.75	0.45	-10.9	13.6	0.41	0.51

Table A.4.18. Using field experimental data (n = 8) from the site at Ste-Anne-de-Bellevue, Quebec, Canada to statistically evaluate DNDC-simulated soil carbon in the 0–10 cm, 10–20 cm, and 20–30 cm soil layer at the start (initial) and end (final) stages of the 3-year field experiment. Total model error is not significant if RMSE < $\text{RMSE}_{95\%}$. Model bias is not significant for E < $E_{95\%}$.

Treatment	**Stage**	**Layer**	**Sim**	**Obs**	**Std. Dev.**	**E**	**$E_{95\%}$**	**RMSE**	**$\text{RMSE}_{95\%}$**
			(Mg C ha^{-1})			**(%)**		(Mg C ha^{-1})	
Unfertilized	A(0-10cm)	Initial	16.60	14.86	1.23	-11.7	13.2	1.74	1.96
Unfertilized	B(10-20cm)	Initial	16.58	15.12	0.83	-9.6	8.7	1.46	1.32
Unfertilized	C(20-30cm)	Initial	12.99	13.98	2.29	7.1	26.0	1.00	3.64
Urea	A(0-10cm)	Initial	15.98	15.03	2.31	-6.3	17.3	0.95	2.60
Urea	B(10-20cm)	Initial	15.82	16.15	2.42	2.1	16.9	0.33	2.72
Urea	C(20-30cm)	Initial	12.66	15.49	4.40	18.3	31.9	2.83	4.95
Digested biosolids	A(0-10cm)	Initial	19.79	14.61	2.71	-35.5	20.9	5.18	3.05
Digested biosolids	B(10-20cm)	Initial	18.81	15.73	1.59	-19.5	11.4	3.07	1.79
Digested biosolids	C(20-30cm)	Initial	14.32	14.85	2.41	3.6	18.3	0.53	2.71
Alkaline-stabilized biosolids	A(0-10cm)	Initial	21.06	14.70	1.07	-43.3	8.2	6.36	1.20
Alkaline-stabilized biosolids	B(10-20cm)	Initial	19.90	15.60	0.69	-27.5	5.0	4.29	0.78

Treatment	**Stage**	**Layer**	**Sim**	**Obs**	**Std. Dev.**	**E**	**$E_{95\%}$**	**RMSE**	**$RMSE_{95\%}$**
			(Mg C ha^{-1})			**(%)**		(Mg C ha^{-1})	
Alkaline-stabilized biosolids	C(20-30cm)	Initial	14.86	14.27	2.54	-4.1	20.1	0.58	2.86
Composted biosolids	A(0-10cm)	Initial	19.85	15.46	1.85	-28.4	13.4	4.39	2.08
Composted biosolids	B(10-20cm)	Initial	19.06	16.10	1.81	-18.4	12.7	2.96	2.04
Composted biosolids	C(20-30cm)	Initial	14.50	14.22	5.47	-2.0	43.2	0.28	6.15
Digested biosolids + Urea	A(0-10cm)	Initial	19.25	15.58	3.18	-23.5	22.9	3.66	3.57
Digested biosolids + Urea	B(10-20cm)	Initial	18.40	15.47	1.94	-18.9	14.1	2.93	2.19
Digested biosolids + Urea	C(20-30cm)	Initial	14.12	14.89	2.71	5.2	20.5	0.77	3.05
Alkaline-stabilized biosolids + Urea	A(0-10cm)	Initial	19.49	15.42	1.09	-26.4	8.0	4.07	1.23
Alkaline-stabilized biosolids + Urea	B(10-20cm)	Initial	18.66	15.45	1.07	-20.8	7.8	3.21	1.21
Alkaline-stabilized biosolids + Urea	C(20-30cm)	Initial	14.27	13.59	3.39	-5.0	28.0	0.68	3.81
Composted biosolids + Urea	A(0-10cm)	Initial	19.52	14.85	1.74	-31.5	13.2	4.67	1.95
Composted biosolids + Urea	B(10-20cm)	Initial	18.69	16.32	2.19	-14.5	15.1	2.37	2.46
Composted biosolids + Urea	C(20-30cm)	Initial	14.28	15.19	1.07	6.0	7.9	0.91	1.20
Unfertilized	A(0-10cm)	Final	15.52	16.72	1.75	7.2	16.7	1.20	2.79

Treatment	**Stage**	**Layer**	**Sim**	**Obs**	**Std. Dev.**	**E**	**$E_{95\%}$**	**RMSE**	**$RMSE_{95\%}$**
			(Mg C ha^{-1})			**(%)**		(Mg C ha^{-1})	
Unfertilized	B(10-20cm)	Final	15.44	15.64	1.36	1.3	13.9	0.20	2.17
Unfertilized	C(20-30cm)	Final	12.64	14.11	1.22	10.4	13.7	1.47	1.93
Urea	A(0-10cm)	Final	15.42	18.57	3.59	17.0	21.7	3.15	4.04
Urea	B(10-20cm)	Final	15.27	16.59	2.10	8.0	14.2	1.32	2.36
Urea	C(20-30cm)	Final	12.58	14.87	1.28	15.4	9.7	2.29	1.44
Digested biosolids	A(0-10cm)	Final	21.18	18.89	4.16	-12.1	24.8	2.29	4.68
Digested biosolids	B(10-20cm)	Final	20.97	17.23	2.46	-21.8	16.1	3.75	2.77
Digested biosolids	C(20-30cm)	Final	15.38	16.20	1.92	5.0	13.3	0.82	2.15
Alkaline-stabilized biosolids	A(0-10cm)	Final	23.12	19.86	4.09	-16.4	23.2	3.25	4.60
Alkaline-stabilized biosolids	B(10-20cm)	Final	22.95	17.02	1.73	-34.8	11.4	5.93	1.94
Alkaline-stabilized biosolids	C(20-30cm)	Final	16.13	16.19	1.38	0.4	9.6	0.06	1.56
Composted biosolids	A(0-10cm)	Final	21.47	17.71	2.25	-21.2	14.3	3.76	2.53
Composted biosolids	B(10-20cm)	Final	21.32	16.76	2.01	-27.2	13.5	4.56	2.27
Composted biosolids	C(20-30cm)	Final	15.46	15.83	0.69	2.3	4.9	0.37	0.77

Treatment	**Stage**	**Layer**	**Sim**	**Obs**	**Std. Dev.**	**E**	**$E_{95\%}$**	**RMSE**	**$RMSE_{95\%}$**
			(Mg C ha^{-1})			**(%)**		(Mg C ha^{-1})	
Digested biosolids + Urea	A(0-10cm)	Final	20.68	19.64	3.17	-5.3	18.2	1.04	3.57
Digested biosolids + Urea	B(10-20cm)	Final	20.50	16.40	1.67	-25.0	11.5	4.10	1.88
Digested biosolids + Urea	C(20-30cm)	Final	15.17	15.09	1.50	-0.6	11.2	0.09	1.69
Alkaline-stabilized biosolids + Urea	A(0-10cm)	Final	22.05	16.52	2.24	-33.5	15.3	5.53	2.52
Alkaline-stabilized biosolids + Urea	B(10-20cm)	Final	21.93	15.16	1.79	-44.6	13.3	6.77	2.02
Alkaline-stabilized biosolids + Urea	C(20-30cm)	Final	15.59	14.42	0.63	-8.2	4.9	1.18	0.71
Composted biosolids + Urea	A(0-10cm)	Final	22.79	16.61	3.01	-37.2	20.4	6.18	3.38
Composted biosolids + Urea	B(10-20cm)	Final	22.67	13.96	2.18	-62.4	17.5	8.71	2.45
Composted biosolids + Urea	C(20-30cm)	Final	15.85	14.02	1.91	-13.0	15.3	1.82	2.14

Table A.4.19. Using field experimental data (n = 4) from the site at Ste-Anne-de-Bellevue, Quebec, Canada to statistically evaluate DNDC-simulated soil nitrogen (Mg N ha^{-1}) in the 0–10 cm, 10–20 cm, and 20–30 cm soil layer at the start (initial) and end (final) stages of the 3-year field experiment. Total model error is not significant if RMSE < RMSE$_{95\%}$. Model bias is not significant for E < E$_{95\%}$.

Treatment	**Stage**	**Layer**	**Sim**	**Obs**	**Std. Dev.**	**E**	**E$_{95\%}$**	**RMSE**	**RMSE$_{95\%}$**
			(Mg N ha^{-1})			(%)		(Mg N ha^{-1})	
Unfertilized	A(0-10cm)	Initial	1.35	1.72	0.15	21.23	13.81	0.36	0.24
Unfertilized	B(10-20cm)	Initial	1.35	1.74	0.16	22.66	14.64	0.39	0.25
Unfertilized	C(20-30cm)	Initial	1.16	1.68	0.26	30.83	25.09	0.52	0.42
Urea	A(0-10cm)	Initial	1.35	1.74	0.18	22.62	11.31	0.39	0.20
Urea	B(10-20cm)	Initial	1.34	1.82	0.16	26.11	9.92	0.47	0.18
Urea	C(20-30cm)	Initial	1.17	1.67	0.21	30.04	13.90	0.50	0.23
Digested biosolids	A(0-10cm)	Initial	1.43	1.69	0.24	15.61	16.06	0.26	0.27
Digested biosolids	B(10-20cm)	Initial	1.43	1.78	0.20	19.65	12.68	0.35	0.23
Digested biosolids	C(20-30cm)	Initial	1.23	1.71	0.24	28.17	15.55	0.48	0.27
Alkaline-stabilized biosolids	A(0-10cm)	Initial	1.39	1.73	0.11	19.74	7.25	0.34	0.13
Alkaline-stabilized biosolids	B(10-20cm)	Initial	1.40	1.75	0.12	20.14	7.74	0.35	0.14

Treatment	**Stage**	**Layer**	**Sim**	**Obs**	**Std. Dev.**	**E**	**$E_{95\%}$**	**RMSE**	**$RMSE_{95\%}$**
			(Mg N ha^{-1})			(%)		(Mg N ha^{-1})	
Alkaline-stabilized biosolids	C(20-30cm)	Initial	1.21	1.67	0.21	27.33	14.47	0.46	0.24
Composted biosolids	A(0-10cm)	Initial	1.43	1.75	0.16	18.37	9.97	0.32	0.17
Composted biosolids	B(10-20cm)	Initial	1.44	1.80	0.16	20.36	10.12	0.37	0.18
Composted biosolids	C(20-30cm)	Initial	1.23	1.67	0.42	26.06	28.62	0.44	0.48
Digested biosolids + Urea	A(0-10cm)	Initial	1.42	1.73	0.22	18.20	14.04	0.31	0.24
Digested biosolids + Urea	B(10-20cm)	Initial	1.42	1.76	0.20	18.97	12.82	0.33	0.23
Digested biosolids + Urea	C(20-30cm)	Initial	1.22	1.76	0.26	30.46	16.74	0.54	0.29
Alkaline-stabilized biosolids + Urea	A(0-10cm)	Initial	1.42	1.78	0.13	20.21	8.40	0.36	0.15
Alkaline-stabilized biosolids + Urea	B(10-20cm)	Initial	1.43	1.77	0.12	19.33	7.51	0.34	0.13
Alkaline-stabilized biosolids + Urea	C(20-30cm)	Initial	1.23	1.69	0.25	27.41	16.47	0.46	0.28
Composted biosolids + Urea	A(0-10cm)	Initial	1.42	1.77	0.12	19.42	7.46	0.34	0.13
Composted biosolids + Urea	B(10-20cm)	Initial	1.43	1.85	0.09	22.59	5.76	0.42	0.11
Composted biosolids + Urea	C(20-30cm)	Initial	1.23	1.78	0.12	31.13	7.44	0.56	0.13
Unfertilized	A(0-10cm)	Final	1.34	1.19	0.26	-12.77	34.40	0.15	0.41

Treatment	**Stage**	**Layer**	**Sim**	**Obs**	**Std. Dev.**	**E**	**$E_{95\%}$**	**RMSE**	**$RMSE_{95\%}$**
			(Mg N ha^{-1})			(%)		(Mg N ha^{-1})	
Unfertilized	B(10-20cm)	Final	1.35	1.06	0.26	-27.33	39.80	0.29	0.42
Unfertilized	C(20-30cm)	Final	1.14	1.13	0.05	-0.47	7.64	0.01	0.09
Urea	A(0-10cm)	Final	1.34	1.43	0.44	6.16	34.33	0.09	0.49
Urea	B(10-20cm)	Final	1.34	1.26	0.32	-6.39	28.57	0.08	0.36
Urea	C(20-30cm)	Final	1.14	1.11	0.21	-2.62	20.89	0.03	0.23
Digested biosolids	A(0-10cm)	Final	1.60	1.42	0.55	-12.83	43.76	0.18	0.62
Digested biosolids	B(10-20cm)	Final	1.51	1.37	0.21	-10.67	17.28	0.15	0.24
Digested biosolids	C(20-30cm)	Final	1.24	1.23	0.34	-0.79	31.00	0.01	0.38
Alkaline-stabilized biosolids	A(0-10cm)	Final	1.67	1.54	0.55	-8.61	40.08	0.13	0.62
Alkaline-stabilized biosolids	B(10-20cm)	Final	1.52	1.43	0.25	-6.35	19.65	0.09	0.28
Alkaline-stabilized biosolids	C(20-30cm)	Final	1.23	1.22	0.23	-0.83	21.71	0.01	0.26
Composted biosolids	A(0-10cm)	Final	1.71	1.45	0.29	-17.82	22.48	0.26	0.33
Composted biosolids	B(10-20cm)	Final	1.56	1.25	0.33	-25.29	30.18	0.32	0.38
Composted biosolids	C(20-30cm)	Final	1.25	1.09	0.23	-14.86	23.83	0.16	0.26

Treatment	**Stage**	**Layer**	**Sim**	**Obs**	**Std. Dev.**	**E**	**$E_{95\%}$**	**RMSE**	**$RMSE_{95\%}$**
			(Mg N ha^{-1})			(%)		(Mg N ha^{-1})	
Digested biosolids + Urea	A(0-10cm)	Final	1.54	1.64	0.31	5.76	21.62	0.09	0.35
Digested biosolids + Urea	B(10-20cm)	Final	1.48	1.34	0.13	-10.53	11.24	0.14	0.15
Digested biosolids + Urea	C(20-30cm)	Final	1.23	1.21	0.25	-1.06	23.21	0.01	0.28
Alkaline-stabilized biosolids + Urea	A(0-10cm)	Final	1.64	1.27	0.23	-29.66	20.74	0.38	0.26
Alkaline-stabilized biosolids + Urea	B(10-20cm)	Final	1.53	1.11	0.28	-38.43	28.71	0.43	0.32
Alkaline-stabilized biosolids + Urea	C(20-30cm)	Final	1.24	1.05	0.19	-18.88	20.62	0.20	0.22
Composted biosolids + Urea	A(0-10cm)	Final	1.62	1.30	0.33	-24.29	28.68	0.32	0.37
Composted biosolids + Urea	B(10-20cm)	Final	1.56	1.02	0.29	-52.14	31.75	0.53	0.33
Composted biosolids + Urea	C(20-30cm)	Final	1.24	1.08	0.30	-14.54	30.92	0.16	0.34

4.8.3. Appendix C: Equations

$$r = \frac{\sum_{i=1}^{n}(O_i - \bar{O})(P_i - \bar{P})}{\sqrt{\sum_{i=1}^{n}(O_i - \bar{O})^2}\sqrt{\sum_{i=1}^{n}(P_i - \bar{P})^2}} \qquad \text{(Eq. A.4.1)}$$

Where r is Pearson's correlation coefficient, O_i is the *i*th measured value, $\bar{O}$ is the average measured value, P_i is the *i*th simulated value, and $\bar{P}$ is the average simulated value.

$$F\ value = \frac{(n-2) \times r^2}{(1-r^2)} \qquad \text{(Eq. A 4.2)}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(O_i - P_i)^2}{n}} \qquad \text{(Eq. A 4.3)}$$

$$RMSE_{95\%} = \sqrt{\frac{\sum_{i=1}^{n}\left(SE_i \times t_{m,95}\right)^2}{n}} \qquad \text{(Eq. A 4.4)}$$

Where $RMSE_{95\%}$ is the root mean-square error (*RMSE*) at 95% confidence interval, SE_i is the standard error in the *i*th measurement, $t_{m,95}$ is the Student's t value for *m* replicates and 95% probability (P-value of 0.95), and *n* is the number of measurements.

$$E\ (\%) = \frac{100}{\bar{O}} \times \frac{\sum_{i=1}^{n}(O_i - P_i)}{n} \qquad \text{(Eq. A 4.5)}$$

$$E_{95\%}(\%) = \frac{100}{\bar{O}}\frac{\sum_{i=1}^{n}\left(SE_i \times t_{m,95}\right)}{n} \qquad \text{(Eq. A 4.6)}$$

Where $E_{95\%}$ is the relative error (*E*) at 95% confidence interval.

4.8.4. Appendix D: Additional Figures

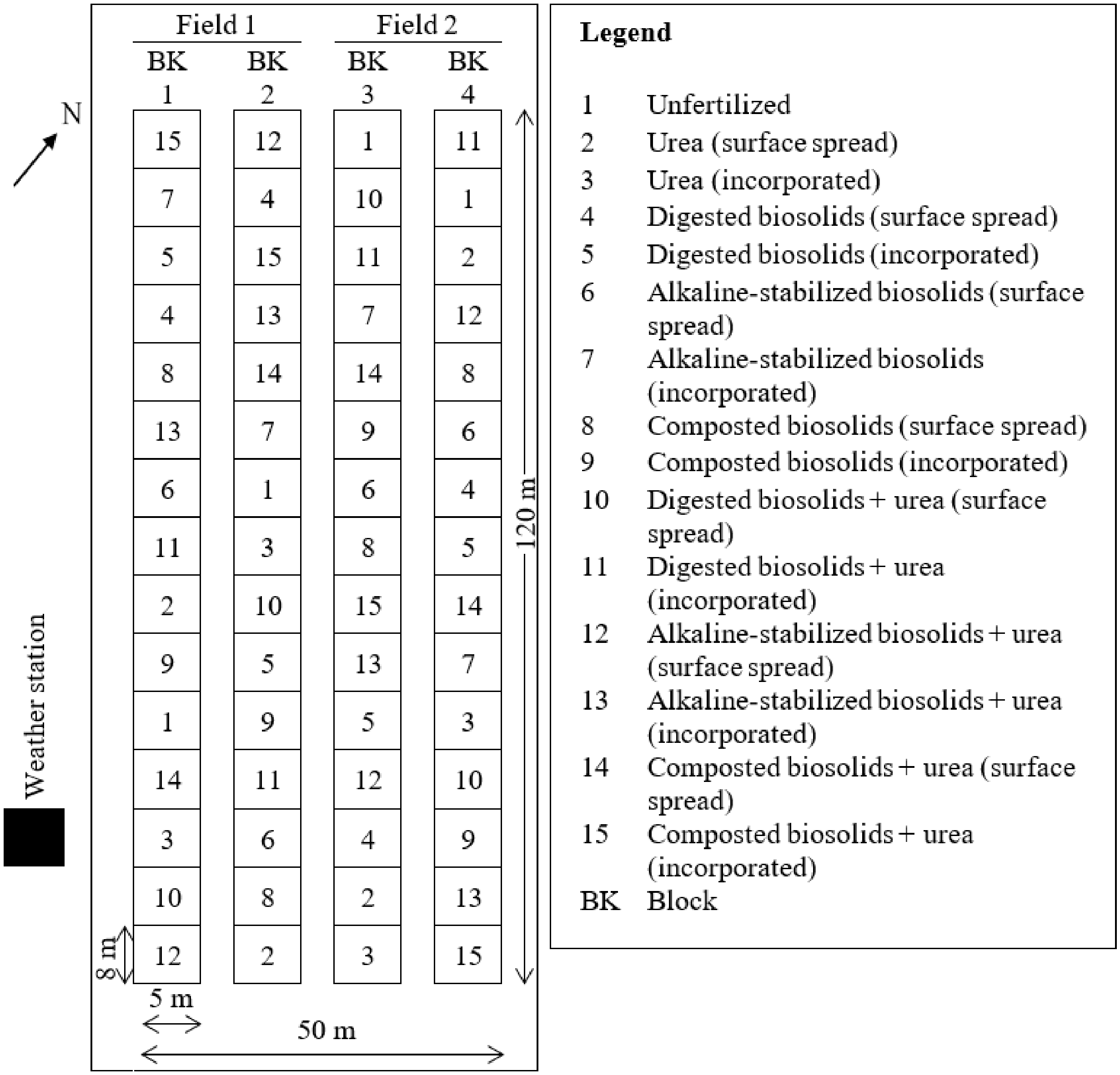
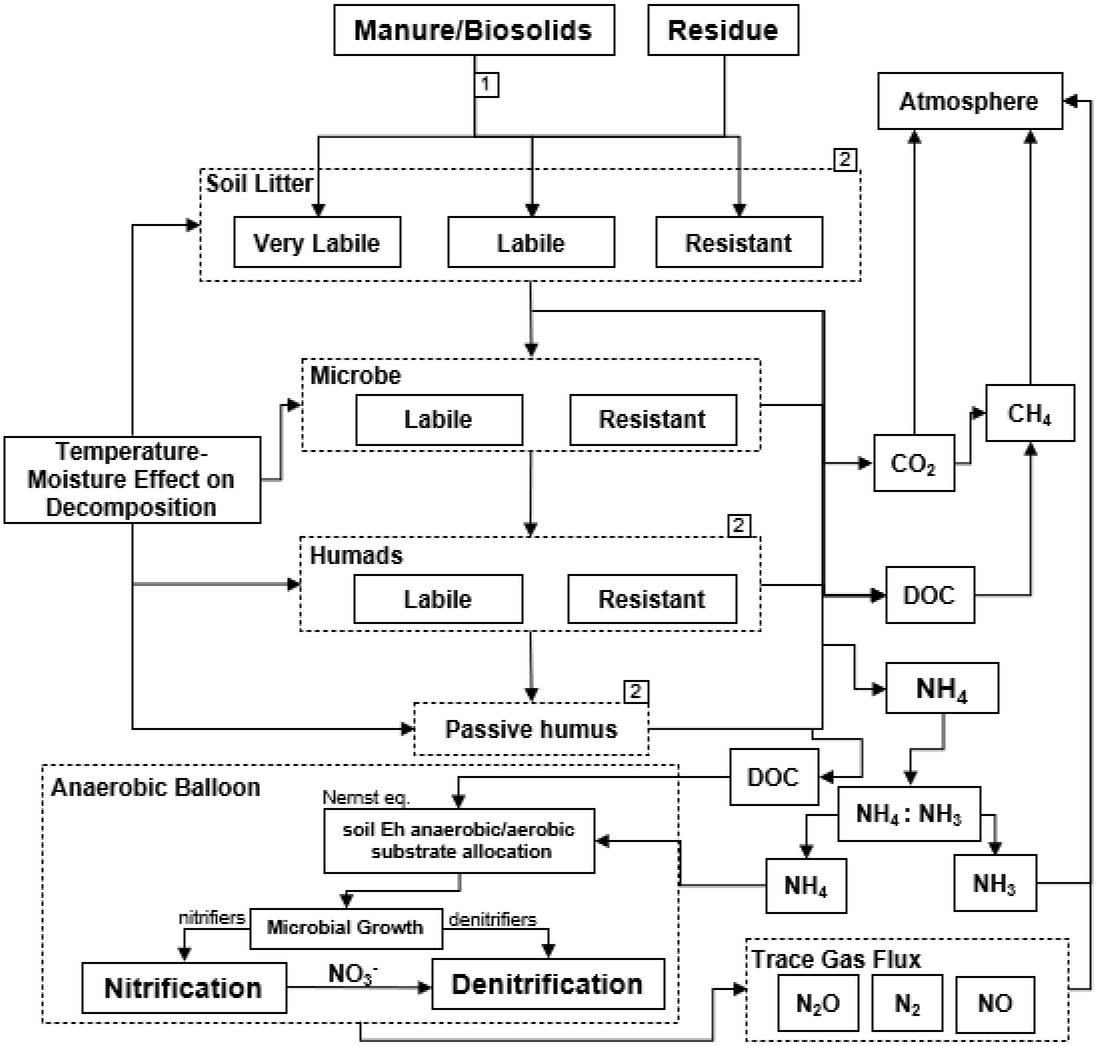


Figure A 4.1. Layout of experimental treatments (not to scale) from 1 to 15 replicated four times (Blocks 1 to 4) across Fields 1 and 2. Numbers 1 to 15 represent the applied fertilizer and method of application in brackets. Environment and Climate Change Canada’s weather station (located about 50 m from Field 1, on the left) at the Emile Lod’s Agronomy Research Centre Ste-Anne-de-Bellevue, QC, Canada.



1 Fractional C Allocation of Manure/Residues to 3 Litter Pools based on C:N manure N regulated by defined manure pH, N source (urea, organic N, NH4, NO3), application depth, dry matter%

2 User defined C Pool decomposition rate adjustment factor (default=1.0) – Litter, Humads, Passive humus

Figure A 4.2. Schematic of manure/biosolids carbon and nitrogen flow schematic for DNDC

Decomposition of each C-pool occurs independently using first-order kinetics and is regulated by soil temperature and moisture conditions as shown in the equation below. The anaerobic balloon (regulated by soil Eh via the Nernst equation) cycles the mineralized organic N /ammoniacal N from manure/biosolid application into the nitrification and denitrification pathways to evolve trace gas emissions (N_2O, NO, N_2). The NH_4:NH_3 equilibrium framework derives the partitioning of N that may be subject to NH_3 volatilization (see Congreves et al., 2016).

Microbial-mediated first-order decomposition kinetics of organic C pools

$$dC/dt = CNR * \mu * (S * k_l + (1-S) * k_r) * [C] \qquad \text{(Eq. A 4.7)}$$

[C], decomposed organic C (kg C/kg manure per day)

t, time (day)

S, labile fraction of organic C compounds in the pool

(1 - S), resistant fraction of organic C compounds

k_l, specific decomposition rate (SDR) of labile fraction (1/day)

k_r, SDR of the resistant fraction (1/day)

l, temperature and moisture reduction

factor

CNR = 0.2 + 7.2/(CP/NP), C:N ratio reduction factor

CP,C produced by potential residue decomposition per day (without CNR reduction factor) (kg C/ha)

NP, N produced by potential residue decomposition per day plus free NH_4 and NO_3^- in soil (kg N/ha). C:N ratio = 02.35, 20, 20, 8, 8, 8 and 8

SDR = 0.074, 0.074, 0.02, 0.33, 0.04, 0.16 and 0.006 (1/day) for very labile litter, labile litter, resistant litter, labile microbes, resistant microbes, labile humads and resistant humads, respectively

Anaerobic Balloon Main Principles

- Nernst equation determines soil Eh used for anaerobic/aerobic soil partitioning and determines substrate allocation (DOC, NO_3^-, NH_4^+ etc)
- Michaelis-Menten equations regulate nitrifier/denitrifier growth

Organic Matter Pools C:N ratio and pool specific decomposition rates described in *Table 2 (https://doi.org/10.1007/s10705-012-9507-z)*

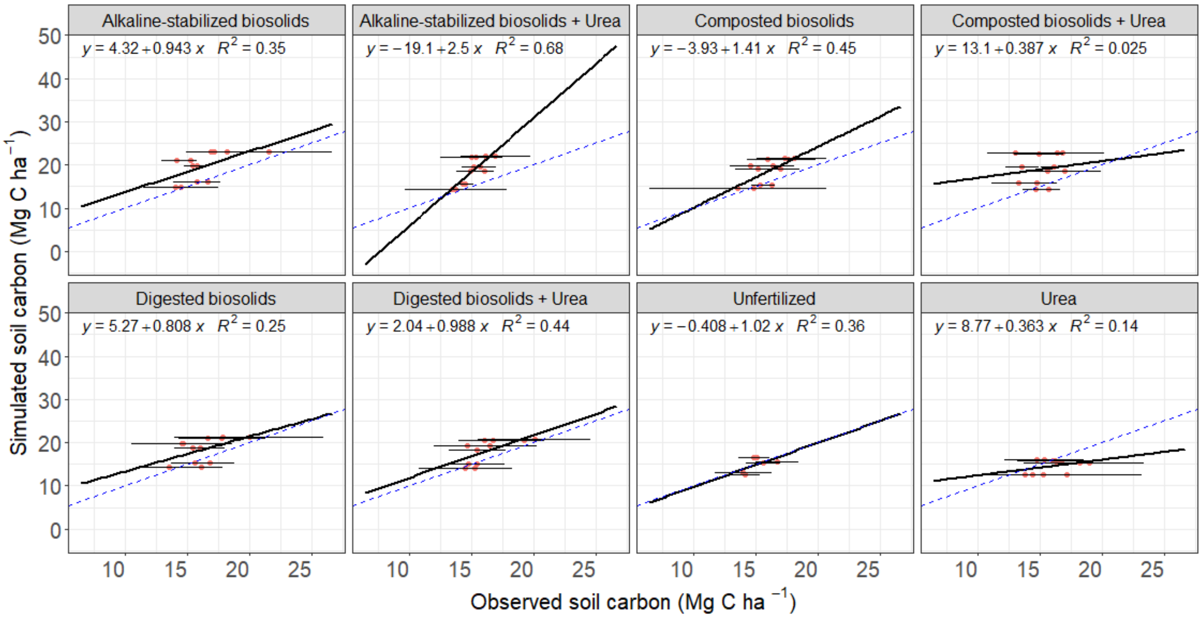


Figure A 4.3. Measured vs. simulated total soil carbon (indicated by red markers) at the start (April 2017) and end (November 2019) of the experiment at 0–30 cm soil depth. Measured mean values within treatments; n = 8 for fertilized and n = 4 for unfertilized treatments; error bars indicate standard deviation; blue lines indicate identity (1:1) lines; and black lines indicate the trend lines. The method of application had no significant effect on total soil carbon ($\alpha = 0.05$), so data from surface-spread and soil-incorporated treatments were pooled.

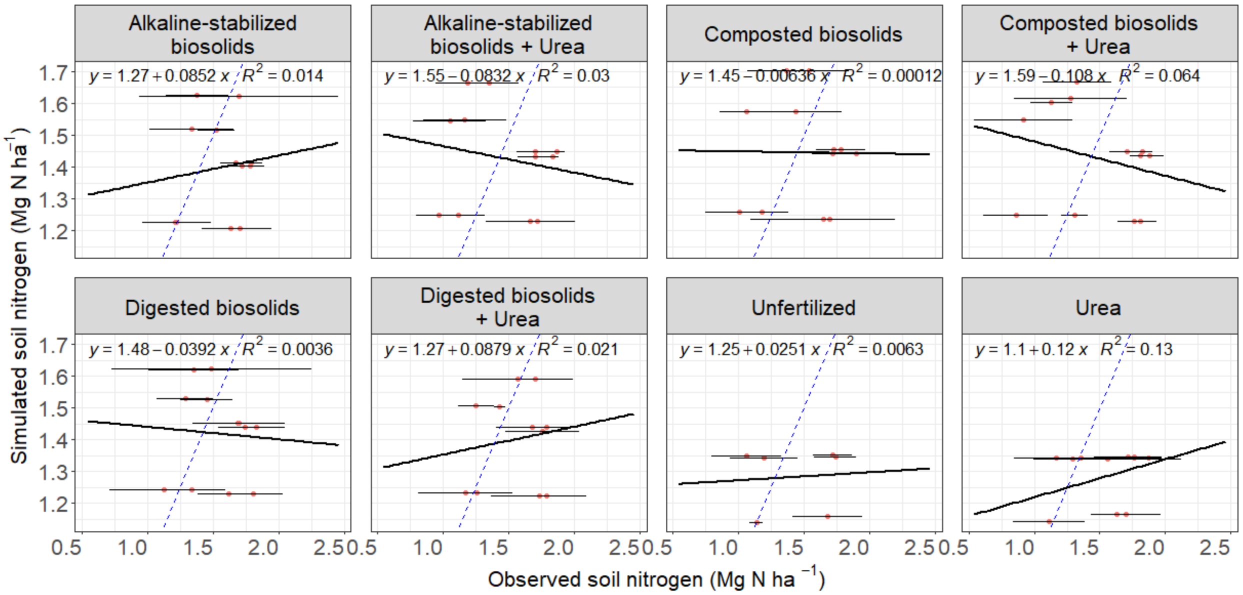


Figure A 4.4. Measured *vs.* simulated total soil nitrogen (indicated by red markers) at the start (April 2017) and end (November 2019) of the experiment at 0–30 cm soil depth. Measured mean values within treatments; n = 8 for fertilized and n = 4 for unfertilized treatments; error bars indicate standard deviation; blue lines indicate identity (1:1) lines; and black lines indicate the trend lines. The method of application had no significant effect on total soil nitrogen (α = 0.05), so data from surface-spread and soil-incorporated treatments were pooled.

Connecting text to Chapter 5

The DNDC model estimated GHG emissions, crop yields, and select underlying soil climate and chemical conditions within the standard errors of the observed means when tested on a system level for estimating C and N dynamics in a Quebec corn agroecosystem amended with biosolids. This site-specific performance of DNDC against empirical data shows the potential of process models as tools for estimating and reporting Canada-wide GHG emissions. In the next chapter, in addition to the Quebec site (Ste-Anne-de-Bellevue), we test DNDC across two more sites (Truro and Edmonton) and compare the DNDC-, IPCC Tier 1-, and IPCC Tier 2 – estimates against measured seasonal N_2O emissions across the three sites: Ste-Anne-de-Bellevue, QC; Truro, NS; and Edmonton, AB.

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Chapter 5. Comparing IPCC Tier 1, 2, and 3 methodologies for estimating nitrous oxide emissions from biosolids-amended soils in three different climatic ecozones in Canada

Okenna Obi-Njoku, Ward Smith, Brian Grant, Michael Yongha Boh, Corey Flemming, Carmen Roman-Perez, Gurwinder Singh, Zheya Lin, Guillermo Hernandez-Ramirez, David Burton, G.W. Price, O. Grant Clark

Abstract

There is an increasing use of municipal biosolids in farmlands across Canada to grow crops. However, due to sparse empirical data, Canada currently does not have biosolids-specific N_2O emission factors required to estimate and report emissions from land-application of biosolids in the national inventory. In this study, N_2O emissions during the growing season were estimated using Tier 1, Tier 2 (Canadian), and Tier 3 (Denitrification and Decomposition model [DNDC]) methodologies recommended by the Intergovernmental Panel on Climate Change (IPCC) and compared with measured emission factors from agricultural soils amended with different types of biosolids in Canada. The experiments were conducted in the Canadian provinces of Quebec (mixed wood plains), Nova Scotia (Atlantic maritime), and Alberta (prairie) between 2017 and 2019. Nitrogen was applied in amounts recommended for the given crop and location in the form of either mesophilic anaerobically digested biosolids, composted biosolids, alkaline-stabilized biosolids, urea, or a 1:1 combination of biosolids and urea. N_2O emissions were measured periodically during the growing season using manual chambers and compared against the estimates from the IPCC methods. In all locations, the mean N_2O emissions during the growing season were higher from plots receiving digested biosolids than from other plots. Also, N_2O emissions from plots receiving composted or alkaline-stabilized biosolids were not statistically different from the unfertilized treatment. The root mean-square error (RMSE) was used to evaluate the N_2O emissions estimated by the IPCC methods relative to the measured values across the three sites. Akin to the performance of the Tier 3 method, a Tier 2 method adapted with empirically determined biosolid-specific correction factors improved N_2O estimates relative to the current Tier 2 and Tier 1 methods. These results will be used by researchers and government scientists to improve methods for estimating N_2O emissions from agricultural soils amended with biosolids, and to generate more accurate GHG inventories to fulfil reporting obligations.

Keywords: Biosolids; DNDC model; N_2O emissions; IPCC methodology; Land application; National GHG inventory

5.1. Introduction

Greenhouse gas (GHG) emissions from cultivated soils contribute up to 10% of the 50 Gt CO_2e (carbon dioxide equivalent) of global emissions each year. Countries with a large industrialized agricultural sector are the largest emitters of these soil gases, with nitrous oxide (N_2O) being the most potent (Reay et al., 2012). In Canada, for example, about 40% of the 60 Mt CO_2e of agricultural GHG emissions are from soils. Countries are mandated to report soil GHG emissions, except (biogenic) CO_2 emissions to the United Nations Framework Convention on Climate Change (UNFCCC). However, many countries currently do not report GHG emissions from land-application of treated municipal wastewater sludge (*i.e.*, biosolids) to, or do not report those emissions accurately. In the Canadian national GHG inventory, it is assumed that biosolids and urea emit the same fraction of applied N amount as N_2O. This shortcoming is due mainly to the lack of empirical data about GHG emissions from agricultural soils amended with biosolids (ECCC, 2017).

It is important that Canada's national GHG inventory include an accurate estimate of the N_2O emissions from soils fertilized with biosolids. From 1990 to 2015, land application of biosolids in Canada increased by 60% (780 Tg in 2015), partly due to policies intended to divert biosolids from landfills and thus avoid the generation of methane (Cheminfo Services Inc., 2018). About 500 Tg of biosolids are now applied annually by Canadian farmers to supply plant nutrients, adjust the pH of acidic soils, and increase soil organic carbon (SOC) (Cheminfo Services Inc., 2018). The land-application of biosolids is expected to keep increasing in Canada and with it the associated emission of GHGs from the amended soil. The emissions of GHGs resulting from this practice differ according to location. There are about 68 million ha of agricultural land spread across numerous ecodistricts in Canada (Statistics Canada, 2014), with each ecodistrict having characteristic agroclimatic conditions, soil types, and management practices that differently influence GHG emissions (Kirschbaum, 1995; Sass et al., 2002; Paul, 2016).

The Intergovernmental Panel on Climate Change (IPCC, 2006) recommends three methods for reporting national soil GHG emissions to the UNFCCC. Canada uses a Tier 2 approach, which uses information about climate, soil type, crops, and management practices to estimate annual soil N_2O emissions at an ecodistrict scale. These estimates are then aggregated at the provincial and national scales (Rochette et al., 2008). The Canadian approach is based on domestic studies of the relationship between precipitation and N_2O emissions during the growing season (Rochette et al., 2008; Rochette et al., 2018). The Tier 2 method is an improvement over Tier 1, which uses a generic, globally-derived emission factor to compute N_2O emissions as a fraction of applied N and neglects local conditions (IPCC, 2006; 2019). The Tier 3 method is even more accurate because it also accounts for the physiochemical and biological properties of different fertilizers, which influence the transformation of C and N in soils (Grewer et al., 2016). Given the variability of moisture, carbon-to-nitrogen ratio (C/N), and types of organic compounds in different kinds of biosolids, modelling studies consider these variables as important model inputs to accurately estimate N_2O emissions.

Tier 2 and 3 methods are more accurate than the Tier 1 method, but collecting the enormous amounts of data required for these methods is challenging and expensive if done empirically (Li, 2000; Bouwman et al., 2002; Oertel et al., 2016). The use of process-based models such as the Denitrification and Decomposition (DNDC) model (Li et al., 1992) or DayCent (Parton et al., 1994) provides an alternative method for estimating GHGs that is more accurate than Tier 1 but less expensive than an entirely empirical approach. Many model inputs, simulation runs, and statistical analyses are still required, however, to develop a model that accurately relates ecological parameters to soil N_2O emissions. Different mathematical approaches have been adapted for this purpose, such as the Morris (1991), Monte Carlo (Fryer & Rubinstein, 1983), and Sobol′ (2001) methods.

The objective of this paper was to estimate N_2O fluxes using Tier 1, Tier 2 (Canadian), and Tier 3 (Denitrification and Decomposition model [DNDC]) methodologies and compare these with measured emissions from agricultural soils amended with different types of biosolids in Canada's mixed wood plain, Atlantic maritime, and prairie ecozones. We then evaluated which approach is the most accurate and amenable for estimating soil N_2O emissions from land-applied biosolids at the national scale.

5.2. Methodology

5.2.1. Site Description and Field Experiment

5.2.1.1. Physicochemical Characteristics of Biosolids

The chemical characteristics of the biosolids are described in Table 5.1 and Table A.5.1 to Table A.5.3 (Appendix 5.1). The mesophilic anaerobically digested biosolids (henceforth called digested biosolids) applied in Ste-Anne-de-Bellevue, QC and Truro, NS were collected from a municipal biomethanization centre (St-Hyacinthe, QC), where wastewater sludge was co-digested with food waste under mesophilic conditions. The digested biosolids used in Edmonton, AB were collected from Edmonton Waste Management Centre. The alkaline-stabilized biosolids applied in Ste-Anne-de-Bellevue and Truro were produced at the Aerotech Biosolids Processing Facility (Walker Environmental Inc.), Goffs, NS while those used in Edmonton were produced at the Wastewater Treatment Facility in Banff, AB. Both were produced using the N-Viro® technique, which involves addition of cement kiln dust and quicklime to wastewater sludge at a temperature of 52–62°C to raise the pH over 12 for at least 12 hours (Wang et al., 2007). The composted biosolids applied in Ste-Anne-de-Bellevue, Truro, and Edmonton were produced by Gaudreau Compost (Victoriaville, QC), Fundy Compost Incorporated (Brookfield, NS), and the Edmonton Waste Management Centre (Edmonton, AB), respectively. In each case, biomethanized wastewater sludge was co-composted with different proportions of wood chips as a bulking agent for structure and additional carbon.

Table 5.1. Chemical characteristics of mesophilic anaerobically digested, composted, and alkaline-stabilized biosolids applied to agricultural soils in the Ste-Anne-de-Bellevue, QC; Truro, NS; and Edmonton, AB sites. Value are means ± standard deviation (n = 3).

Parameter	Ste-Anne-de-Bellevue			Truro			Edmonton[†]		
	Digested	Composted	Alkaline-stabilized	Digested	Composted	Alkaline-stabilized	Digested	Composted	Alkaline-stabilized
Dry Matter (kg kg^{-1})	0.20 ± 0.02	0.44 ± 0.04	0.62 ± 0	0.21 ± 0.01	0.43 ± 0.01	0.62 ± 0	0.2 ± 0	0.71 ± 0.05	0.72 ± 0.02
pH	8.2 ± 0.1	7.3 ± 0.3	9.8 ± 0.9	8.0 ± 0.2	7.3 ± 0.2	9.5 ± 0.6	7.7 ± 0	5.0 ± 0	12.8 ± 0
Nitrogen (g N kg^{-1})	65.3 ± 4.1	15.8 ± 6.1	9.3 ± 2.0	60.7 ± 3.4	12.3 ± 1.3	9.5 ± 1.7	30.2 ± 10.0	21.0 ± 1.2	8.0 ± 0.1
Ammonium-N (g N kg^{-1})	12.6 ± 1.1	2.2 ± 1.3	0.9 ± 0.2	13.0 ± 0	0.7 ± 0.5	1.0 ± 0	8.2 ± 0	1.4 ± 0	1.3 ± 0
Potassium (g kg^{-1})	4.4 ± 3.8	1.0 ± 0.6	1.1 ± 0	6.3 ± 1.8	2.0 ± 0	6.0 ± 3.5	n/a	n/a	n/a
Phosphorus (g kg^{-1})	21.2 ± 17.9	3.7 ± 2.8	5.9 ± 0	32.7 ± 5.8	8.0 ± 1.4	6.6 ± 0.5	n/a	n/a	n/a
Calcium (g kg^{-1})	30.5 ± 7.5	29.0 ± 0	163.7±107.6	28.3 ± 7.8	15.3 ± 3.4	186.3 ± 30.2	n/a	n/a	n/a
Magnesium (g kg^{-1})	4.7 ± 0.2	2.7 ± 0	1.3 ± 0.3	4.0 ± 0.8	2.0 ± 0	2.3 ± 0.9	n/a	n/a	n/a
Sodium (g kg^{-1})	3.4 ± 0.9	11.2 ± 0	0.4 ± 0	3.0 ± 0.8	0.7 ± 0.5	0.8 ± 0.3	n/a	n/a	n/a
Iron (g kg^{-1})	28.6 ± 0.5	6.6 ± 0	4.8 ± 1.4	27.7 ± 6.3	6.3 ± 0.2	6.4 ± 2.1	n/a	n/a	n/a
Boron (mg kg^{-1})	11.6 ± 0.6	16.0 ± 0	12.3 ± 0	12.6 ± 0.8	11.3 ± 0.7	19.1 ± 0.3	n/a	n/a	n/a
Copper (mg kg^{-1})	244.3 ± 105.8	91.0 ± 0	49.3 ± 22.6	141.8 ± 6.0	51.2 ± 17.5	88.4 ± 11.9	n/a	n/a	n/a
Zinc (mg kg^{-1})	300.5 ± 19.5	266.0 ± 0	151.0 ± 27.0	243.6± 28.3	165.8 ± 31.2	211.2 ± 28.7	n/a	n/a	n/a
C:N ratio (g g^{-1})	4.7 ± 0.3	38.3 ± 0.4	20.9 ± 2.0	8.9 ± 0.1	38.3 ± 0.4	34.7 ± 3.8	6.7 ± 0	12.4 ± 0	15.7 ± 0

[†] n/a = not available.

5.2.1.2.Study Areas and Materials

Three experimental sites were chosen to represent the diversity of soils and climates of Canada’s main agricultural regions. The field experiments were run concurrently for three years (2017-2019): the Emile A. Lods Agronomy Research Centre, Ste-Anne-de-Bellevue, QC, (45°28’N, 73°45’W); the Bio-Environmental Engineering Complex, Bible Hill (Truro), NS, (45°22’N, 63°14’W); and the Ellerslie (53°25’N, 113°27’W) Research Station, near Edmonton, AB. Geographic location, soil, and climate information for the sites are described in Table A.5.4 and Table A.5.5. Each experiment was conducted using management practices and crops appropriate to the region: silage corn (*Zea mays* L.) was grown in Ste-Anne-de-Bellevue and Truro, while barley (*Hordeum vulgare* L.) was grown in Edmonton.

5.2.1.3. Experimental Design

The experiments followed an unbalanced factorial design, the three treatment factors being fertilizer type, rate of biosolid application, and fertilizer application method. The fertilizer types included three different biosolids: composted biosolids, alkaline-stabilized biosolids, and mesophilic anaerobically digested (digested) biosolids. The application rates provided sufficient biosolids to meet plant N requirements or 50% of that rate with additional urea to provide an equivalent amount of N. The two fertilizer application methods were surface-spreading and incorporation by tillage. Positive control plots were fertilized solely with urea and negative control plots received no fertilizer at all. Fertilizers were applied annually based on recommended rates of 120 kg N ha^{-1} for corn and 96 kg N ha^{-1} for barley. N mineralization rates were assumed to be 50% for all biosolids except for digested biosolids in Truro, for which a 75% mineralization rate was assumed based on preliminary tests conducted on the three biosolids in Truro. The total N applied at each site for the majority-biosolids (full rate) and split-application (half rate) treatments, respectively, was as follows: the Edmonton site received 192 and 96 kg N ha^{-1}, all applied during planting of barley; the Ste-Anne-de-Bellevue site received 201 and 180 kg N ha^{-1}, with 39 kg N ha^{-1} of these amounts applied as urea during planting of corn and the rest applied at a later date; and the Truro site received 210 and 150 kg N ha^{-1} as digested or composted biosolids, or 390 and 210 kg N ha^{-1} as alkaline-stabilized biosolids, with 30–36 kg N ha^{-1} applied during planting of corn for all treatments and the rest applied at a later date. Biosolids were uniformly distributed on the surface prior to planting and then either left on the surface or incorporated to a depth of 10 to 15 cm within 24 h of application, using a cultivator or rototiller. Surface spread treatments in Truro were not tilled during the course of the experiment to approximate the application of biosolids to a no-till production system. In total, there were 15 treatments replicated 4 times, resulting in 60 experimental plots per site. The plot dimensions, treatments, and site management practices specific to each site are shown in Table A.5.6.

5.2.2. Sampling and Analysis of N_2O Emissions

Manual non-steady-state vented chambers were used for gas sampling from every plot during the growing seasons from 2017 to 2019 in Ste-Anne-de-Bellevue, Truro (Singh & Burton, unpublished data), and Edmonton (Roman-Perez & Hernandez-Ramirez, 2021). In Ste-Anne-de-Bellevue and Truro, the manual chambers consisted of a square acrylic collar (50 cm × 50 cm × 15 cm high) buried to a depth of 10 cm in the centre of each plot, while in Edmonton, the collars (64.1 cm × 15.6 cm × 15 cm high) of the manual chambers were placed perpendicular to the crop rows, in the middle of each plot to a depth of 5 cm. The top 5 cm of each chamber served as the base over which an equally sized insulated cover was placed during each sampling event (Hung et al., 2021). After covering the chamber, 20 mL of headspace gas was sampled from each chamber at 15-min intervals from 0 to 60 min and transferred into 12-ml pre-evacuated glass Exetainers™ (Labco Limited, Lampeter, Wales, UK). Manual gas sampling was conducted twice weekly immediately after biosolids and urea fertilizer application, once weekly thereafter, and within 48 h after major rainfall events to capture any spikes in gas flux as a consequence of increased soil moisture (Barton et al., 2015). N_2O concentrations in the gas samples were measured using a gas chromatograph (Bruker 450-GC, Bruker Corporation, Billerica, MA, USA) fitted with a ^{63}Ni electron capture detector (ECD) for N_2O analysis and using high purity He as a carrier gas. The 2017 gas measurements at the Ste-Anne-de-Bellevue site were excluded from further analysis due to failure to meet the quality criteria as described by Rochette and Eriksen-Hamel (2008). Also, 2019 gas measurements from Edmonton were excluded in this study as the treatments in 2019 received significantly higher amounts of N than in previous years.

The emission rates of N_2O were estimated using the Hutchinson-Mosier R (HMR) software package (v1.0.1; Pedersen, 2020) assuming the molar mass of N in N_2O equals 28 g mol^{-1}. During each sampling event, a Kestrel Drop 3 environmental data logger (Kestrel Meters, Boothwyn, PA, USA) was placed inside a chamber to record the air temperature and water vapor pressure. The calculated N_2O fluxes were adjusted accordingly, as per Hung et al. (2021). The cumulative emissions for the growing season were estimated by linear interpolation of the flux between successive sampling dates (De Klein & Harvey, 2012). In Ste-Anne-de-Bellevue and Truro, soil temperature was measured by inserting a thermometer probe 10 cm into the soil, while soil moisture was measured by collecting about 50 g of soil from the top 10 cm, drying it at 60^{o}C for 48 h, and noting the change in mass. For the Edmonton site, soil moisture and soil temperature were measured at depths of 5 and 10 cm with 5TM sensors interfaced with EM50 data loggers (Decagon Devices, Inc., Pullman, WA).

5.2.3. Statistical Analysis

All statistical analyses were conducted in R 3.6.1 (R Core Team, 2020) using an alpha level of 0.05 to indicate statistical significance. Measurements of N_2O (g N ha^{-1}) emissions during the growing season at the three sites failed to satisfy the assumptions of normality and homoscedasticity, based on the Shapiro-Wilk test and residuals plots, respectively, and therefore were log-transformed. A five-way analysis of variance (ANOVA) was used to test for statistical differences between treatment effects, with site, fertilizer type, method of application, rate of application, annual effects (year) and their interactions considered as fixed effects. The fertilizer type and rate of application were colinear, as such the rate of application was dropped from the ANOVA. At each site, ANOVA was also used to test for statistical differences between treatment effects, with fertilizer type, method of application, annual effects, and their interactions considered as fixed effects. If the ANOVA indicated significant differences among treatment effects, then Tukey's Honest Significant Difference (HSD) post-hoc test was used to test the cumulative N_2O emissions for pairwise differences between treatments.

5.2.4. Estimating N_2O Emissions and Uncertainty Using the IPCC Tier 1 Method

The refined IPCC Tier 1 method (Eq. 5.1) was used to estimate growing season N_2O emissions from biosolids-amended soils on the three sites. According to the *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories*, the emission factor was disaggregated according to climate into wet (ratio of annual precipitation: potential evapotranspiration > 1) and dry (ratio of annual precipitation: potential evapotranspiration < 1), as well as the fertilizer type (IPCC, 2019); in this case, biosolids, mineral N, and crop residue. In dry climates, the recommended emission factor is 0.005 kg N_2O-N per kg N for all N sources. Meanwhile, in wet climates (e.g., Truro and Ste-Anne-de-Bellevue), the recommended emission factor is 0.006 kg N_2O-N per kg N for organic N sources and 0.016 kg N_2O-N per kg N for mineral N sources (e.g., urea). The uncertainty of this Tier 1 emission factor ranges from 0.00–0.019 kg-N_2O-N per kg of total N applied, depending on the fertilizer type and climate.

$$N_2O\text{-}N_{i,j} = EF \times N_{inputs_{i,j}} \qquad \textbf{Eq. 5.1}$$

N_2O-N is the amount of N emitted as N_2O on site i by fertilizer type j during the growing season; EF is the IPCC Tier 1 emissions factor (kg N_2O-N kg^{-1} N); and N_{inputs_i}, j is the amount of N applied on site i from fertilizer type j (kg ha^{-1}).

Crop residue N ($Nres$) was calculated using crop-specific parameters from Jansen et al. (2003) to convert the site-specific crop production (kg ha^{-1}) amounts to total above and below ground residual N, following Eq. 5.2:

$$Nres = (AGprod(k) \times AGN(k) + BGprod(k) \times BGN(k)) \times DMi,k \times \left(\frac{1}{Renew(k)}\right) \qquad \textbf{Eq. 5.2}$$

$AGprod(k)$ is the fraction of above-ground biomass remaining as residue for crop k; $AGN(k)$ is the fraction of N in the above-ground residue; $BGprod(k)$ is the ratio of below-ground biomass remaining as residue for crop k; $BGN(k)$ is the fraction of N in the below-ground residue; DMi,k is the quantity of dry matter produced for crop k at site i; and $Renew(k)$ represents a correction for the duration of forage crop k. About 10% of crop residue was left on the field each year after harvest.

5.2.5. Estimating Cumulative N_2O Emissions and Uncertainty During the Growing Season Using Two IPCC Tier 2 Approach

Three

Three country-specific Tier 2 methods: Canada's 2020 National Inventory Report (NIR) (Rochette et al. 2008; NIR 2020), henceforth called the Tier 2 (2008); a proposed update to the Tier 2 (2008) methodology using a manure-derived correction factor to estimate N_2O emissions from land-applied organics (Rochette et al., 2018; Liang et al., 2020), henceforth called the Tier 2 (2018); and the Tier 2 (2018) method with proposed biosolids-derived correction factors based on the results of this study, henceforth called the corrected Tier 2 (2018) were individually used to estimate growing season N_2O emissions from land-application of biosolids on the three sites.

The Tier 2 (2018) methodology uses a non-linear (exponential) function based on a relationship between growing season precipitation and N_2O emissions (Eq. 5.3), with further adjustments for cropping system, nitrogen source, tillage, soil texture, and topography. The approach was implemented for each treatment across the three sites according to Liang et al. (2020). Cropping system had no effect on N_2O emissions since only annual crops (corn and barley) were used in this study. Conventional tillage is the baseline tillage type in this method, hence; had no effect on N_2O emissions across the sites. As such, surface spread treatments in Truro, with no- to minimal tillage during the course of the experiment were accounted for in the Tier 2 (2018) emission factor estimate. The effects of soil texture (Eq. 5.4) and N input were also relevant in estimating the emission factor at our site locations. The overall contributions of climate, soil texture, tillage, and N inputs are shown in Eq. 5.5.

$$\text{Tier 2 (2018) emission factor}, EF_{eco_i} = e^{0.00558P_i - 7.701} \qquad \textbf{Eq. 5.3}$$

P_i is the precipitation during the growing season in ecodistrict i.

$$\mathrm{RF}_{text_i} = \mathrm{RF}_{text,fine_{\mathrm{i}}} \times F_{text,fine_i} + \mathrm{RF}_{text,medium_{\mathrm{i}}} \times F_{text,medium_i} + \mathrm{RF}_{text,coarse_{\mathrm{i}}} \times F_{text,coarse_i} \qquad \textbf{Eq. 5.4}$$

RF_{text_i} is the ratio factor for coarse, medium, and fine soils, while and F_{text_i} is the corresponding proportion of the soil texture on site *i*. Following Rochette et al. (2018), RF_{text} values of 2.55, 0.49, and 0.49 were assigned to clay (fine), silt (medium), and sand (coarse), respectively, for the sites in Eastern Canada (Ste-Anne-de-Bellevue and Truro), while the Edmonton site had RF_{text} value of 1.0 irrespective of soil texture.

$$N_2O_{inputs_i} = [\mathrm{N}_{\mathrm{applied}_{\mathrm{i,j}}} \times (EF_{eco_i} \times RF_{text_j} \times RF_{till_j} \times RF_{N,j})] \qquad \textbf{Eq. 5.5}$$

$N_2O_{inputs_i}$ represents N_2O emissions from site *i* due to nitrogen source (kg N ha^{-1}); *j* = N source type (mineral N, manure, crop residue, or biosolids treatment). RF_N is the correction factor for each N source (fertilizer type): mineral N = 1, manure = 0.84, and crop residue = 0.28. RF_{till} due to minimum tillage in Truro = 1.1.

The emission factors in Tier 2 (2018) were adjusted using the empirical ratio of growing season N_2O emissions from biosolids to that of urea. In place of the 0.84 coefficient used for manure in Eq. 5.5, the correction factors 0.71, 0.43, and 2.77 were used for alkaline-stabilized, composted, and digested biosolids, respectively. These biosolids correction factors were derived by dividing the average values of measured N_2O emissions across the three sites from the respective biosolids treatment by the average measured N_2O emissions from urea treatment .

The Tier 2 (2008) methodology is based on a linear regression between N_2O emissions and the ratio of precipitation to potential evapotranspiration, with modifications for topography, soil texture, summer fallow, irrigation, and tillage (Rochette et al. 2008). A soil N_2O emission factor (kg N_2O-N kg N applied^{-1}) was calculated for each site location based on the average soil and climate characteristics for the ecodistrict in which the site is located. Given that none of the sites in this study were located in the lower portion of the toposequence, and that irrigation and summer fallow, only P/PE and soil texture were considered (Eq. 5.6). The effect of minimum tillage was considered in Truro but not for the Ste-Anne-de-Bellevue and Edmonton sites. In both cases, the site-specific emission factors were multiplied by the quantity of biosolids N, synthetic N fertilizer (urea and calcium ammonium nitrate), and crop residue N, to estimate N_2O emissions from each fertilizer type (Eq. 5.7).

$$EF_{eco_i} = \left(0.022 \times \frac{P_i}{PE_i} - 0.0048\right) \qquad \textbf{Eq. 5.6}$$

$$N_2O_{inputs_i} = \sum(N_{inputs_{i,j}}) \times EF_{eco_i} \qquad \textbf{Eq. 5.7}$$

EF_{eco_i} is the calculated emission factor in ecodistrict *i* (kg N_2O-N per kg N); PE is the growing season (May to October) potential evapotranspiration in ecodistrict *i*, estimated using the Thornthwaite method; N_{input} is the quantity of nitrogen input (kg N ha^{-1}) for ecodistrict *i* and for nitrogen source *j* (biosolids, synthetic fertilizer, crop residue; kg N ha^{-1}).

Rochette et al. (2008) in developing the Tier 2 approach estimated that 70% of annual N_2O emissions occur during the Canadian growing season. Therefore, emissions were calculated on an annual basis for each source of N input, and then multiplied by 0.7 to estimate growing season N_2O emissions from individual sources, following Eq. 5.8.

$$N_2O\text{-}N = 0.7 \times N_2O_{\text{inputs}_i} \times [((RF_{till} - 1) \times F_{till_i}) + (1 + (RF_{text,fine_i} - 1) \times F_{text,fine_i} + (RF_{text,medium_i} - 1) \times F_{text,medium_i} + (RF_{text,coarse_i} - 1) \times F_{text,coarse_i}] \quad \textbf{Eq. 5.8}$$

According to Rochette et al. (2008), RF_{text} values of 0.8, 0.8, and 1.0 were assigned to the fraction of silt (medium) and sand (coarse) in soils of the Ste-Anne-de-Bellevue, Truro, and Edmonton sites, respectively, while RF_{text} values of 1.2, 1.2, and 1.0 were assigned to clay (fine), respectively. RF_{till} is the ratio factor determined in the region where ecodistrict *i* is located and F_{till_i} is the fraction of agricultural land under tillage. RF_{till} is 1.0 for the sites under conventional tillage and 1.1 for surface spread treatments receiving minimum tillage in Truro.

5.2.6. Estimating N_2O Emissions Using the Denitrification and Decomposition (DNDC) Model

5.2.6.1. Initializing the DNDC Model

The DNDC model (Li et al., 1994; version DNDC.vCAN) was used to simulate daily N_2O emissions, which were summed over the growing season. Three types of data were used to initialize DNDC: 1) soil physical characteristics including soil texture, bulk density, clay content, hydraulic conductivity, organic carbon concentration, soil pH, field capacity, wilting point, and porosity; 2) historical daily climate data obtained from Environment and Climate Change Canada (ECCC) weather stations near the test sites (years 2007-2019), including wind speed, relative humidity, maximum and minimum air temperature, solar radiation and precipitation; and 3) crop characteristics, e.g. temperature and water requirements, crop biomass fractions, potential crop yield, carbon and nitrogen concentrations, as well as historical farm management practices, e.g. tillage, N application rate and method, crop rotation, and planting and harvest dates, which were provided by the farm managers at each site. Literature values or DNDC default values were used as substitutes for missing data.

The site characteristics and management information were compiled as lists of input parameters to initialize the model (Table A.5.7). The DNDC model was run using these lists of input parameters and climate data files specific to each site. A simulation spin-up of 10 years was used to allow the simulated SOC to stabilize. The simulated outputs were then converted into the same standard units as used for the measured datasets.

5.2.6.2. Calibration and Validation of DNDC Model to Simulate N_2O Emissions

DNDC calibration followed the method described by Li (2007). Datasets (N_2O and CO_2 emissions, crop yield, and soil moisture and temperature) from the negative control (unfertilized), positive control (urea only), and surface-spread biosolids treatments on each site were used for calibration, while data from the incorporated biosolids and biosolids + urea treatments were used for validation. First, crop parameters in DNDC were adjusted iteratively, such that the simulated above-ground biomass closely approximated the measured mean values. The means and standard errors time series of simulated soil water content, soil temperature, and N_2O flux values over the growing season were compared with those of the measured values for all calibration treatments. The performance of the calibrated model was evaluated using R^2, RMSE, relative root means square error (rRMSE), and relative error (E), as shown in Equations A.5.1 to A.5.6 and described by Smith & Smith (2007). For model validation, the fertilizer parameters were changed to reflect the field management practices while the calibrated soil and crop parameters were kept the same. Model validation followed the same statistical evaluation methods used for calibration.

5.2.6.3. Sensitivity Analysis

To identify the DNDC parameters with the most influence on simulated soil N_2O emissions across the three sites, a sensitivity analysis (SA) was conducted using the sensitivity package (v1.26.0; Iooss et al., 2021) in R 3.6.1, following Morris (1991) method, modified as shown in Qin et al. (2016). The Morris method can detect whether the effect of an input (factor or variable) is linear and additive, non-linear and/or interact with other inputs, or have a negligible effect on the simulated outputs. The method calculates for each selected model parameter a number of incremental ratios, called Elementary Effects (EE), from which three sensitivity measures are computed: the mean of the distribution of the EE, μ, which assesses the overall influence of the input on the simulated output; Morris sensitivity index, μ^*, which is the estimate of the mean of the distribution of the absolute values of the elementary effects; and the standard deviation of the distribution of the EE, σ, which estimates the collective effects of the input due to non-linearity and/or interactions with other factors. Using the estimated range of values for crop, soil, and climate variables for each site, based on informed opinion of site researchers and expert modelers (Table A.5.8), the elementary effect of each input on cumulative growing season N_2O emissions was determined. The inputs were then ranked according to their μ^* values.

5.2.6.4. Simulating N_2O Emissions due to Variations in Measured Soil, Climate, and Crop Variables During the Growing Season

Using the most significant factor (MSF) approach, the set of maximum and minimum values of the eight most sensitive factors identified at each site during the sensitivity analysis were used to simulate N_2O emissions. While keeping other input values the same, the set of maximum values of the selected variables were used in one model run and the set of minimum values were used in another run, to generate N_2O emissions, as described by Li et al. (2004) and Fitton et al. (2014).. This approach was carried out to estimate the potential range of N_2O emissions during the growing season, using the most significant site-specific input variables to minimize computational expense. Then, the mean and standard deviation of the simulated cumulative N_2O emissions during the growing season were calculated with values simulated using the minimum, maximum, and baseline (measured mean) of all the chosen input variables.

5.2.7. Error Analyses

N_2O emissions during the growing season were estimated using the IPCC Tier 1, 2, and 3 methods and compared to the emissions measured on each site. RMSE was used to determine the degree of coincidence, accuracy, and predictive power, relative error (E) was used to determine model bias for DNDC simulations alone, while R^2 was used to determine the degree of association between the measured and estimated values.

5.3. Results

5.3.1. Site, Treatment, and Weather Effects on N_2O Emissions During the Growing Season

The ANOVA results show that differences between the sites, fertilizer types, annual effects (Year; as written in the tables), and method of application led to significant differences in N_2O emissions during the growing season (Table A.5.9). The magnitude of N_2O emissions depend on fertilizer type, annual effects, and site-specific conditions as seen in the interaction effects between site, annual effect, and fertilizer type on N_2O emissions in Table A.5.9. In general, N_2O emissions were highest in Ste-Anne-de-Bellevue, followed by Truro, then Edmonton (Table A.5.10). Between the fertilizer types, emissions were highest for treatments receiving digested biosolids either in full or half rate (Table A.5.11). The least emissions were from the unfertilized and full rate composted biosolids treatments, while emissions from the other treatments were not significantly different from each other. The method of application significantly influenced N_2O emissions as seen in Table A.5.12, but this was true only in Edmonton. Annually, N_2O emissions increased significantly from 2017 to 2019 (Table A.5.13).

At Ste-Anne-de-Bellevue (Mixed Wood Plain Ecozone), N_2O emissions during the growing season differed with fertilizer type (Table A.5.14). Annual differences in weather and perhaps the cumulative effect of repeated applications of biosolids in 2018 and 2019 resulted in higher N_2O emissions in the 2019 growing season than in 2018 (Table A.5.15). The differences among treatments were significant. N_2O emissions from the plots that received digested biosolids were similar whether or not they also received urea, and their emissions were significantly higher than those of other treatments (Table A.5.16). N_2O emissions during the growing season from the negative control plots (no fertilizer) were lower than those from treatments receiving urea alone (positive control) or in combination with composted biosolids, but the same as emissions from treatments receiving alkaline biosolids with or without urea, and those receiving only composted biosolids.

At Truro (Atlantic Maritime Ecozone), N_2O emissions during the growing season differed with fertilizer type, as well as by interaction between fertilizer type and annual effects (Table A.5.17). While N_2O emissions from treatments receiving digested biosolids alone or at half-rate with urea were the same as those receiving full-rate alkaline-stabilized biosolids, they were significantly higher than emissions from treatments receiving composted biosolids at full-rate or half-rate with urea (Table A.5.18). N_2O emissions during the growing season from half-rate alkaline-stabilized biosolids were greater in 2018 than in 2017 (Table A.5.19).

At Edmonton (Prairie Ecozone), N_2O emissions during the growing season differed with type of fertilizer, annual effects, and fertilizer application method (Table A.5.20). The N_2O emissions from treatments receiving full-rate digested biosolids or half-rate + urea were the same but were significantly higher than emissions from all the other treatments, except composted biosolids + urea (Table A.5.21). There was no significant difference in emissions between the control and treatments receiving alkaline-stabilized and composted biosolids, with or without urea. Also, there were no differences in N_2O emissions between each of the biosolids when applied at full-rate or applied at half-rate with urea. Annual effects influenced N_2O emissions, which in 2018 were generally higher than in 2017 (Table A.5.22). Notably, N_2O emissions were generally higher in incorporated than in surface spread treatments (Table A.5.23).

5.3.2. Comparison between IPCC Tier 1-Estimated and Measured Growing Season N_2O Emissions Estimates

In general, relative to the measured N_2O emissions across sites, the Tier 1 method performed poorly as seen in the R^2 (association) values in Tables 5.2, which ranged from 0 to 0.14, and the divergence between the trendline and 1:1 line as seen in Figures A.5.1 (Appendix D). However, except for Ste-Anne-de-Bellevue (total difference, rRMSE = 48%), the rRMSE for the other sites were low: Truro (21%) and Edmonton (3%). These error values indicate a poor performance of the Tier 1 method in the humid sites but not in the semi-arid Edmonton site (see Table 5.2 and Figure 5.1). At the Edmonton site, the mean of the measured emissions across the treatments were lower than those of the Tier 1 estimates, except for those of the digested biosolids (full- and half-rate) treatments (Figure 5.1). At the humid sites (Truro and Ste-Anne-de-Bellevue), only the composted biosolids and the alkaline-stabilized biosolids treatments, both full-rate and half-rate with urea, were within the ranges of the Tier 1-estimated emissions (see Figure 5.1). The measured mean emissions from the urea (full-rate) treatments in Truro was similar to the Tier 1-estimated emissions but not in Ste-Anne-de-Bellevue.

Across the treatments, the total difference between the Tier 1-estimated and measured emissions ranged from 1% (for alkaline-stabilized biosolids) to 135% (for composted biosolids), as seen in the rRMSE values in Table 5.3. Tier 1 N_2O estimates *vs* measurements for urea (rRMSE = 5%, $R^2 = 0.36$), unfertilized (rRMSE = 21%, $R^2 = 0.46$), and composted biosolids + urea (rRMSE = 22%, $R^2 = 0.50$) treatments despite having relatively low error values, showed divergence between the trendline and 1:1 line as seen in Figures A.5.2.

Table 5.2. Comparing R^2, RMSE, and rRMSE for measured vs. IPCC Tier 1, 2, and 3 - estimated N_2O emissions during the growing season, averaged across all treatments in each of the sites.

Method	Metric	Edmonton	Ste-Anne-de-Bellevue	Truro
Measured	Mean N_2O emission (kg N ha^{-1})	0.61	3.07	1.51
	S.D. (kg N ha^{-1})	0.52	2.87	0.93
Tier 1	Mean N_2O emission (kg N ha^{-1})	0.77	1.60	1.55
	S.D. (kg N ha^{-1})	0.21	0.28	0.33
	R^2	0.14	0.07	0.00
	RMSE (kg N ha^{-1})	0.13	1.47	0.05
	rRMSE (%)	21.0	47.9	3.04
Tier 2 (2008)	Mean N_2O emission (kg N ha^{-1})	1.22	1.72	2.03
	S.D. (kg N ha^{-1})	0.44	0.69	0.66
	R^2	0.17	0.15	0.03
	RMSE (kg N ha^{-1})	0.55	1.44	0.43
	rRMSE (%)	90.9	46.8	28.2
Tier 2 (2018)	Mean N_2O emission (kg N ha^{-1})	0.40	1.29	1.53
	S.D. (kg N ha^{-1})	0.16	0.81	0.81
	R^2	0.15	0.13	0.05
	RMSE (kg N ha^{-1})	0.23	1.84	0.05
	rRMSE (%)	37.6	59.9	3.04
Corrected Tier 2 (2018)	Mean N_2O emission (kg N ha^{-1})	0.56	1.72	1.87
	S.D. (kg N ha^{-1})	0.52	1.71	1.45

	R^2	0.86	0.42	0.48
	RMSE (kg N ha^{-1})	0.08	1.44	0.27
	rRMSE (%)	13.2	46.7	18.0
Tier 3	Mean N_2O emission (kg N ha^{-1})	0.62	2.69	1.85
	S.D. (kg N ha^{-1})	0.21	0.45	1.15
	R^2	0.64	0.81	0.31
	RMSE (kg N ha^{-1})	0.01	0.39	0.35
	rRMSE (%)	2.4	12.6	22.9

R^2, RMSE, and rRMSE values for the estimation methods were derived based on comparison between simulated and empirical values. Note: S.D. = standard deviation.

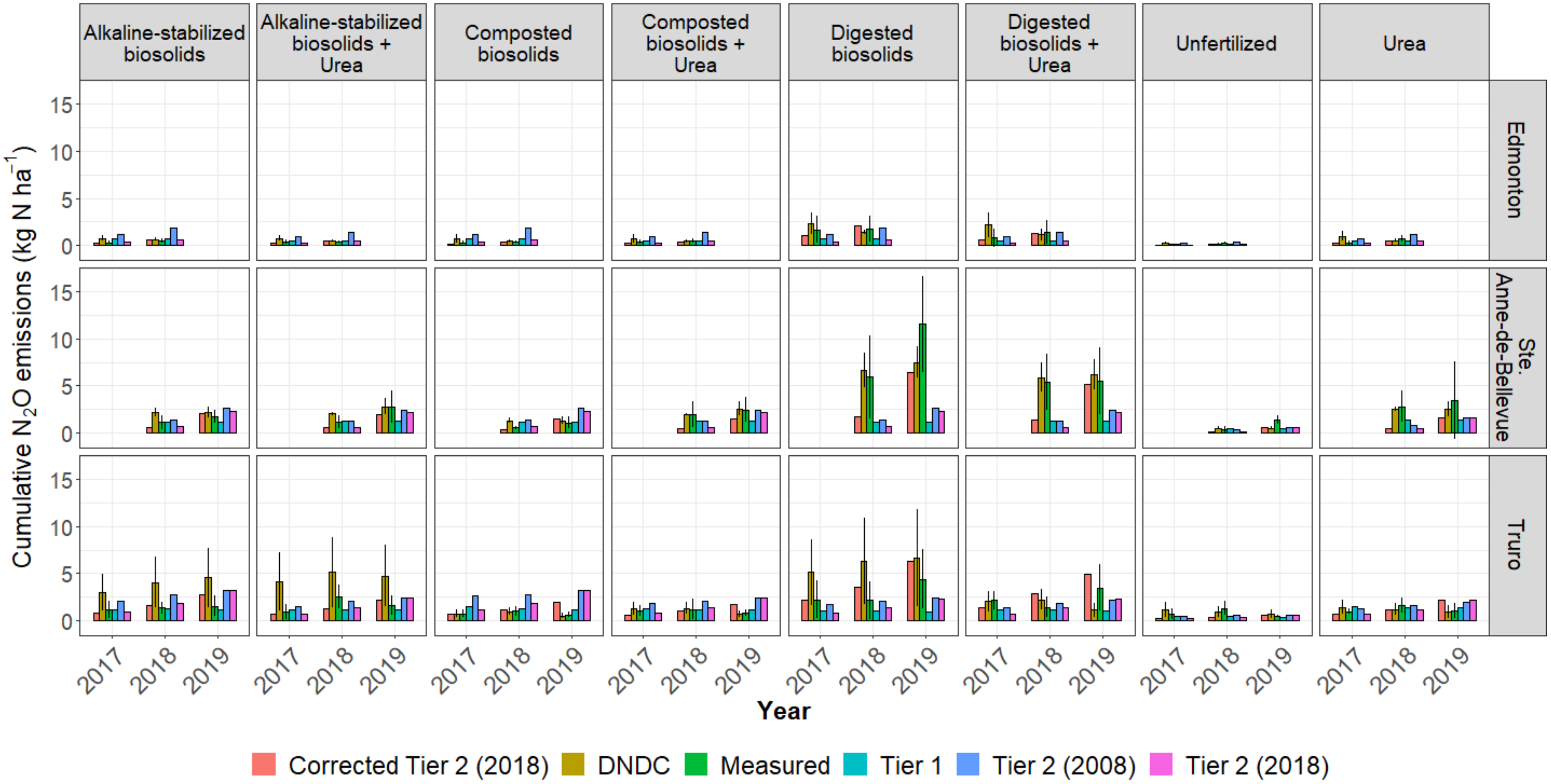

Figure 5.1. Comparison between measured nitrous oxide emissions (with standard deviation) during the growing season and those estimated using the IPCC Tier 1, Tier 2 (2008), Tier 2 (2018), corrected Tier 2 (2018), and Tier 3 (DNDC) methods from agricultural soils in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea from 2017 to 2019.

Table 5.3. Comparing R^2, RMSE, and rRMSE for measured vs. IPCC Tier 1, 2, and 3 - estimated N_2O emissions during the growing season for each treatment, averaged across the three sites (Ste-Anne-de-Bellevue, QC; Truro, NS; and Edmonton, AB).

Method	Metric	Alkaline-stabilized biosolids	Alkaline-stabilized biosolids + urea	Composted biosolids	Composted biosolids + urea	Digested biosolids	Digested biosolids + urea	Unfertilized (negative control)	Urea (positive control)
Measured	Mean (kg N ha^{-1})	1.08	1.39	0.65	1.18	4.24	2.87	0.64	1.53
	S. D. (kg N ha^{-1})	0.55	0.98	0.31	0.78	3.61	1.95	0.50	1.17
Tier 1	Mean (kg N ha^{-1})	1.47	1.41	1.52	1.43	1.35	1.37	0.51	1.60
	S. D. (kg N ha^{-1})	0.33	0.43	0.38	0.46	0.27	0.42	0.23	0.63
	R^2	0.79	0.55	0.51	0.50	0.45	0.50	0.46	0.36
	RMSE (kg N ha^{-1})	0.39	0.01	0.88	0.25	2.89	1.50	0.13	0.07
	rRMSE (%)	36.2	0.99	135.0	21.5	68.2	52.1	20.7	4.65
Tier 2 (2008)	Mean (kg N ha^{-1})	2.15	1.68	2.23	1.72	1.88	1.62	0.43	1.30
	S. D. (kg N ha^{-1})	0.75	0.57	0.77	0.57	0.51	0.54	0.17	0.43
	R^2	0.59	0.29	0.44	0.17	0.35	0.22	0.62	0.04
	RMSE (kg N ha^{-1})	1.06	0.29	1.58	0.54	2.35	1.25	0.20	0.23
	rRMSE (%)	98	21	243	46	55	44	32	15
Tier 2 (2018)	Mean (kg N ha^{-1})	1.41	1.14	1.45	1.16	1.20	1.10	0.29	0.96
	Std (kg N ha^{-1})	1.06	0.85	1.05	0.84	0.83	0.81	0.21	0.70
	R^2	0.66	0.61	0.40	0.16	0.42	0.25	0.43	0.09

	RMSE (kg N ha^{-1})	0.33	0.25	0.79	0.02	3.04	1.77	0.35	0.58
	rRMSE (%)	31	18	121	2	72	62	55	38
Corrected Tier 2 (2018)	Mean (kg N ha^{-1})	1.23	1.04	0.87	0.83	3.34	2.50	0.29	0.96
	Stdev (kg N ha^{-1})	0.94	0.77	0.65	0.61	2.19	1.85	0.21	0.70
	R^2	0.67	0.61	0.44	0.14	0.43	0.30	0.43	0.09
	RMSE (kg N ha^{-1})	0.15	0.35	0.22	0.35	0.90	0.38	0.35	0.58
	rRMSE (%)	14	25	34	30	21	13	55	38
Tier 3	Mean (kg N ha^{-1})	2.06	1.15	0.83	0.89	4.67	2.35	0.61	1.36
	S.D. (kg N ha^{-1})	1.40	0.02	0.24	0.04	0.32	2.73	0.25	0.46
	R^2	0.69	0.43	0.49	0.86	0.46	0.65	0.23	0.80
	RMSE (kg N ha^{-1})	0.98	0.24	0.18	0.30	0.44	0.53	0.03	0.17
	rRMSE (%)	91	17	28	25	10	18	4	11

5.3.3. Comparison between IPCC Tier 2-Estimated and Measured Growing Season N_2O Emissions Estimates

5.3.3.1. Tier 2 (2008)

Relative to the measured N_2O emissions across sites and treatments, the Tier 2 (2008) method performed poorly as seen in the rRMSE and R^2 values in Tables 5.2 and 5.3, as well as the divergence between the trendline and 1:1 line as seen in Figures A.5.3 and A.5.4. In terms of estimating N_2O emissions magnitudes, the Tier 2 (2008) method underperformed relative to the Tier 1 method. Overall, it estimated N_2O emissions in Truro (rRMSE = 28%) better than in Ste-Anne-de-Bellevue (rRMSE = 47%) and Edmonton (rRMSE = 91%) (Table 5.2). In estimating treatment-specific emissions, the rRMSE values for the Tier 2 (2008) method were only slightly better than those for the Tier 1 estimates of N_2O emissions during the growing season from treatments amended with digested biosolids (Table 5.3). Noticeably, N_2O emissions estimated using the Tier 1 method had lower rRMSE for treatments receiving half-rate biosolids with urea than for treatments receiving full-rate biosolids.

5.3.3.2. Tier 2 (2018)

In general, general, the Tier 2 (2018) method estimated N_2O emissions during the growing season across the three sites was better than the Tier 2 (2008) method but was not better than the Tier 1 method. On average, the Tier 2 (2018) emissions estimates were mostly lower than the Tier 2 (2008) emissions estimates for the Edmonton site but were the same as Tier 2 (2008) emission estimates for the Ste-Anne-de-Bellevue and Truro sites (Figure 5.1). The total difference between the estimated and measured emissions showed that the Tier 2 (2018) estimates were better than the Tier 2 (2008) estimates for Edmonton (rRMSE: from 91% to 38%) and Truro (from 28% to 3%) but worse for Ste-Anne-de-Bellevue (rRMSE: from 47% to 60%), particularly for treatments receiving full-rate or half-rate digested biosolids or urea alone (positive control). The N_2O emissions estimated for the growing season using the Tier 2 (2018) method had lower rRMSE values for the half-rate biosolids treatments than for the full-rate biosolids treatments. However, there was visible divergence between the trendline and 1:1 line as seen in plots in Figures A.5.5 and A.5.6.

5.3.3.3. Corrected Tier 2 (2018)

In general, using the corrected Tier 2 (2018) method to estimate growing season N_2O emissions across the three sites led to smaller rRMSE values and increase in R^2 values (between the simulated and measured values) over the Tier 2 (2008), Tier 2 (2018), and Tier 1 estimates. Also, the convergence between the trendline and 1:1 line improved across the sites, as seen in plots in Figure A.5.7, but not for the treatments (Figure A.5.8). The ratio of measured biosolids-induced N_2O-N to urea-induced N_2O-N resulted to biosolids-specific corrections factors for the emission factors as follows: 0.71 for alkaline-stabilized, 2.77 for digested, and 0.43 for composted biosolids, instead of the 0.84 (manure correction factor) used for the Tier 2 (2018) method. These improvements in Tier 2 (2018) estimates were observed across the sites, but to a lesser extent in Ste-Anne-de-Bellevue. In Truro and Edmonton, the rRMSE values between the measured and estimated emissions were < 20%, while Ste-Anne-de-Bellevue was ~47% as shown in Table 5.2. In addition, the estimated (*i.e.*, corrected) emissions were generally within the range of the measured emissions (Figure 1). Meanwhile, across the treatments, rRMSE values were < 40%, except for the unfertilized treatment with rRMSE of 55%.

5.3.4. Comparison between IPCC Tier 3-Estimated and Measured N_2O Emissions During the Growing Season

5.3.4.1. DNDC Calibration and Validation Results

DNDC was calibrated to simulate N_2O emissions for the growing season. Validation of the simulated emissions showed that they were within the 95% confidence intervals of the measured N_2O emissions across the three sites (Tables A.5.24 and A.5.25). The total model error and bias across the sites were not significant in either the calibration or validation stages.

5.3.4.2. DNDC-Estimated N_2O Emissions During the Growing Season

The rRMSE values comparing the measured N_2O emissions and those simulated using DNDC for the growing season were: 2% for Edmonton, 13% for Ste-Anne-de-Bellevue, and 23% for Truro. The rRMSE values for DNDC were lower than those for Tier 1 and 2 estimates across the three sites and for most treatments (Tables 5.2 and 5.3). There was convergence between the trendline and 1:1 line across the sites, as seen in plots in Figure A.5.9, but not for the treatments (Figure A.5.10). Also, the R^2 values between the measured N_2O emissions and DNDC estimates across all sites ranged from 0.31 to 0.81 and were greater than those for Tier 1 and 2 estimates, before the biosolids correction factors were applied. For N_2O emissions specifically from treatments amended with digested biosolids at full and half rates, respectively, there was only a 10% and 18% rRMSE between the measured emissions and those estimated using DNDC, while Tier 1 and Tier 2 methods before correction factor was applied, underestimated the emissions by at least 44%. The rRMSE values for ranged from 4% to 28% across the treatments except for treatments receiving alkaline-stabilized biosolids with rRMSE of 91%.

5.3.4.3. Influence of DNDC Input Parameters on Simulated N_2O Emissions

The sensitivity analysis using the Morris method (Morris, 1991) showed how simulated N_2O emissions during the growing season were affected by varying characteristics of biosolids, soil, weather, and management practices (Tables 5.4 and A.5.26). Input variables with higher Morris sensitivity index (μ^*) have a greater effect on a simulated output (e.g., N_2O emissions) than those with lower values of μ^*. Meanwhile, the standard deviation (σ) reflects whether the effect of a variable is linear or nonlinear (*i.e.*, interacts with other inputs). A high value of σ indicates that the elementary effect of a given input variable depends on the values of other input variables.

As seen in Table 5.4 (also Table A.5.26; in this text, the names of the model inputs and parameters shown in the tables are written in brackets while referring to the physical parameter they represent), across the three sites, soil pH was the dominant variable and had a non-linear relationship with soil N_2O emissions. In Ste-Anne-de-Bellevue, soil pH ($\mu^* = 8.61$) had the highest influence on N_2O emissions followed by biosolid C/N (written as manure C/N in DNDC with $\mu^* = 5.0$), and their effects were non-linear with σ equals 3.05 and 2.16, respectively. Increases in soil pH, C/N, clay fraction, and depth of N application (fertilizer depth, which in this study differentiates surface spread from soil incorporated N application) were correlated with decreasing N_2O emissions. However, the correlations were weak for clay fraction ($r = -0.2$) and depth of N application ($r = -0.13$). Meanwhile, increasing the amount of biosolids N (Manure org. N), temperature degree days (Acc. temp.), precipitation, or field capacity of the soil led to an increase in N_2O emissions. In Truro, soil pH ($\mu^* = 2.59$) and active humus fraction (humads fraction, with $\mu^* = 2.30$ is a DNDC parameter, which represents the unstable fraction of soil humus) were the most sensitive model variables, and N_2O emissions responded non-linearly to changes in these variables. In DNDC, an increase in soil pH from 5.4 to 6.0 led to an increase in N_2O emissions with $\mu = 2.59$, while an increase in soil active humus fraction led to a decrease in N_2O emissions ($\mu = -2.30$). N_2O emissions during the growing season were also sensitive to- and positively correlated with soil bulk density (bulk density, $\mu^* = 1.27$ and $r = 0.28$), precipitation ($\mu^* = 1.16$ and $r = 0.37$), soil organic C (Top SOC, $\mu^* = 0.91$ and $r = 0.18$), and air temperature (Max. air temp and Min. air temp). As seen in the simulated results of the Ste-Anne-de-Bellevue site, in the Truro site simulations, the effect of depth of N application (fertilizer depth) also had a negative correlation with N_2O emission during the growing season. The effect of soil bulk density on N_2O emission was non-linear ($\sigma = 0.42$). In Edmonton, soil clay content was the most sensitive parameter with respect to N_2O emissions with $\mu^* = 0.81$. Increasing the soil clay fraction without changing the soil hydraulic parameters led to a decrease in N_2O emissions during the growing season. To a lesser extent, N_2O emissions during the growing season were also sensitive to temperature degree days (Acc. Temp.), soil pH, soil organic C (Top SOC), air temperature (Max. air temp and Min. air temp), precipitation, and porosity.

Table 5.4. Simulation input parameters and variables ranked according to the Morris sensitivity index (μ*) with respect to simulated cumulative N_2O emissions in Ste-Anne-de-Bellevue (2018 and 2019), Truro (2017–2019), and Edmonton (2017 and 2018). The standard deviation (**σ)** indicates whether linear or nonlinear effects exist due to interactions with other inputs. The Pearson correlation coefficient (r) is an alternative measure of the strength of the association between the input and the N_2O emissions.

Ste-Anne-de-Bellevue					Truro					Edmonton				
†Parameter	**μ**	**μ***	**σ**	**r**	**†Parameter**	**μ**	**μ***	**σ**	**r**	**†Parameter**	**μ**	**μ***	**σ**	**r**
Soil pH	-8.61	8.61	3.05	-0.62	Soil pH	2.59	2.59	0.43	0.51	Clay fraction	-0.81	0.81	0.12	-0.47
Manure C/N	-5.00	5.00	2.16	-0.41	Humads frac.	-2.30	2.30	0.72	-0.33	Acc. Temp.	-0.27	0.31	0.21	-0.15
Manure Org. N	3.08	3.08	0.89	0.12	Bulk density	1.27	1.27	0.42	0.28	Soil pH	-0.30	0.30	0.07	-0.08
Acc. temp.	2.20	2.20	0.98	0.10	Precipitation	1.16	1.16	0.25	0.37	Top SOC	0.25	0.25	0.11	0.09
Clay fraction	-1.69	1.69	0.48	-0.20	Top SOC	0.91	0.91	0.32	0.18	Min. air temp	0.20	0.20	0.11	0.16
Precipitation	1.37	1.37	0.31	0.27	Max. air temp	0.74	0.74	0.24	0.09	Precipitation	0.20	0.20	0.12	0.22
Field capacity	1.12	1.12	0.38	0.01	Min. air temp	0.67	0.67	0.19	0.36	Max. air temp	0.17	0.18	0.15	0.16
Fert. depth	-0.47	0.78	0.87	-0.13	Fert. depth	-0.23	0.23	0.21	-0.05	Porosity	-0.14	0.14	0.08	0.12
Urea	0.76	0.76	0.23	0.08	Field capacity	0.21	0.21	0.08	0.16	Humads frac.	0.12	0.12	0.03	-0.06
Top SOC	0.68	0.68	0.45	0.07	Manure depth	-0.15	0.17	0.18	-0.03	Hydro cond.	0.11	0.11	0.08	-0.07

[†] Manure C/N = C to N ratio in biosolids, Manure org. N = biosolids N, Acc. Temp. = temperature degree days, Fert. depth = fertilizer depth, Top SOC = soil organic carbon in topsoil, Humads frac. = fraction of active humus in soil organic carbon based on measurements made in several field experiments (Li et al., 1994), Max./min air temp = maximum/minimum daily air temperature.

Note: μ = the mean of the distribution of the elementary effects (EE), which assesses the overall influence of the input on the simulated output; μ* = Morris sensitivity index, which is the estimate of the mean of the distribution of the absolute values of the elementary effects; and σ = the standard deviation of the distribution of the EE, which estimates the collective effects of the input due to non-linearity and/or interactions with other inputs.

5.4. Discussion

5.4.1. Assessment of Measured Growing Season N_2O Emissions: Site, Treatment, Weather Effects

The individual or combined effects of fertilizer type, rate of application, method of application, and annual effects on N_2O emissions measured during the growing season varied in response to the unique biotic and abiotic features of each site. Among the sites, the average N_2O emissions in Ste-Anne-de-Bellevue were about 5 times the average values in Edmonton and 2.5 times those in Truro. These findings corroborate those of many other studies in which N_2O emissions differed among sites due to differences in soil types and climatic zones (e.g. Aliyu et al., 2018). Of particular importance were differences in precipitation, agricultural practices (e.g., amount of N applied), and soil organic carbon content, which were dominant factors influencing N_2O emissions.

At the sites in humid Eastern Canada (Ste-Anne-de-Bellevue and Truro), N_2O emissions were dominantly driven by denitrification while nitrification was the dominant process driving N_2O emissions in Edmonton, in the semi-arid Canadian Prairies (Rochette et al., 2018; Thilakarathna & Hernandez-Ramirez, 2021). The total average precipitation during the three growing seasons was 606 mm in Ste-Anne-de-Bellevue and 555 mm in Truro, while Edmonton received an average of 211 mm (Table A.5.5). Also, fields in humid regions have higher plant yield potential than those in arid regions and farmers therefore apply more N. Barley, moreover, requires less N than corn for vegetative growth. In this study, the total N applied in Ste-Anne-de-Bellevue (corn; 120 kg N ha^{-1} for urea and 180 or 201 kg N ha^{-1} for half- and full-rate biosolids treatments, respectively) and Truro (corn; 120 kg N ha^{-1} for urea and 150 or 220 kg N ha^{-1} for half- and full-rate biosolids treatments, respectively) was higher than in Edmonton (barley; 96 and 192 kg N ha^{-1}). Given that precipitation is the most significant factor influencing the rate of denitrification in soil in humid climates and that less N was applied in Edmonton, it is understandable that N_2O emissions in the humid ecozones were higher than in the semi-arid ecozone.

The N_2O emissions, averaged across all growing seasons and the three sites, were generally higher from treatments receiving digested biosolids (full-rate or half-rate) than from other treatments. Digested biosolids have relatively lower C/N and more labile C forms and thus higher mineralization rates relative to the other biosolids (Wang et al., 2016). This suggests that soil inorganic N level was more influential than the amount of organic C being added. Adding the urea effectively nullified the effect of reducing the rate of biosolids application by half.

The differences in N_2O emissions between treatments due to method of fertilizer application in the semi-arid Edmonton site were perhaps due to a combination of factors as follows: mineral N availability in the fertilizers, the high SOC (~55 g C kg^{-1} soil) in the Black Chernozemic soils, and the likely increase in SOC decomposition and soil N mineralization rates due to soil disturbance through incorporation of fertilizers using a rotary plough. Chernozemic soils of the Canadian prairies are generally characterized by high SOC in the topsoil, unlike gleysolic and podzolic/luvisolic soils in Eastern Canada which have SOC < 20 g C kg^{-1} soil. Annual tillage at the Edmonton site is expected to trigger increased SOC decomposition than when left undisturbed. As such, further soil disturbance through soil incorporation of biosolids in Chernozemic soils could potentially result to higher SOC decomposition and microbial activity than in relatively lesser disturbed surface-spread treatments. However, an empirical assessment of the N budget, especially likely N losses due to volatilization and run-off in surface-spread treatments, is required prior to a definitive conclusion.

In addition to climate and SOC differences between the sites, soil clay content, and soil pH also influence the magnitude of soil N_2O emissions in agroecosystems. On the one hand, soil clay content affects soil aeration (porosity), moisture retention, and provides binding sites for NH_4^+ and influences N availability for denitrification (Bateman & Baggs, 2005). Increasing concentration of clay in the soil provides more binding sites for NH_4^+ and then to have higher water contents (lower aeration) favouring complete denitrification, lowering N_2O emissions. Overall, soil texture and clay content differed between the sites. Ste-Anne-de-Bellevue (loam; clay = ~190 g kg^{-1} soil), Truro (sandy loam; clay = ~100 g kg^{-1} soil), Edmonton (silty clay loam; clay = ~327 g kg^{-1} soil). On the other hand, N_2O:N_2 ratio reduces as soil pH tends to neutral (Saggar et al., 2013; Hénault et al., 2019). However, the effect of soil pH on growing season emissions across the sites appear to be masked by climate differences. N_2O emissions from the Ste-Anne-de-Bellevue site with mean pH of ~7 was higher than those of Truro which had a mean pH of 5.7. Besides the alkaline-stabilized biosolids which had a relatively high pH (> 9), other soil amendments may not be able to buffer the soil pH as effectively at the Truro site. Perhaps, this explains why N_2O emissions from Truro soils receiving alkaline-stabilized biosolids were not significantly different from those receiving digested biosolids.

A limiting factor in GHG measurement using manual chambers is the sampling frequency and spatial coverage which can introduce gaps in emissions data impacting the level of uncertainty in estimating cumulative emissions on both national and sub-national scales (Barton et al., 2015). Also, the linear *vs.* exponential interpolation approaches of estimating cumulative N_2O emissions produce different values (Levy et al., 2017).

5.4.2. Comparing Estimated and Measured N_2O Emissions During the Growing Season

5.4.2.1. IPCC Tier 1 Method

The poor results from the Tier 1 method does not come as a surprise since it is well established that biotic and abiotic differences between agroecosystems influence the rates of N mineralization, nitrification, and denitrification, and are only partially represented in the Tier 1 methodology. Similar studies conducted in Canada and other temperate countries using manure, identified disparities of about 15% between the measured and estimated N_2O emissions (Bell et al., 2015). These disparities occur broadly due to differences in site and in type of amendment. In addition to the Tier 1 method's lack of representation of biosolids in the dataset used for developing the emissions factors, the Tier 1 method broadly categorizes climate differences into wet and dry conditions. It does not account for the magnitudes of growing season precipitation, which vary in their marginal effects on N_2O emissions between sites. Also, organic materials are not segregated according to more definitive characteristics such as the inherent C/N and form of the organic C in the organic amendment. In addition to these, variations in soil conditions, management practices, and vegetation between the sites influence N_2O emissions significantly but were not strongly accounted for in the analysis. The Tier 1 methodology differentiates between management practices only when there is a change quantity of the applied N. Tillage, fertilizer placement, timing and source are not considered. It surprising however, that on average, the Tier 1 method estimated the emissions magnitudes better than the Tier 2 (2008 and 2018) methods.

5.4.2.2. IPCC Tier 2 Method

Irrespective of the localized datasets used in developing the Tier 2 method, the uncorrected (Tier 2 (2008) and Tier 2 (2018)) Tier 2-estimated growing season N_2O emissions in this study were more poorly simulated relative to the Tier 1-estimates. A similar performance was found in another study where the Tier 2 method underestimated N_2O emissions by 75% for inorganic amendment additions at a site in Manitoba, Canada (Uzoma et al., 2015). This is despite the accounted regional/ecodistrict-scale effects of moisture regime, soil texture, spring thaw in Western Canada, topography, tillage, summer fallow, and irrigation on N_2O emissions. Also, the Tier 2 (2008) method was adjusted for growing season emissions by a factor of 0.7, *i.e.*, according to Rochette et al. (2008) that 70% of annual N_2O emissions occur during the growing season. Other studies report that 50–70% of annual emissions could occur during the growing season depending on the site (Chantigny et al., 2016); thus, leaving room for marginal error due to estimation uncertainty.

The effects of moisture regime on N_2O emissions were accounted for in the form of either precipitation or ratio of precipitation to potential evapotranspiration (P/PE). However, the discrepancies between the measured and estimated growing season N_2O emissions occurred in the Tier 2 estimates due to their different approaches in expressing the relationships between ecodistrict moisture regime and N_2O emission factor. While the relationship between emission factor and moisture regime was linear for the Tier 2 (2008) method, the Tier 2 (2018) method was based on an exponential relationship. Being sensitive parameters, changes in precipitation will lead to exponential changes in emissions factors for the Tier 2 (2018) and corrected Tier 2 (2018) methods but linear for the Tier 2 (2008) method. Moreover, considering that the Tier 2 methods were developed using 30-year regional precipitation averages, which was mostly < 700 mm, site specific growing season precipitation values exceeding 700 mm in a target year will lead to exaggerated changes in the magnitude of emissions factors. These challenges highlight the limitations of the IPCC Tier 2 method to accurately estimate site scale emissions on an annual basis.

Besides the challenges of applying the Tier 2 method on a site scale, additional shortcomings of the Tier 2 method include its lacking representation of several sensitive soil and fertilizer parameters. For instance, the Tier 2 methods do not account for the differences in soil pH, which has been found in several studies to significantly differentiate N_2O emissions magnitudes between sites. In addition, the dataset used in developing the Tier 2 (2008) method were biased towards sites in Brown-Dark Brown and Black soil regions in the Canadian Prairies, of which most sites were mineral N-fertilized. Meanwhile, the Tier 2 (2018) method used more recent data covering organic- and mineral N-fertilized sites across Canada, including pacific maritime ecozone. However, its inability to accurately estimate biosolids-induced N_2O emissions led to implementation of correction factors in the so-called corrected Tier 2 (2018) method.

The corrected Tier 2 (2018) method minimized deviations between the measured and estimated growing season N_2O emissions relative to the Tiers 1 and 2 (2008 and 2018) methods by incorporating biosolids-specific correction factors into the Tier 2 (2018) equation. The correction factors represent sensitive biosolids parameters such as C/N, pH, and organic carbon forms, which are major distinguishing factors between biosolids. As such, the corrected Tier 2 (2018) method estimated digested biosolids-related N_2O emissions better than the previous Tier 2 and Tier 1 methods.

The use of the relatively simple corrected Tier 2 (2018) method for Canada’s national GHG inventory requires validation and better alignment with the existing national inventory infrastructure. Despite the addition of site-specific effects of moisture on N_2O emissions and the proposed biosolids-specific correction factors, minimal deviations still exist between the measured and estimated N_2O emissions. These deviations occur because the correction factors are global (calculated across the three sites) and as such the site-specific effects of temperature were unaccounted for in this Tier 2 method. Also, the meta-data used in deriving the emission factors did not account for the differences in research objectives and protocols used in the selected empirical studies and how they might influence the deduced emissions factors. Therefore, this method needs to be tested on independent datasets prior to deployment in the national inventory. Despite these shortcomings, the corrected Tier 2 (2018) method offers a better approach than the Tier 1 and previous Tier 2 methods for estimating biosolids-induced N_2O emissions across the studied sites. The improvement in the fit between the corrected Tier 2 (2018) estimates and the measured emissions justifies the added task of including the correction factors in the inventory methodology. Further requirements include availability of activity data and technical/scientific requirements to employ and defend methodology to regional/national and international partners-stakeholders.

5.4.2.3.IPCC Tier 3 Method

The improvement of the Tier 3- over the Tiers 1- and 2-estimates support the original hypothesis that the Tier 3 method would produce the most accurate N_2O emission estimates in reference to growing season measurements. The main reason for these improved estimates is that the interaction between management, soils and climate are well captured in the Tier 3, unlike the Tier 1 and 2 approaches. The Tier 3 method via process-based modelling accounts for the effects of influential soil, fertilizer (e.g., biosolid), climate, and crop variables, as well as management practices on N_2O emissions, irrespective of spatial scale. However, there are limitations and challenges associated with the Tier 3 method. Firstly, process-based models must be calibrated and validated against empirical data for each site/region prior to use. Secondly, running such data-intensive modelling exercise requires extensive data collection, which are challenging in terms of both labour and time. Thirdly, process-based models are complex and often limited in their mechanistic explanation of soil processes. Also, to use DNDC in the national GHG inventory requires the development of a transparent and complete documentation of the Canada model version. Finally, expertise is required to employ process-based models and uncertainty due to model structure needs to be quantified at high computational expense.

The data requirement of the Tier 3 method in estimating biosolids-induced soil N_2O emissions limit its immediate implementation in the national GHG inventory. To minimize the data requirements for making accurate estimates of N_2O emissions, effort could be focused on identifying the most important parameters influencing region-specific N_2O emissions as seen in the sensitivity analysis. Through such approach, measurements, in coordination with process-based modelling could be used to develop improved meta-equations for use in the Tier 2 framework. For instance, to estimate direct N_2O emissions from grazed pastures in New Zealand, Giltrap et al. (2013) and Giltrap & Ausseil (2016) used DNDC to develop regression models with N_2O-sensitive input parameters which predicted national emissions in agreement with national emission factor-estimated emissions. However, using this approach requires additional datasets to test and validate estimates to minimize model/estimation errors. Computational efficiency is an advantage of this method, while a major limitation is the under-representation of nationwide differences in site-sensitive inputs due to limited empirical data. For instance, in this study, N_2O emissions were sensitive to soil bulk density only in Truro. Such discrepancy could be transmitted to the meta-equation to produce biased N_2O emissions estimates across sub-national units.

5.5. Conclusions

Mean growing season N_2O emissions were significantly higher in treatments receiving digested biosolids than composted and alkaline-stabilized biosolids across the three sites. Considering that emissions from the control treatment were not different from emissions from the alkaline-stabilized and composted biosolids, the use of these two biosolids offer a means to reduce emissions relative to the digested biosolids. Reducing the rate of application of biosolids from a rate sufficient to meet plant N requirements to half that rate with supplemental urea did not influence N_2O emissions. This suggest N availability and not organic C availability may be more influential in determining N_2O emissions from land receiving biosolids. In Chernozemic soils, surface spreading of digested and composted biosolids and soil incorporation of alkaline-stabilized biosolids does not necessarily reduce N_2O emissions. Surface spreading likely leads to increased ammonia volatilization in the composted and mesophilic biosolids. In addition, surface application is outside most provincial regulations across Canada for several good reasons. Then, in the current study, emissions from New Brunswick, Manitoba, and British Columbia which represent other ecozones such as the Pacific maritime ecozone were not accounted for, due to the practical limitations (e.g., logistics) of conducting empirical studies on a national scale. Still, we see the value to science as this enables comprehensive understanding of biosolids effects on environment and plant productivity. However, empirical determination of N budgets across Canadian agroecosystems is required to properly understand the N pathways when biosolids are land-applied.

Given the poor performance of the Tiers 1 and 2 (2008 and 2018) methods as seen in this study and the challenges associated with deploying the Tier 3 method for national GHG accounting, the corrected Tier 2 (2018) method offers the best chance for accounting national biosolids-induced soil GHG emissions in the near future. On a regional scale, the Tier 2 and 3 methods can be combined to better estimate national scale soil N_2O emissions. However, regionalized activity data at the inventory level may not currently be sufficient to support this kind of application of Tier 3 models. Global market access based on country specific Tier 3 approaches to quantify and benchmark current farm practices and emission levels could face additional scrutiny (compared to Tier 1 and Tier 2) if robust calibration/validation procedures are not demonstrated and model processes are not sufficiently documented for evaluation. The ramifications can be that local producers may feel arbitrarily misrepresented by a complex mechanistic modelling approach compared to a Tier 2 or Tier 1, although every approach has its merits. Then, there are no global standards or criteria determining how to use the Tier 3 modelling approach for GHG inventory, which can result in a lot of disparity/uncertainty in the integrity in country-country assessments. Finally, the comparison between Tier 1, Tier 2, and Tier 3 approaches has some inherent bias in that the Tier 3 approach was employed after the model was "trained" –calibrated for the site level emissions, unlike the Tiers 1 and 2 approaches which were "trained" with regional and international datasets, respectively. This is both a strength (improved outcomes) and limitation (in its applicability nationally) in the approach and will inherently impact the comparability of the Tier 3 approach with the other 2 approaches. However, models can be calibrated regionally using what data is available.

5.6. Path Forward

In the short-term, the Tier 2 (2008) method could be used for national biosolids-induced soil N_2O emissions accounting prior to the development of activity data, additional measurement, and validation of the Tier 3 method. Due to the high data requirement of the Tier 3 method, and its marginal improvement over the corrected Tier 2 (2018) method in estimating emissions, the corrected Tier 2 (2018) method presents a more practical approach in developing an N_2O accounting tool in the mid-term. Firstly, engagement of producers is much easier using a Tier 2 approach. Secondly, the application of the Tier 2 approach avoids the pitfalls that a Tier 3 approach inherently has. Also, the Tier 2 approach is much more transparent in how the current scientific understanding is being applied towards quantifying GHG emissions from farm practices. Considering these points, utilizing a Tier 3 approach to improve Tier 2 methodologies as well as highlighting where additional resources for measuring scientific gaps can be allocated could be an area for future research. Producer groups and Fertilizer Canada are concerned that Tier 2 approaches do not include 4R practices (right source, right rate, right time, and right place). As such, the Tier 2 approach could be updated or a complete move to a process-based modelling approach could be implemented in the long-term.

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5.8. Appendix

5.8.1. Appendix A: Tables Showing Measured Variables and Model Parameter Values

Table A.5.1. Macro and micronutrients content of biosolids applied to agricultural soils for the three years (2017–2019) of field experiment in Ste-Anne-de-Bellevue, QC, Canada. †

Parameter	Digested biosolids			Composted biosolids			alkaline-stabilized biosolids		
	2017	2018	2019	2017	2018	2019	2017	2018	2019
Dry Matter (kg kg^{-1})	0.20	0.23	0.17	0.38	0.48	0.45	0.62	0.61	0.62
pH (pH Units)	8.2	8.2	8.1	7.6	7.4	7	10.8	9.8	8.7
Nitrogen (g N kg^{-1})	71.0	63.3	61.7	24.5	11.7	11.3	n/a	11.3	7.3
Ammonium-N (g N kg^{-1})	11.0	13.4	13.3	4.1	1.3	1.3	n/a	0.7	1.0
Potassium (g kg^{-1})	0.6	n/a	8.1	0.4	n/a	1.6	n/a	n/a	1.1
Phosphorus (g kg^{-1})	3.3	n/a	39.1	0.9	n/a	6.4	n/a	n/a	5.9
Calcium (g kg^{-1})	23	n/a	38	29	n/a	n/a	250	12	229
Magnesium (g kg^{-1})	4.8	n/a	4.5	2.7	n/a	n/a	n/a	1.6	1.0
Sodium (g kg^{-1})	2.5	n/a	4.2	11.2	n/a	n/a	n/a	0.4	0.4
Iron (g kg^{-1})	29.0	n/a	28.1	6.6	n/a	n/a	n/a	6.2	3.4
Boron (mg kg^{-1})	11.0	n/a	12.1	16.0	n/a	n/a	n/a	12.3	<10.0
Copper (mg kg^{-1})	350	n/a	139	91	n/a	n/a	n/a	27	72
Zinc (mg kg^{-1})	320	n/a	281	266	n/a	n/a	n/a	124	178
C:N ratio	4.7	5.1	4.4	n/a	38.6	37.9	22.3	18.1	22.2

Table A.5.2. Macro and micronutrients content of biosolids applied to agricultural soils for the three years (2017–2019) of field experiment in Truro, NS, Canada. †

Parameter	Digested biosolids			Composted biosolids			alkaline-stabilized biosolids		
	2017	2018	2019	2017	2018	2019	2017	2018	2019
Dry Matter (kg kg^{-1})	0.23	0.23	0.17	0.42	0.42	0.45	0.62	0.62	0.62
pH (pH Units)	7.8	8.2	8.1	7.4	7.4	7.0	10.0	9.8	8.7
Nitrogen (g N kg^{-1})	56.0	64.0	62.0	14.0	12.0	11.0	10.0	11.3	7.3
Ammonium-N (g N kg^{-1})	13.0	13.0	13.0	0.0	1.0	1.0	n/a	1.0	1.0
Potassium (g kg^{-1})	3.8	7.0	8.1	2.0	2.0	2.0	8.0	9.0	1.1
Phosphorus (g kg^{-1})	25.0	34.0	39.0	9.0	9.0	6.0	7.0	7.0	5.9
Calcium (g kg^{-1})	19.0	28.0	38.0	20.0	14.0	12.0	165.0	165.0	229
Magnesium (g kg^{-1})	3.0	4.0	5.0	2.0	2.0	2.0	3.0	3.0	1.0
Sodium (g kg^{-1})	2.0	3.0	4.0	1.0	1.0	0.0	1.0	1.0	0.4
Iron (g kg^{-1})	19.8	35.2	28.1	6.1	6.6	6.2	7.7	8.1	3.4
Boron (mg kg^{-1})	13.7	12.1	12.0	10.9	10.7	12.3	18.8	19.4	<10.0
Copper (mg kg^{-1})	150.2	136.7	138.5	61.0	66.0	26.7	99.4	93.9	72
Zinc (mg kg^{-1})	212	238	281	175	198	124	208	248	178
Manganese (mg kg^{-1})	287	118	122	1172	1094	1114	219	449	256
C:N ratio	n/a	8.8	8.9	n/a	38.6	37.9	n/a	30.9	38.5

Table A.5.3. Macro and micronutrients content of biosolids applied to experiment field in Edmonton, AB, Canada in 2017 and 2018. †

Parameter	Digested biosolids		Composted biosolids		alkaline-stabilized biosolids	
	2017	2018	2017	2018	2017	2018
Dry Matter (kg kg^{-1})	0.23	0.23	0.59	0.72	0.69	0.74
pH	7.7‡	n/a	5.01§	n/a	12.8§	n/a
Nitrogen† (g N kg^{-1})	17.9	42.4	19.5	22.5	8.1	7.8
Ammonium-N (g N kg^{-1})	8.2	n/a	1.4	n/a	1.3	n/a
C to N ratio	n/a	6.7	n/a	12.4	n/a	15.7
TC† (g C kg^{-1})	n/a	283.3	n/a	278.4	n/a	122.5
Electrical conductivity‡ (dS m^{-1})	4.5	n/a	n/a	n/a	n/a	n/a
Moisture (mass basis)	0.77	0.77	0.41	0.28	0.31	0.26

†Total carbon (TC) and total nitrogen (TN) were measured by dry combustion.

‡Measured in saturated paste 1:2.

§Measured by the TMECC 04.11 Electrometric pH Determinations for Compost. 1:5 Slurry Method.

Table A.5.4. Site descriptions of the Ste-Anne-de-Bellevue, QC; Truro, NS; and Edmonton, AB sites where experiments were conducted across Canada from 2017 to 2019.

Site climate and soil parameters	Ste-Anne-de-Bellevue Site	Truro Site	Edmonton Site
Ecozone	Mixed wood plain	Atlantic maritime	Prairies
Ave. annual rainfall (mm)	785	928	339
Ave. annual snowpack (cm)	206	162	115
Ave. annual temperature (°C)	6.5	6.2	3.9
Ave. growing season temp. (°C)	16	15	16.5
Crop grown	Silage corn	Silage corn	Barley
Growing season for crop	May to October	May to September	June to September
Soil class	Gleysolic	Podzolic/Luvisolic	Chernozomic
Soil texture	Loam	Sandy loam	Silty clay loam
Bulk density (g cm^{-3})	1.21 ± 0.06	1.31 ± 0.05	1.18 ± 0.05
Soil pH	6.1 ± 0.2	5.7 ± 0.2	6.1 ± 0.2
Clay content (g kg^{-1})	190 ± 10	103 ± 15	342 ± 15
Sand (g kg^{-1})	490 ± 20	589 ± 15	70 ± 10
Silt (g kg^{-1})	320 ± 15	309± 12	460 ± 10
Porosity (cm^3 cm^{-3})	0.54 ± 0.02	0.51 ± 0.01	0.56 ± 0.02
Conductivity (m hr^{-1})	0.015 ± 0.008	0.046 ± 0.005	0.008 ± 0.001

field capacity (cm^3 cm^{-3})	0.46 ± 0.05	0.382 ± 0.05	0.391 ± 0.05
wilting point (cm^3 cm^{-3})	0.243 ± 0.04	0.161 ± 0.05	0.251 ± 0.05
Initial Soil NO_3^-(mg N kg^{-1}) 10cm[†]	9.0 ± 0.2	24.2 ± 0.3	13.3 ± 0.1
Initial Soil NH_4^+(mg N kg^{-1}) 10cm[†]	1.52 ± 0.15	3.91 ± 0.01	4.00 ± 0.01
SOC at 0-10cm of soil (kg C kg^{-1})[†]	0.013 ± 0.005	0.012 ± 0.005	0.055 ± 0.005

[†] NO_3^-= nitrate, NH_4^+= ammonium, and SOC = soil organic carbon.

Table A.5.5. Values of mean air temperature (ºC), total potential evapotranspiration (mm), total precipitation (mm), and ratio of precipitation to potential evapotranspiration during the growing season in the Ste-Anne-de-Bellevue, QC (May to October); Truro, NS (May to October); and Edmonton, AB (June to August) sites between 2017 and 2019.

Site	**Year**	**Air temperature** (ºC)	**Potential evapotranspiration (mm)**	**Precipitation (mm)**	**Precipitation/ potential evapotranspiration**
Edmonton	2017	14.0	243.2	136.8	0.56
Edmonton	2018	11.9	242.3	168.8	0.70
Edmonton	2019	11.0	236.9	328.6	1.39
Ste-Anne-de-Bellevue	2017	17.3	549.9	648.4	1.18
Ste-Anne-de-Bellevue	2018	17.1	559.3	392.6	0.70
Ste-Anne-de-Bellevue	2019	16.0	546.2	624.8	1.14
Truro	2017	14.5	532.6	491.3	0.92
Truro	2018	13.8	538.5	611.3	1.14
Truro	2019	12.9	531.5	715.9	1.35

Table A.5.6. Management practices (tillage, fertilizer and biosolids application, planting, and harvesting) at Ste-Anne-de-Bellevue, QC; Truro, NS; and Edmonton, AB sites during field experiments from 2017 to 2019.

Management practice	**Year**	**Ste-Anne-de-Bellevue**	**Truro**	**Edmonton**
Chamber base dimensions (L × W × H) (cm)	n/a	50 × 50 × 15	40 × 20 × 15	64.1 × 15.6 × 15
Chamber cover dimensions (L × W × H) (cm)	n/a	50 × 50 × 15	40 × 20 × 15	50 × 50 × 15
Plot dimension (L × W) (m)	n/a	8 × 5	8 × 6	8 × 2
Quantity of crop residue N (kg N ha^{-1})	**2017**	0	0	0
Date of biosolids application		23-May	10-May	31-May
Quantity of applied biosolids N (kg N ha^{-1}) (biosolids only/half-rate + urea)		162/120	145/72 (digested), 173/86 (alkaline-stabilized), 239/120 (composted)	192/96
Date of tillage/incorporation		15-May	11-May	31-May
Type of till		Chisel plough	Disk plough	Rotary plough

Date of planting with initial mineral N		8-Jun	20-May	1-Jun
Mineral N applied at planting (kg N ha^{-1})		39	36	96
Planting rate (seeds per hectare)		76,000	84,000	n/a
Date of urea application		5-Jul	4-Jul	31-May
Quantity of urea N applied (kg N ha^{-1}) (urea only/half-rate + urea)		120/60	126/66	96/48
Date of harvest		4-Oct	17-Oct	17-Aug
Date of termination till		-	20-Oct	17-Aug
Quantity of crop residue N (kg N ha^{-1})	2018	9.4	11.1	2.0
Date of biosolids application		15-May	17-May	4-Jun
Quantity of applied biosolids N (kg N ha^{-1}) (biosolids only/half-rate + urea)		162/120	120/80 (digested), 180/90 (alkaline-stabilized), 180/90 (composted)	192/96
Date of tillage/incorporation		3-May	18-May	4-Jun
Type of till		Chisel plough	Disk plough	Rotary plough
Date of planting with initial mineral N		14-Jun	24-May	5-Jun

Mineral N applied at planting (kg N ha^{-1})		36	30	96
Planting rate (seeds per hectare)		76,000	84,000	n/a
Date of urea application		19-Jul	23-Jul	4-Jun
Quantity of urea N applied (kg N ha^{-1}) (urea only/half-rate + urea)		120/60	120/68	96/48
Date of harvest		18-Oct	15-Oct	15-Aug
Date of termination till		20-Oct	18-Oct	15-Aug
Quantity of crop residue N (kg N ha^{-1})	2019	9.4	11.1	2.0
Date of biosolids application		15-May	7-May	5-Jun
Quantity of applied biosolids N (biosolids only/half-rate + urea)		162/120	145/72 (digested), 173/86 (alkaline-stabilized), 239/120 (composted)	1230/615 (digested), 402/201 (alkaline-stabilized), 351/176 (composted)
Date of tillage/incorporation		6-May	8-May	5-Jun
Type of till		Chisel plough	Disk plough	Rotary plough
Date of planting with initial mineral N		24-May	31-May	5-Jun
Mineral N applied at planting (kg N ha^{-1})		36	30	96

Planting rate (seeds per hectare)		76,000	84,000	n/a
Date of urea application		30-May	7-Aug	2-Jun
Quantity of urea N applied (kg N ha^{-1}) (urea only/half-rate + urea)		120/60	120/60	96/48
Date of harvest		21-Oct	22-Oct	22-Aug
Date of termination till		22-Oct	25-Oct	22-Aug

Table A.5.7. List of crop, soil and climate parameters used in DNDC calibration and simulation of carbon and nitrogen cycling on the Ste-Anne-de-Bellevue, QC; Truro, NS; and Edmonton, AB sites. [†]

Model parameter [†]	**Ste-Anne-de-Bellevue**	**Truro**	**Edmonton**	**Unit**[†]
Land-use type	Upland	Upland	Upland	-
Bulk density	1.21	1.18	1.18	g cm^{-3}
Soil pH	7.0	5.7	6.1	-
Clay fraction	0.19	0.10	0.34	-
Porosity	0.45	0.46	0.55	cm^3 cm^{-3}
Field capacity	0.46	0.60	0.66	WFPS
Wilting point	0.20	0.30	0.46	WFPS
Hydraulic conductivity	0.015	0.046	0.015	m hr^{-1}
Top layer SOC to 20 cm depth	0.015	0.014	0.054	kg C kg^{-1}
Litter fraction	0.01	0.01	0.01	-
Humads fraction	0.19	0.09	0.02	-
Humus fraction	0.80	0.90	0.97	-
Crop residue left in field	0.10	0.10	0.10	-
Snow melt factor[#]	1.10	1.50	1.50	-
Soil evaporation factor[#]	0.80	0.70	0.80	-
Run-off snow melt fraction	0.20	0.20	0.20	-
N_2O rain intensity factor[#]	0.70	0.50	0.50	-
Litter decomposition factor[#]	0.80	1.00	0.01	-
Humads decomposition factor[#]	0.80	1.00	0.10	-

Humus decomposition factor#	0.80	1.00	0.10	-
Denitrifier growth rate#	1.95	1.35	0.50	-
Grain yield	4,800	4,700	2,150	kg C ha^{-1} yr^{-1}
Grain fraction of crop biomass	0.25	0.25	0.30	-
Leaf fraction of crop biomass	0.30	0.30	0.23	-
Stem fraction of crop biomass	0.30	0.30	0.23	-
Root fraction of crop biomass	0.15	0.15	0.24	-
TDD	2600	2600	1500	°C d
Optimum crop temperature	25	30	18	°C
Crop water requirement	151	150	150	g water g^{-1} DM
N in rainfall	0.19	0.15	5.90	mg g^{-1}
Maximum air NH_3 concentration	0.15	0.06	0.45	µg N m^{-3}
Air CO_2 concentration	407	400	405	mg g^{-1}

dimensionless variables influencing soil carbon and nitrogen mineralization and water flow

Table A.5.8. Ranges of values used to conduct DNDC sensitivity analysis on the effects of changing crop, soil, and climate parameters on growing season N_2O emissions from soils amended with biosolids in Ste-Anne-de-Bellevue, QC; Truro, NS; and Edmonton, AB. Mesophilic anaerobically digested biosolids were used as the default for the model simulations. Def = default, Min. = minimum, and Max. = maximum values.

Parameter and parameter type		Data source	Ste-Anne-de-Bellevue			Truro			Edmonton		
			Def.	Min.	Max.	Def.	Min.	Max.	Def.	Min.	Max.
Topsoil organic C (kg C Kg^{-1} soil)	-------Soil-------	Estimated	0.015	0.012	0.018	0.014	0.011	0.017	0.054	0.04	0.063
Clay fraction (kg kg^{-1} soil)		Measured	0.19	0.15	0.23	0.12	0.1	0.14	0.34	0.27	0.41
Bulk density (g cm^{-3})		Measured	1.31	1.27	1.4	1.4	1.12	1.68	1.18	1.15	1.21
Conductivity (m hr^{-1})		Estimated	0.015	0.0135	0.0165	0.046	0.0414	0.0506	0.015	0.0135	0.0165
Porosity (cm^{3} cm^{-3})		Estimated	0.45	0.405	0.495	0.46	0.414	0.506	0.55	0.495	0.605
Soil pH (-)		Estimated	7.0	6.6	7.4	5.7	5.4	6.0	6.1	5.8	6.4
Field capacity (WFPS)		Estimated	0.46	0.40	0.52	0.60	0.54	0.66	0.70	0.63	0.77
Wilting point (WFPS)		Estimated	0.20	0.16	0.24	0.30	0.27	0.33	0.46	0.41	0.51
Litter fraction (kg C kg^{-1} C)		Estimated	0.01	0.005	0.02	0.01	0.005	0.02	0.01	0.005	0.02
Humads fraction (kg C kg^{-1} C)		Estimated	0.19	0.05	0.25	0.09	0.05	0.14	0.02	0.015	0.025

Maximum yield (kg C ha^{-1} yr^{-1})	Crop management-	Estimated	4800	4400	5200	4700	4230	5170	2150	1900	2400
Grain C:N ratio (-)		Estimated	50	45	65	59	45	65	35	30	50
Water demand (g water g^{-1} DM)		Estimated	151	120	181	150	120	181	141	113	169
Thermal degree days (ºC d)		Estimated	2600	2340	2860	2600	2340	2860	1200	1080	1440
Optimum temperature (ºC)		Estimated	22	22.5	27.5	30	22.5	27.5	18	16.2	19.8
Biosolids N applied (kg N ha^{-1})		Estimated	162	129.6	194.4	162	129.6	194.4	96	86.4	105.6
Crop residue (kg C kg^{-1} C ha^{-1})		Estimated	0.2	0.1	0.3	0.2	0.1	0.3	0.1	0.05	0.15
Fertilizer depth (cm)		Estimated	15	5	20	15	5	20	15	5	20
Urea N applied (kg N ha^{-1})		Estimated	39	30	45	30	24	36	10	8	12
Manure depth (cm)		Estimated	15	5	20	15	5	20	15	5	20
Manure C/N		Estimated	6.0	4.0	7.5	6.0	4.0	7.5	7.73	6.2	9.3
Manure pH		Estimated	8.22	6.7	9.2	8.22	6.7	9.2	8.15	6.5	9.9
Solar radiation (MJ m^{-2} d^{-1})	Environment	Estimated	value	-10%	+10%	value	-10%	+10%	value	-10%	+10%
Precipitation (cm)		Estimated	value	-10%	+10%	value	-10%	+10%	value	-10%	+10%
Air temperature (ºC)		Estimated	value	-1	+1	value	-1	+1	value	-1	+1

5.8.2. Appendix B: Tables Showing the Results of Statistical and Error Analysis

Table A.5.9. Four-way ANOVA table for the effects of Site, fertilizer N source (Fert), method of application (MA) and annual effects (Year) on N_2O emissions during the growing season across Ste-Anne-de-Bellevue (QC; 2018 and 2019), Truro (NS; 2017 to 2019), and Edmonton (AB; 2017 and 2018) sites at $\alpha = 0.05$.

Source	DF	Sum of Squares	Mean Square	F value	Pr(>F)	Significance
Fert	7	112.518	16.074	32.1498	<2.0E16	***
Year	2	81.814	40.907	81.8186	<2.0E16	***
MA	1	2.752	2.752	5.504	0.0196007	*
Site	2	85.837	42.918	85.8419	<2.0E16	***
Fert:Year	14	12.34	0.881	1.7629	0.04329	*
Fert:MA	6	3.559	0.593	1.1865	0.3131656	
Year:MA	2	0.39	0.195	0.3896	0.6776863	
Fert:Site	14	16.549	1.182	2.3643	0.0039358	**
Year:Site	2	8.661	4.331	8.6617	0.0002184	***
MA:Site	2	2.765	1.383	2.7654	0.0644973	.
Fert:Year:MA	12	5.351	0.446	0.8919	0.5555328	
Fert:Year:Site	14	16.127	1.152	2.304	0.0050728	**
Fert:MA:Site	12	1.862	0.155	0.3103	0.987379	
Year:MA:Site	2	0.88	0.44	0.8803	0.415687	
Fert:Year:MA:Site	12	3.423	0.285	0.5706	0.8653979	
Residuals	311	155.491	0.5			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on growing season N_2O emission at the p value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.5.10. Tukey HSD pairwise comparison of means of growing season N_2O emission due to site-specific differences where the respective soils were amended with either surface spread or soil incorporated biosolids and/or urea between 2017 and 2019. Mean differences are significant at $\alpha = 0.05$.

Site	$\log(N_2O)$	std	N	se	††groups
Ste-Anne-de-Bellevue	7.5376	1.07225	120	0.09788	a
Truro	7.04557	0.81128	176	0.06115	b
Edmonton	5.97094	0.92782	120	0.0847	c

[††] Different letters within the “group” column represent significant differences at $p < 0.05$ based on Tukey’s test for pairwise comparison.

Table A.5.11. Tukey HSD pairwise comparison of means of growing season N_2O emission due to fertilizers (biosolids and/or urea) applied on the surface or incorporated into the soil in Ste-Anne-de-Bellevue (QC; 2018 and 2019), Truro (NS; 2017 to 2019), and Edmonton (AB; 2017 and 2018) sites at $\alpha = 0.05$.

Fertilizer	$\log(N_2O)$	std	N	se	[††]groups
Digested biosolids	7.752	1.2505	56	0.16711	a
Digested biosolids + urea	7.56127	0.99715	55	0.13446	a
Urea	6.80985	1.03591	56	0.13843	b
Alkaline-stabilized biosolids + urea	6.79322	0.9984	56	0.13342	b
Composted biosolids + urea	6.67992	0.91364	56	0.12209	b
Alkaline-stabilized biosolids	6.67811	0.8712	55	0.11747	b
Composted biosolids	6.25693	0.75367	55	0.10162	c
Unfertilized	6.06624	1.01316	27	0.19498	c

[††] Different letters within the “group” column represent significant differences at $p < 0.05$ based on Tukey’s test for pairwise comparison.

Table A.5.12. Tukey HSD pairwise comparison of means of growing season N_2O emission due to method of application (MA) of the fertilizers (biosolids and/or urea) in Ste-Anne-de-Bellevue (QC; 2018 and 2019), Truro (NS; 2017 to 2019), and Edmonton (AB; 2017 and 2018) sites at $\alpha = 0.05$.

Method of application	$\log(N_2O)$	std	n	se	[††]groups
Soil incorporated	7.01831	1.11148	195	0.07959	a
Surface spread	6.84889	1.07291	194	0.07703	b

[††] Different letters within the “group” column represent significant differences at $p < 0.05$ based on Tukey’s test for pairwise comparison.

Table A.5.13. Tukey HSD pairwise comparison of means of growing season N_2O emission due to annual effects (Year) across Ste-Anne-de-Bellevue (QC; 2018 and 2019), Truro (NS; 2017 to 2019), and Edmonton (AB; 2017 and 2018) sites where the respective soils were amended with biosolids and/or urea. Mean differences are significant at α = 0.05.

Year	log(N_2O)	std	N	se	††groups
2019	7.43548	1.00874	120	0.09209	a
2018	6.89677	0.97744	179	0.07306	b
2017	6.27577	1.09615	117	0.10134	c

†† Different letters within the "group" column represent significant differences at $p < 0.05$ based on Tukey's test for pairwise comparison.

Table A.5.14. The three-way ANOVA table for the effects of fertilizer N source (Fert), method of application (MA) and annual effects (Year) on N_2O emissions during the growing season in 2018 and 2019 at the Ste-Anne-de-Bellevue, QC site at α = 0.05.

Source	DF	Sum of Squares	Mean Square	F value	Pr(>F)	Significance
Fert	7	72.484	10.3548	20.334	3.99E-16	***
MA	1	0.196	0.1962	0.3852	0.536383	
Year	1	7.571	7.5714	14.8681	0.000216	***
Fert:MA	6	0.67	0.1116	0.2192	0.969715	
Fert:Year	7	7.09	1.0129	1.9891	0.06516	
MA:Year	1	1.525	1.5247	2.994	0.087	
Fert:MA:Year	6	1.448	0.2414	0.474	0.826023	
Residuals	90	45.831	0.5092			

Note: ***, indicates significant influence of effect ((factor or combination of factors)) on growing season N_2O emission at $p < 0.001$.

Table A.5.15. Tukey HSD pairwise comparison of means of growing season N_2O emission due to annual effects at the Ste-Anne-de-Bellevue, QC site where soil was amended with biosolids and/or urea in 2018 and 2019. Mean differences are significant at $\alpha = 0.05$.

Year	log(N_2O)	std	n	se	††groups
2019	7.79	1.00	60	0.13	a
2018	7.29	1.09	60	0.14	b

†† Different letters within the "group" column represent significant differences at p < 0.05 based on Tukey's test for pairwise comparison.

Table A.5.16. Tukey HSD pairwise comparison of means of growing season N_2O emission in 2018 and 2019 due to fertilizer (biosolids and/or urea) type applied at the Ste-Anne-de-Bellevue, QC site ($\alpha = 0.05$).

Fertilizer type	log(N_2O)	std	n	se	††groups
Digested biosolids	8.85	0.76	16	0.19	a
Digested biosolids + urea	8.47	0.53	16	0.13	a
Urea	7.62	0.99	16	0.25	b
Composted biosolids + urea	7.46	0.80	16	0.20	b
Alkaline-stabilized biosolids + urea	7.31	0.76	16	0.19	bc
Alkaline-stabilized biosolids	7.10	0.62	16	0.16	bc
Composted biosolids	6.54	0.57	16	0.14	c
Control	6.38	1.06	8	0.37	c

†† Different letters within the "group" column represent significant differences at $p < 0.05$ based on Tukey's test for pairwise comparison. Value are means ± standard deviation (n = 4).

Table A.5.17. The three-way ANOVA table for the effects of fertilizer N source (Fert), method of application (MA) and annual effects (Year) on growing season N_2O emission in 2018 and 2019 at the Truro site ($\alpha = 0.05$).

Source	DF	Sum of Square	Mean Square	F value	Pr(>F)	Significance
Fert	7	23.645	3.3778	6.7555	7.67E-07	***
Year	2	1.951	0.9753	1.9505	0.14631	
MA	1	0.381	0.381	0.7621	0.38428	
Fert:Year	14	16.52	1.18	2.36	0.00596	**
Fert:MA	6	1.596	0.2661	0.5321	0.78306	
Year:MA	2	1.004	0.5018	1.0037	0.36934	
Fert:Year:MA	12	4.583	0.3819	0.7638	0.68641	
Residuals	131	65.501	0.5			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on growing season N_2O emission at the p value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.5.18. Tukey HSD pairwise comparison of means of growing season N_2O emission in 2018 and 2019 due to fertilizer (biosolids and/or urea) type applied at the Truro, NS site ($\alpha = 0.05$).

Fertilizer type	log(N_2O)	std	n	se	[††]groups
Digested biosolids + urea	7.60	0.64	23	0.13	a
Digested biosolids	7.55	1.04	24	0.21	ab
Alkaline-stabilized biosolids + urea	7.10	0.97	24	0.20	abc
Alkaline-stabilized biosolids	7.06	0.64	23	0.13	abc
Urea	6.93	0.56	24	0.11	bc
Composted biosolids + urea	6.72	0.63	24	0.13	c
Composted biosolids	6.58	0.55	23	0.11	c
Control	6.57	0.63	11	0.19	c

[††] Different letters within the “group” column represent significant differences at $p < 0.05$ based on Tukey’s test for pairwise comparison. Value are means ± standard deviation (n = 4).

Table A.5.19. Tukey HSD pairwise comparison of means of logarithms of growing season N_2O emission (g N ha^{-1}) in 2018 and 2019 due to interaction of year and fertilizer (biosolids and/or urea) type applied on at the Truro, NS site ($\alpha = 0.05$).

Year × Fertilizer interaction	log(N_2O)	Std. Dev.	N	SE	††groups
2019:Digested biosolids	8.17	0.71	8	0.25	a
2019:Digested biosolids + urea	7.93	0.75	8	0.27	ab
2018:Alkaline-stabilized biosolids + urea	7.74	0.52	8	0.18	abc
2017:Digested biosolids + urea	7.57	0.48	8	0.17	abcd
2017:Digested biosolids	7.31	1.02	8	0.36	abcd
2018:Urea	7.27	0.48	8	0.17	abcd
2018:Digested biosolids + urea	7.26	0.55	7	0.21	abcd
2019:Alkaline-stabilized biosolids + urea	7.21	0.66	8	0.23	abcd
2018:Digested biosolids	7.17	1.15	8	0.41	abcd
2019:Alkaline-stabilized biosolids	7.11	0.70	8	0.25	abcd
2018:Alkaline-stabilized biosolids	7.05	0.59	8	0.21	abcd
2018:Control	7.01	0.66	4	0.33	abcd
2017:Alkaline-stabilized biosolids	7.00	0.72	7	0.27	abcd
2017:Urea	6.82	0.33	8	0.12	bcd
2018:Composted biosolids + urea	6.80	0.79	8	0.28	bcd
2018:Composted biosolids	6.75	0.66	8	0.23	bcd
2017:Composted biosolids + urea	6.73	0.71	8	0.25	bcd
2017:Control	6.72	0.43	3	0.25	bcd
2019:Urea	6.71	0.71	8	0.25	bcd
2017:Composted biosolids	6.65	0.43	7	0.16	bcd
2019:Composted biosolids + urea	6.62	0.42	8	0.15	cd
2017:Alkaline-stabilized biosolids + urea	6.36	1.13	8	0.40	d
2019:Composted biosolids	6.35	0.49	8	0.17	d
2019:Control	6.02	0.25	4	0.12	d

†† Different letters within the "group" column represent significant differences at $p < 0.05$ based on Tukey's test for pairwise comparison. Value are means ± standard deviation (n = 4).

Table A.5.20. The three-way ANOVA table for the effects of fertilizer N source (Fert), method of application (MA) and annual effects (Year) on growing season N_2O emission in 2018 and 2019 at the Truro, NS site ($\alpha = 0.05$).

Source	DF	Sum Sq	Mean Sq	F value	Pr(>F)	Significance
Fert	7	33.79	4.8272	9.8382	4.68E-09	***
Year	1	10.807	10.8071	22.0257	9.57E-06	***
MA	1	3.586	3.5861	7.3089	0.0082	**
Fert:Year	7	4.035	0.5765	1.1749	0.32514	
Fert:MA	6	3.726	0.6209	1.2655	0.28128	
Year:MA	1	0.006	0.0065	0.0132	0.90869	
Fert:Year:MA	6	2.332	0.3887	0.7921	0.57844	
Residuals	90	44.159	0.4907			

Note: $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), $p < 0.1$ (.), indicates significant influence of effect ((factor or combination of factors)) on growing season N_2O emission at the p value in the brackets. $p < 0.05$ (*) was the tested significance level for the main and interaction effects in this study.

Table A.5.21. Tukey HSD pairwise comparison of means of growing season N_2O emission in 2017 and 2018 due to fertilizer type (biosolids and/or urea) applied on a soil at the Edmonton, AB site ($\alpha = 0.05$).

Fertilizer type	log(flux)	std	N	se	††groups
Digested biosolids	6.95	1.21	16	0.30	a
Digested biosolids + urea	6.60	0.91	16	0.23	ab
Composted biosolids + urea	5.84	0.63	16	0.16	bc
Urea	5.82	0.83	16	0.21	c
Alkaline-stabilized biosolids + urea	5.82	0.44	16	0.11	c
Alkaline-stabilized biosolids	5.71	0.59	16	0.15	c
Composted biosolids	5.51	0.67	16	0.17	c
Control	5.06	0.68	8	0.24	c

†† Different letters within the “group” column represent significant differences at $p < 0.05$ based on Tukey’s test for pairwise comparison. Value are means ± standard deviation (n = 4).

Table A.5.22. Tukey HSD pairwise comparison of means of growing season N_2O emission due to year of fertilizer application at the Edmonton, AB site where soil was amended with biosolids and/or urea in 2017 and 2018. Mean differences are significant at $\alpha = 0.05$.

Year	log(flux)	std	N	se	†† groups
2018	6.27	0.74	60	0.10	a
2017	5.67	1.00	60	0.13	b

†† Different letters within the “group” column represent significant differences at $p < 0.05$ based on Tukey’s test for pairwise comparison. Value are means ± standard deviation (n = 4).

Table A.5.23. Tukey HSD pairwise comparison of means of growing season N_2O emission in 2017 and 2018 due to method of applying fertilizers (biosolids and/or urea) on a soil at the Edmonton, AB site at $\alpha = 0.05$.

Method of application	log(flux)	std	N	se	††groups
Soil incorporated	6.21	1.04	8	0.37	a
Surface spread	5.86	0.73	56	0.10	b

†† Different letters within the “group” column represent significant differences at $p < 0.05$ based on Tukey’s test for pairwise comparison. Value are means ± standard deviation (n = 4).

Table A.5.24. Error analysis between measured and DNDC-simulated N_2O emissions from 2017 to 2019 across the three sites (Edmonton, AB; Ste-Anne-de-Bellevue, QC; and Truro, NS).

Site	Amendment	Year	Measured (kg N ha^{-1})		Simulated (kg N ha^{-1})		M (kg N ha^{-1})	E (%)	$E_{95\%}$ (%)	RMSE (kg N ha^{-1})	$RMSE_{95\%}$ (kg N ha^{-1})
			Mean	**Std. Dev.**	**Mean**	**Std. Dev.**					
Edmonton	Alkaline-stabilized biosolids	2017	0.26	0.16	0.66	0.32	-0.40	-157.34	69.00	0.40	0.18
	Alkaline-stabilized biosolids	2018	0.46	0.23	0.58	0.21	-0.13	-27.96	57.15	0.13	0.26
	Alkaline-stabilized biosolids + Urea	2017	0.36	0.21	0.42	0.00	-0.05	-14.62	64.96	0.05	0.24
	Alkaline-stabilized biosolids + Urea	2018	0.37	0.11	0.33	0.00	0.04	10.41	32.22	0.04	0.12
	Composted biosolids	2017	0.29	0.23	0.48	0.17	-0.19	-64.65	87.30	0.19	0.25
	Composted biosolids	2018	0.31	0.13	0.35	0.08	-0.04	-14.30	47.38	0.04	0.15
	Composted biosolids + Urea	2017	0.35	0.21	0.33	0.14	0.02	6.52	68.89	0.02	0.24
	Composted biosolids + Urea	2018	0.45	0.19	0.28	0.07	0.17	38.80	48.12	0.17	0.22
	Unfertilized	2017	0.09	0.03	0.26	0.13	-0.17	-190.40	51.12	0.17	0.05
	Unfertilized	2018	0.29	0.02	0.16	0.05	0.13	45.42	13.42	0.13	0.04
	Digested biosolids	2017	1.65	1.41	1.65	0.59	0.00	0.18	95.68	0.00	1.58
	Digested biosolids	2018	1.73	1.40	1.22	0.20	0.50	29.19	91.05	0.50	1.57
	Digested biosolids + Urea	2017	0.77	0.96	1.26	0.65	-0.49	-62.97	139.58	0.49	1.08
	Digested biosolids + Urea	2018	1.41	1.26	0.81	0.44	0.60	42.50	100.70	0.60	1.42
	Urea	2017	0.24	0.22	0.74	0.26	-0.51	-213.67	104.68	0.51	0.25
	Urea	2018	0.68	0.35	0.41	0.07	0.27	39.40	57.57	0.27	0.39
Ste-Anne-de-Bellevue	Alkaline-stabilized biosolids	2018	1.09	0.75	1.92	0.18	-0.83	-75.79	77.22	0.83	0.84
	Alkaline-stabilized biosolids	2019	1.76	0.71	2.18	0.51	-0.42	-23.69	45.10	0.42	0.79
	Alkaline-stabilized biosolids + Urea	2018	1.13	0.72	1.73	0.03	-0.60	-52.43	71.15	0.60	0.81
	Alkaline-stabilized biosolids + Urea	2019	2.77	1.72	1.91	0.04	0.86	31.14	70.02	0.86	1.94
	Composted biosolids	2018	0.53	0.20	1.31	0.26	-0.77	-145.33	41.65	0.77	0.22
	Composted biosolids	2019	1.09	0.61	1.28	0.34	-0.19	-17.49	63.13	0.19	0.69
	Composted biosolids + Urea	2018	2.00	1.39	1.66	0.07	0.34	17.03	78.12	0.34	1.56
	Composted biosolids + Urea	2019	2.44	1.33	1.52	0.00	0.92	37.64	61.42	0.92	1.50

Site	**Amendment**	**Year**	**Measured** (kg N ha^{-1})		**Simulated** (kg N ha^{-1})		M (kg N ha^{-1})	E (%)	E$_{95\%}$ (%)	RMSE (kg N ha^{-1})	RMSE$_{95\%}$ (kg N ha^{-1})
			Mean	**Std. Dev.**	**Mean**	**Std. Dev.**					
	Unfertilized	2018	0.36	0.35	0.51	0.16	-0.15	-42.42	155.10	0.15	0.56
	Unfertilized	2019	1.37	0.44	0.51	0.18	0.85	62.45	51.41	0.85	0.70
	Digested biosolids	2018	5.93	4.39	6.86	2.04	-0.93	-15.68	83.32	0.93	4.94
	Digested biosolids	2019	11.58	5.12	6.92	1.68	4.66	40.23	49.77	4.66	5.76
	Digested biosolids + Urea	2018	5.39	2.97	5.64	0.32	-0.25	-4.57	62.04	0.25	3.34
	Digested biosolids + Urea	2019	5.52	3.52	4.39	0.25	1.13	20.54	71.72	1.13	3.96
	Urea	2018	2.81	1.64	2.47	0.29	0.34	12.02	65.82	0.34	1.85
	Urea	2019	3.42	4.13	2.21	0.92	1.21	35.36	135.73	1.21	4.64
Truro	Alkaline-stabilized biosolids	2017	1.16	0.89	2.55	1.95	-1.39	-119.14	86.49	1.39	1.01
	Alkaline-stabilized biosolids	2018	1.32	0.66	3.27	2.88	-1.95	-147.64	56.15	1.95	0.74
	Alkaline-stabilized biosolids	2019	1.52	1.12	3.25	3.76	-1.73	-114.17	83.02	1.73	1.26
	Alkaline-stabilized biosolids + Urea	2017	0.91	0.79	1.56	0.06	-0.64	-70.44	96.77	0.64	0.88
	Alkaline-stabilized biosolids + Urea	2018	2.57	1.27	1.54	0.01	1.02	39.83	55.86	1.02	1.43
	Alkaline-stabilized biosolids + Urea	2019	1.62	1.02	0.57	0.00	1.05	64.59	70.79	1.05	1.15
	Composted biosolids	2017	0.72	0.42	0.88	0.26	-0.16	-22.10	65.26	0.16	0.47
	Composted biosolids	2018	1.00	0.50	1.03	0.33	-0.03	-3.23	55.91	0.03	0.56
	Composted biosolids	2019	0.62	0.24	0.51	0.22	0.11	17.58	44.00	0.11	0.27
	Composted biosolids + Urea	2017	1.01	0.60	1.03	0.00	-0.02	-1.94	66.40	0.02	0.67
	Composted biosolids + Urea	2018	1.20	1.08	1.03	0.01	0.17	13.93	100.90	0.17	1.21
	Composted biosolids + Urea	2019	0.81	0.30	0.34	0.01	0.46	57.29	41.74	0.46	0.34
	Unfertilized	2017	0.65	0.56	1.20	0.71	-0.55	-84.31	136.40	0.55	0.89
	Unfertilized	2018	1.29	0.76	0.98	0.53	0.31	24.36	93.18	0.31	1.20
	Unfertilized	2019	0.42	0.11	0.68	0.49	-0.25	-60.28	42.60	0.25	0.18
	Digested biosolids	2017	2.22	2.00	4.67	2.59	-2.45	-110.11	101.38	2.45	2.26
	Digested biosolids	2018	2.12	1.96	5.73	4.78	-3.61	-170.19	103.74	3.61	2.20
	Digested biosolids	2019	4.42	3.14	5.64	7.21	-1.22	-27.72	80.01	1.22	3.53
	Digested biosolids + Urea	2017	2.13	0.94	1.89	0.03	0.24	11.16	49.59	0.24	1.05

Site	**Amendment**	**Year**	**Measured** (kg N ha^{-1})		**Simulated** (kg N ha^{-1})		M (kg N ha^{-1})	E (%)	$E_{95\%}$ (%)	RMSE (kg N ha^{-1})	$RMSE_{95\%}$ (kg N ha^{-1})
			Mean	**Std. Dev.**	**Mean**	**Std. Dev.**					
	Digested biosolids + Urea	2018	1.43	1.13	1.89	0.03	-0.46	-32.42	88.98	0.46	1.27
	Digested biosolids + Urea	2019	3.47	2.46	0.57	0.00	2.90	83.61	79.75	2.90	2.77
	Urea	2017	0.96	0.32	1.52	0.54	-0.56	-58.66	38.01	0.56	0.36
	Urea	2018	1.59	0.82	1.29	0.46	0.30	19.00	57.77	0.30	0.92
	Urea	2019	1.04	0.83	0.87	0.67	0.17	16.49	90.53	0.17	0.94

Table A.5.25. Statistical analyses of the model performance in simulating cumulative nitrous oxide emissions during the growing season from 2017 to 2019 for the calibration and validation stages across the three sites (Edmonton, AB; Ste-Anne-de-Bellevue, QC; and Truro, NS). Model total error is not significant for $RMSE < RMSE_{95}$. Model bias is not significant for $E < E_{95}$.

Site	Dataset	M (kg N ha^{-1})	E (%)	$E_{95\%}$ (%)	RMSE (kg N ha^{-1})	$RMSE_{95\%}$ (kg N ha^{-1})
Ste-Anne-de-Bellevue	Calibration	0.23	-16.1	84.8	1.16	2.36
	Validation	0.52	-9.2	82.1	1.08	2.77
Truro	Calibration	0.17	9.1	90.1	0.60	1.26
	Validation	0.44	9.0	95.9	0.83	1.68
Edmonton	Calibration	-0.01	-11.0	96.4	0.13	0.41
	Validation	0.07	-17.1	96.0	0.27	0.55

Table A.5.26. Simulation input parameters and variables ranked according to the Morris sensitivity index (μ*) with respect to simulated cumulative N_2O emissions in Ste-Anne-de-Bellevue (2018 and 2019), Truro (2017–2019), and Edmonton (2017 and 2018). The standard deviation (**σ**) indicates whether linear or nonlinear effects exist due to interactions with other inputs. The Pearson correlation coefficient (r) is an alternative measure of the strength of the association between the input and the N_2O emissions.

Ste-Anne-de-Bellevue					Truro					Edmonton				
†Parameter	**μ**	**μ***	**σ**	**r**	**†Parameter**	**μ**	**μ***	**σ**	**r**	**†Parameter**	**μ**	**μ***	**σ**	**r**
Soil pH	-8.61	8.61	3.05	-0.62	Soil pH	2.59	2.59	0.43	0.51	Clay fraction	-0.81	0.81	0.12	-0.47
Manure C/N	-5.00	5.00	2.16	-0.41	Humads frac.	-2.30	2.30	0.72	-0.33	Acc. Temp.	-0.27	0.31	0.21	-0.15
Manure Org. N	3.08	3.08	0.89	0.12	Bulk density	1.27	1.27	0.42	0.28	Soil pH	-0.30	0.30	0.07	-0.08
Acc. temp.	2.20	2.20	0.98	0.10	Precipitation	1.16	1.16	0.25	0.37	Top layer SOC	0.25	0.25	0.11	0.09
Clay fraction	-1.69	1.69	0.48	-0.20	Top layer SOC	0.91	0.91	0.32	0.18	Min. air temp	0.20	0.20	0.11	0.16
Precipitation	1.37	1.37	0.31	0.27	Max. air temp	0.74	0.74	0.24	0.09	Precipitation	0.20	0.20	0.12	0.22
Field capacity	1.12	1.12	0.38	0.01	Min. air temp	0.67	0.67	0.19	0.36	Max. air temp	0.17	0.18	0.15	0.16
Fert. depth	-0.47	0.78	0.87	-0.13	Fert. depth	-0.23	0.23	0.21	-0.05	Porosity	-0.14	0.14	0.08	0.12
Urea	0.76	0.76	0.23	0.08	Field capacity	0.21	0.21	0.08	0.16	Humads frac.	0.12	0.12	0.03	-0.06
Top layer SOC	0.68	0.68	0.45	0.07	Manure depth	-0.15	0.17	0.18	-0.03	Hydro cond.	0.11	0.11	0.08	-0.07
Manure depth	0.24	0.67	0.95	0.20	Solar rad.	0.15	0.15	0.06	-0.05	Manure depth	-0.10	0.10	0.04	-0.03
Humads frac.	0.46	0.46	0.36	-0.20	Acc. temp	-0.03	0.15	0.20	0.15	Field capacity	-0.08	0.09	0.07	0.06

Ste-Anne-de-Bellevue					Truro					Edmonton				
†Parameter	**μ**	**μ***	**σ**	**r**	**†Parameter**	**μ**	**μ***	**σ**	**r**	**†Parameter**	**μ**	**μ***	**σ**	**r**
Max. yield	-0.44	0.44	0.25	0.04	Porosity	-0.12	0.12	0.08	0.07	Max. yield	-0.07	0.07	0.03	0.05
Hydro cond.	0.43	0.43	0.33	0.09	Max. yield	0.07	0.11	0.13	0.23	Bulk density	0.05	0.05	0.03	-0.06
Grain C/N	0.36	0.36	0.20	0.09	Water req.	-0.05	0.11	0.11	-0.11	Manure C/N	-0.05	0.05	0.02	-0.14
Bulk density	0.30	0.30	0.21	0.03	Clay fraction	0.09	0.11	0.10	-0.14	Manure pH	-0.05	0.05	0.01	0.05
Min. air temp.	-0.28	0.29	0.19	0.08	Manure C/N	0.08	0.09	0.08	-0.30	Grain C/N	0.03	0.03	0.02	0.18
Max. air temp.	-0.17	0.25	0.24	0.12	Manure Org. N	0.04	0.07	0.10	0.25	Manure Org. N	0.03	0.03	0.01	-0.06
Crop res. left	0.13	0.15	0.18	-0.01	Grain C/N	0.00	0.06	0.08	0.37	Litter fraction	-0.02	0.02	0.02	0.00
Solar rad.	-0.08	0.14	0.18	0.05	Litter frac.	0.04	0.04	0.06	-0.11	Opt. temp.	0.00	0.01	0.02	-0.28
Wilting point	0.08	0.13	0.21	0.02	Opt. temp.	-0.01	0.04	0.05	-0.02	Wilting point	0.00	0.01	0.02	0.12
Porosity	-0.04	0.06	0.06	-0.14	Wilting point	-0.01	0.03	0.04	-0.05	Water req.	0.00	0.01	0.01	-0.06
Water req.	-0.02	0.05	0.07	0.06	Manure PH	0.01	0.03	0.05	-0.04	Solar rad.	0.00	0.00	0.01	0.12
Manure pH	-0.04	0.04	0.08	0.03	Urea	-0.01	0.03	0.04	0.03	Fert. depth	0.00	0.00	0.01	-0.12
Litter frac.	-0.03	0.03	0.03	0.01	Crop res. left	0.01	0.01	0.01	0.11	Crop res. left	0.00	0.00	0.00	0.09
Opt. temp.	0.02	0.02	0.02	-0.12	Hydro cond.	0.00	0.00	0.00	0.03	Urea	0.00	0.00	0.00	-0.02

Note: †Fert. Depth = fertilizer depth, Acc. Temp. = temperature degree days, Manure Org. N = biosolids N, Manure C/N = C to N ratio in biosolid, Top SOC = soil organic carbon in topsoil, Water req. = crop water requirement, Crop res. Left = crop residue amount left on the field after harvest, Solar rad. = solar radiation, Opt. temp. = optimum crop temperature, Hydro cond. = soil hydraulic conductivity, Litter frac. = fraction of litter organic carbon in soil, Humads frac. = fraction of active humus in soil organic carbon based on measurements made in several field experiments (Li et al., 1994), Max./min air temp = maximum/minimum daily air temperature.

μ = the mean of the distribution of the elementary effects (EE), which assesses the overall influence of the input on the simulated output; μ* = Morris sensitivity index, which is the estimate of the mean of the distribution of the absolute values of the elementary effects; and σ = the standard deviation of the distribution of the EE, which estimates the collective effects of the input due to non-linearity and/or interactions with other inputs.

5.8.3. Appendix C: Equations used for DNDC Error Analysis

$$r = \frac{\sum_{i=1}^{n}(O_i - \bar{O})(P_i - \bar{P})}{\sqrt{\sum_{i=1}^{n}(O_i - \bar{O})^2}\sqrt{\sum_{i=1}^{n}(P_i - \bar{P})^2}} \qquad \text{(Eq. A.5.1)}$$

r is Pearson's correlation coefficient, O_i is the ith measured value, $\bar{O}$ is the average measured value, P_i is the ith simulated value, and $\bar{P}$ is the average simulated value.

$$F\ value = \frac{(n-2) \times r^2}{(1 - r^2)} \qquad \text{(Eq. A 5.2)}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(O_i - P_i)^2}{n}} \qquad \text{(Eq. A 5.3)}$$

$$RMSE_{95\%} = \sqrt{\frac{\sum_{i=1}^{n}\left(SE_i \times t_{m,95}\right)^2}{n}} \qquad \text{(Eq. A 5.4)}$$

$RMSE_{95\%}$ is the root mean-square error (*RMSE*) at 95% confidence interval, SE_i is the standard error in the ith measurement, $t_{m,95}$ is the Student's t value for m replicates and 95% probability (P-value of 0.95), and n is the number of measurements.

$$E\ (\%) = \frac{100}{\bar{O}} \times \frac{\sum_{i=1}^{n}(O_i - P_i)}{n} \qquad \text{(Eq. A 5.5)}$$

$$E_{95\%}(\%) = \frac{100}{\bar{O}}\frac{\sum_{i=1}^{n}\left(SE_i \times t_{m,95}\right)}{n} \qquad \text{(Eq. A 5.6)}$$

$E_{95\%}$ is the relative error (*E*) at 95% confidence interval.

5.8.4. Appendix D: Comparison between Measured and Estimated N_2O Emissions during the Growing Season

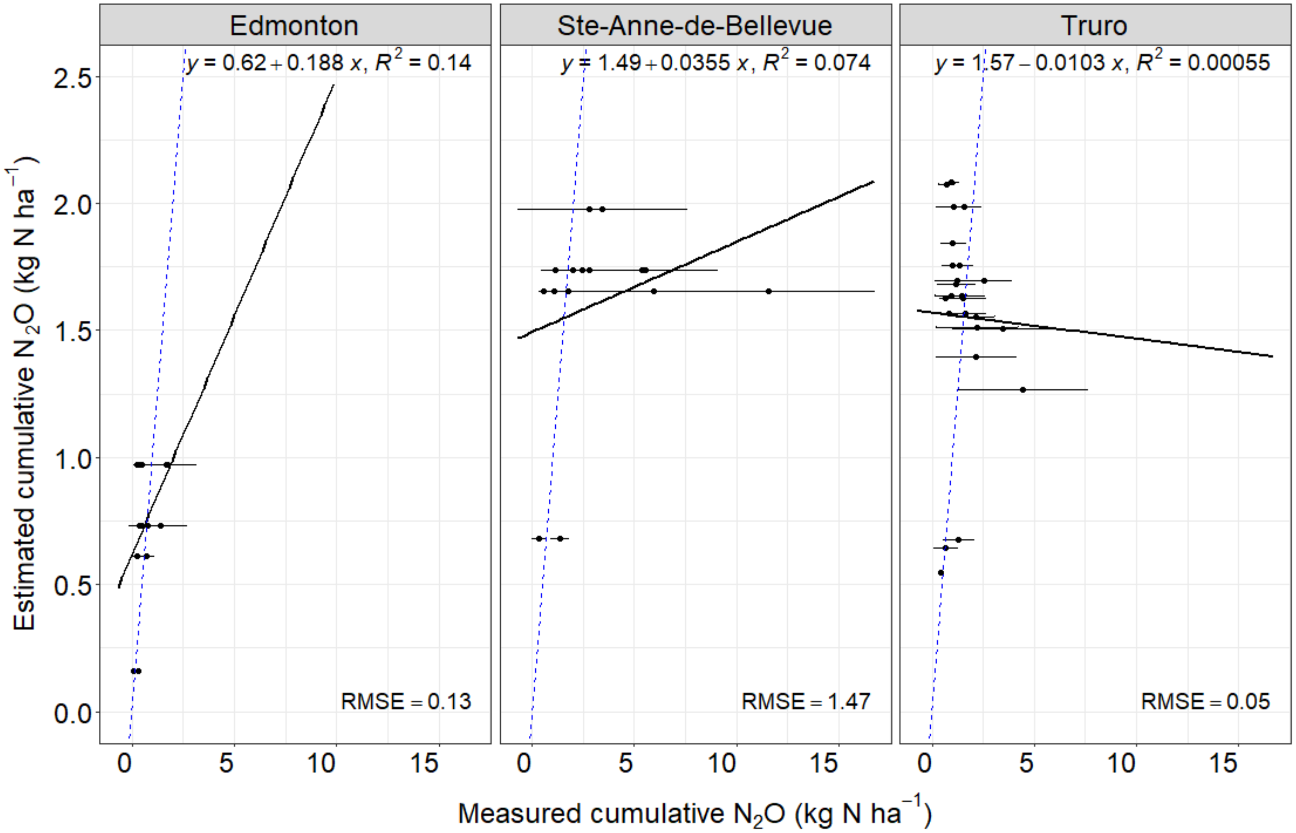

Figure A 5.1. Comparison between measured mean and standard deviation (n=4) values (X-axis) and IPCC Tier 1-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from a field in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

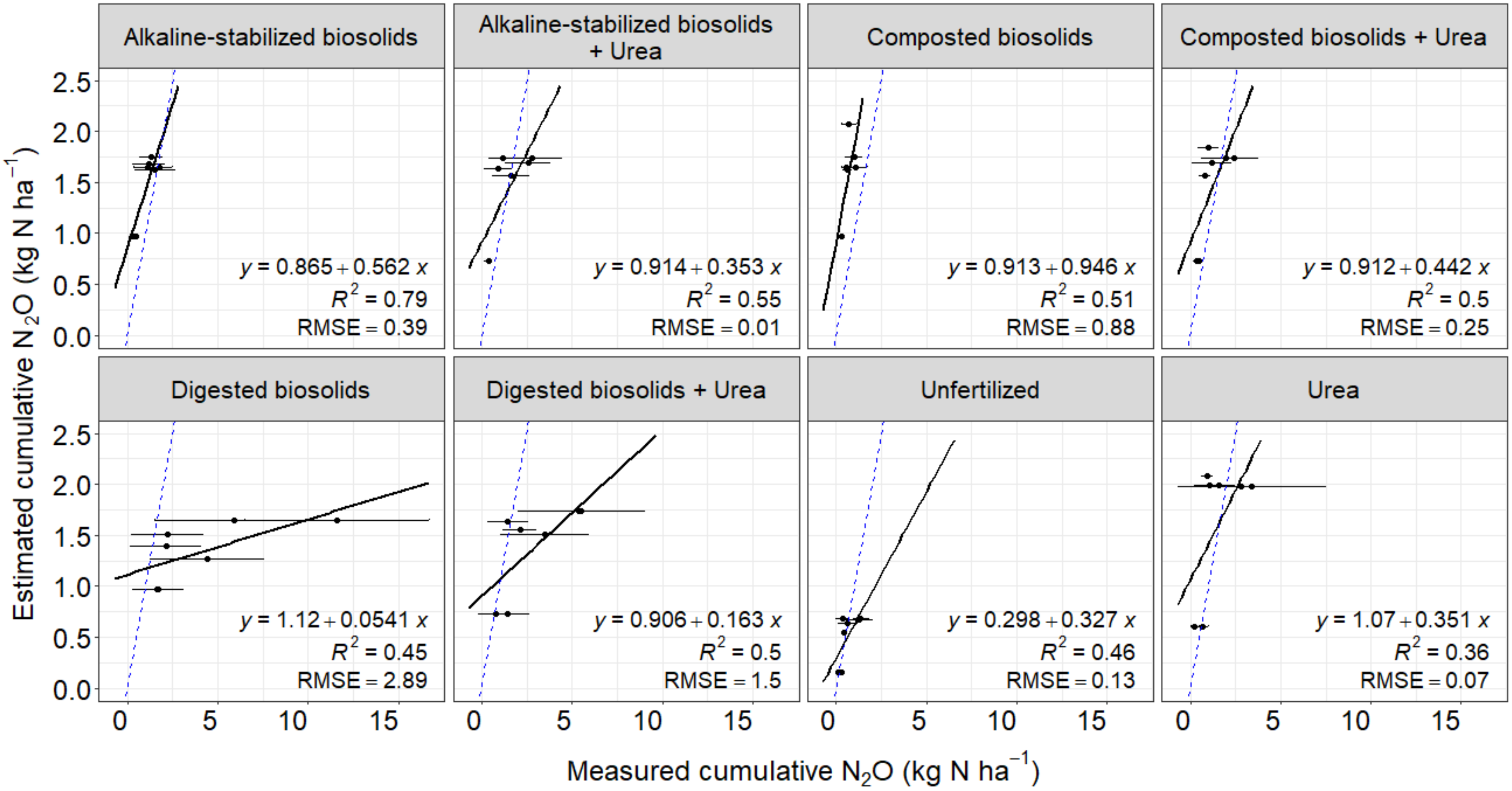

Figure A 5.2. Comparison between measured mean and standard deviation (n=4) values (X-axis) and IPCC Tier 1-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from all treatments across fields in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

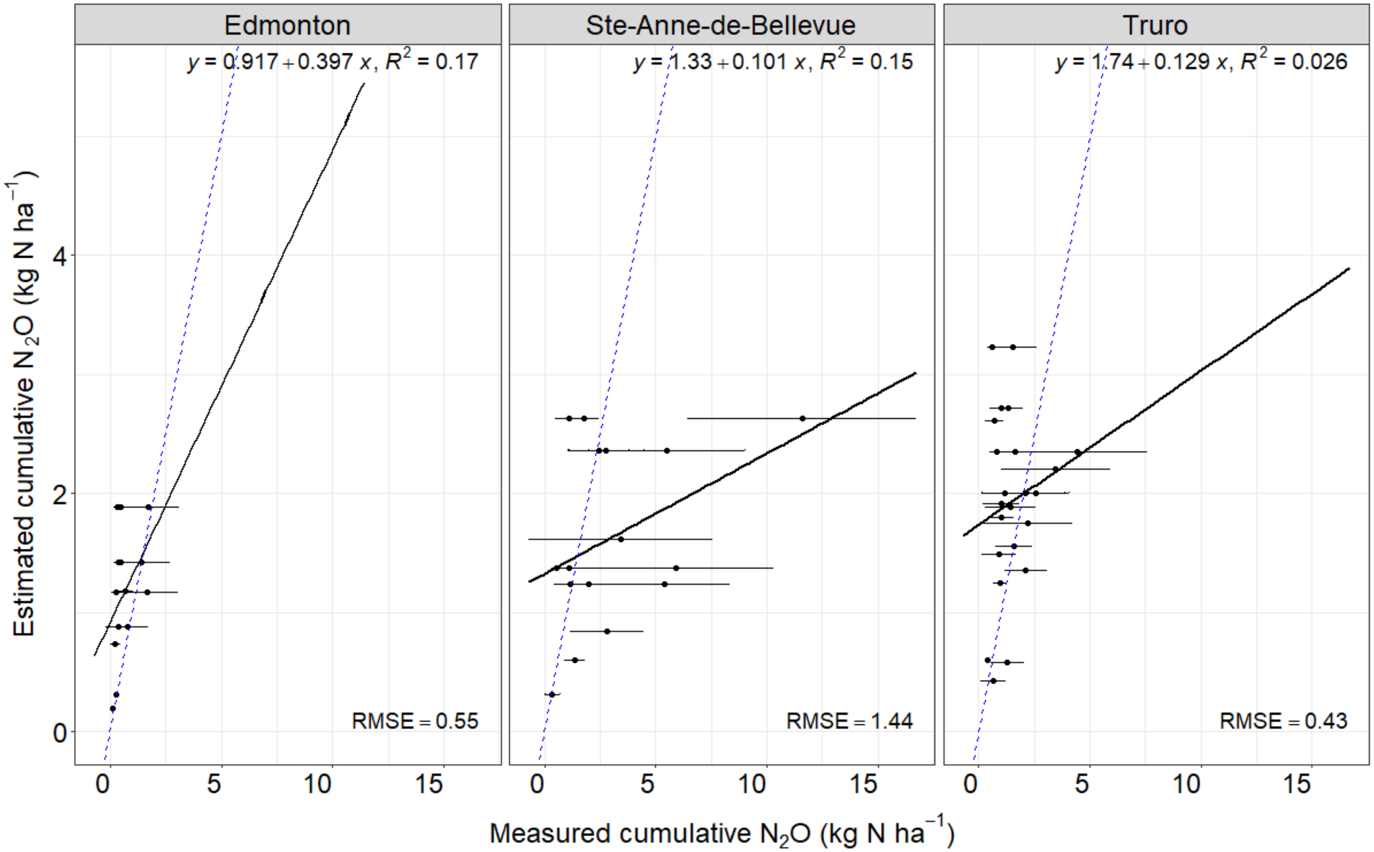

Figure A 5.3. Comparison between measured mean and standard deviation (n=4) values (X-axis) and IPCC Tier 2 (2008)-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from a field in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

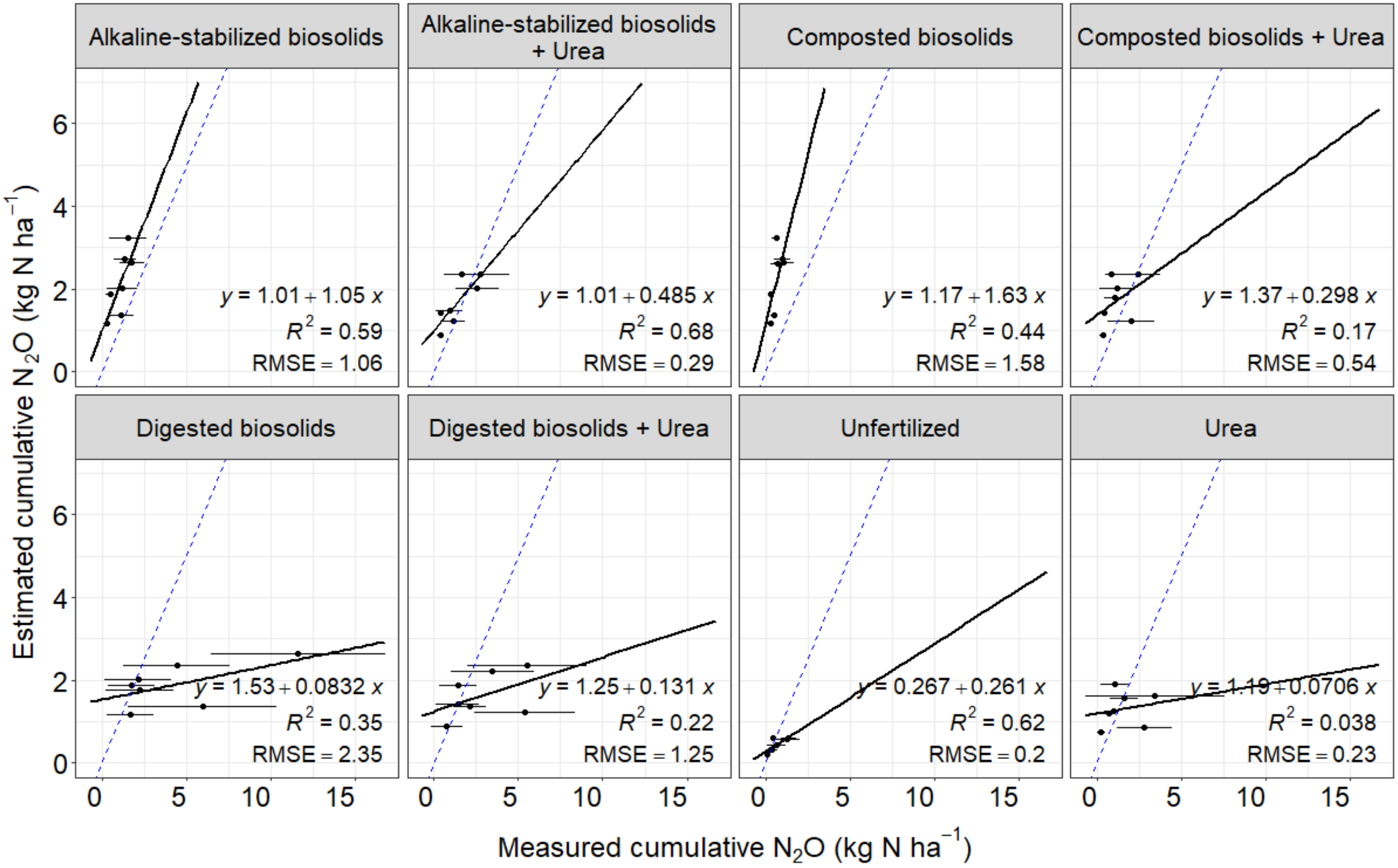

Figure A 5.4. Comparison between measured mean and standard deviation (n=4) values (X-axis) and IPCC Tier 2 (2008)-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from all treatments across fields in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019.

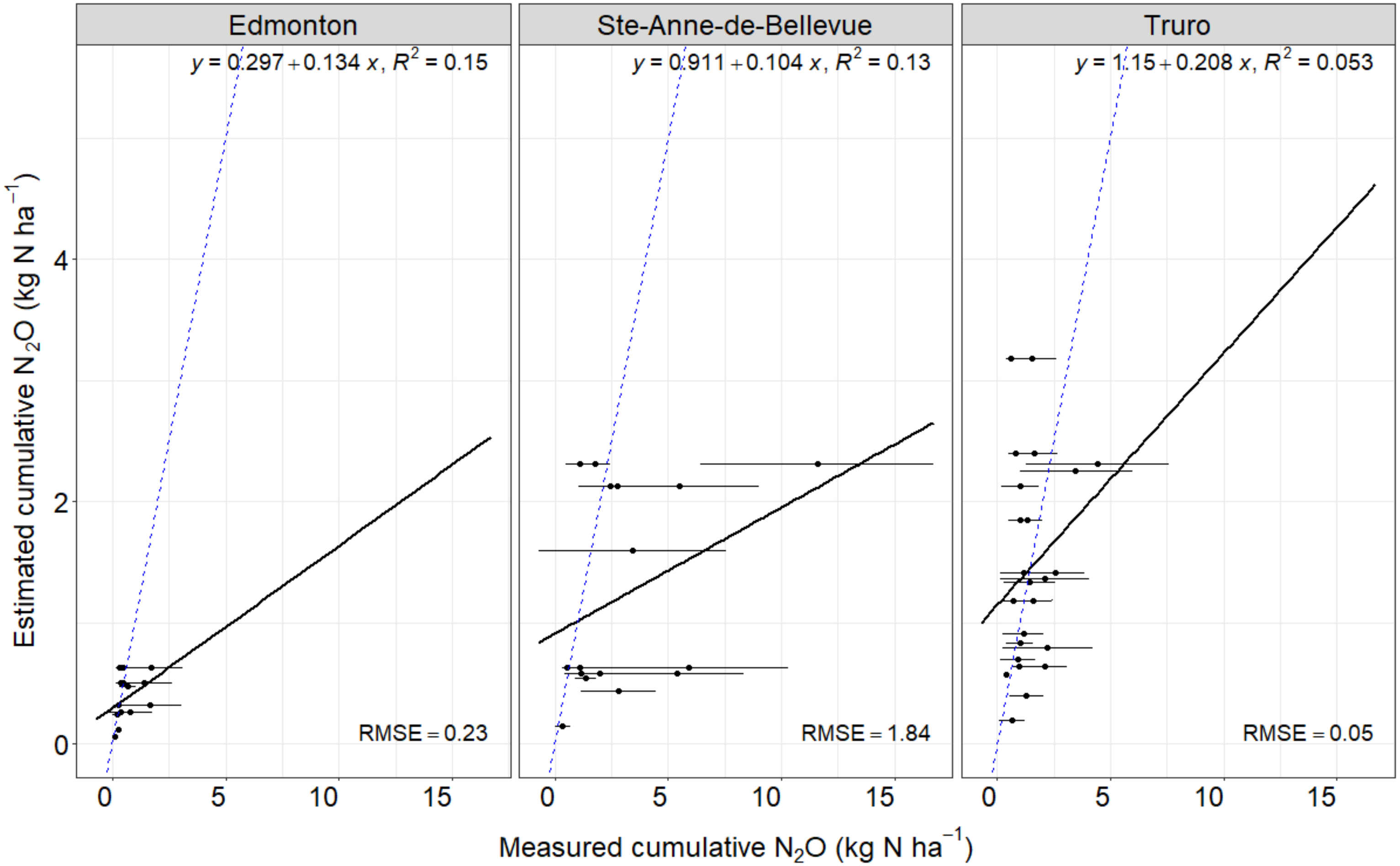

Figure A 5.5. Comparison between measured mean and standard deviation (n=4) values (X-axis) and IPCC Tier 2 (2018)-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from a field in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

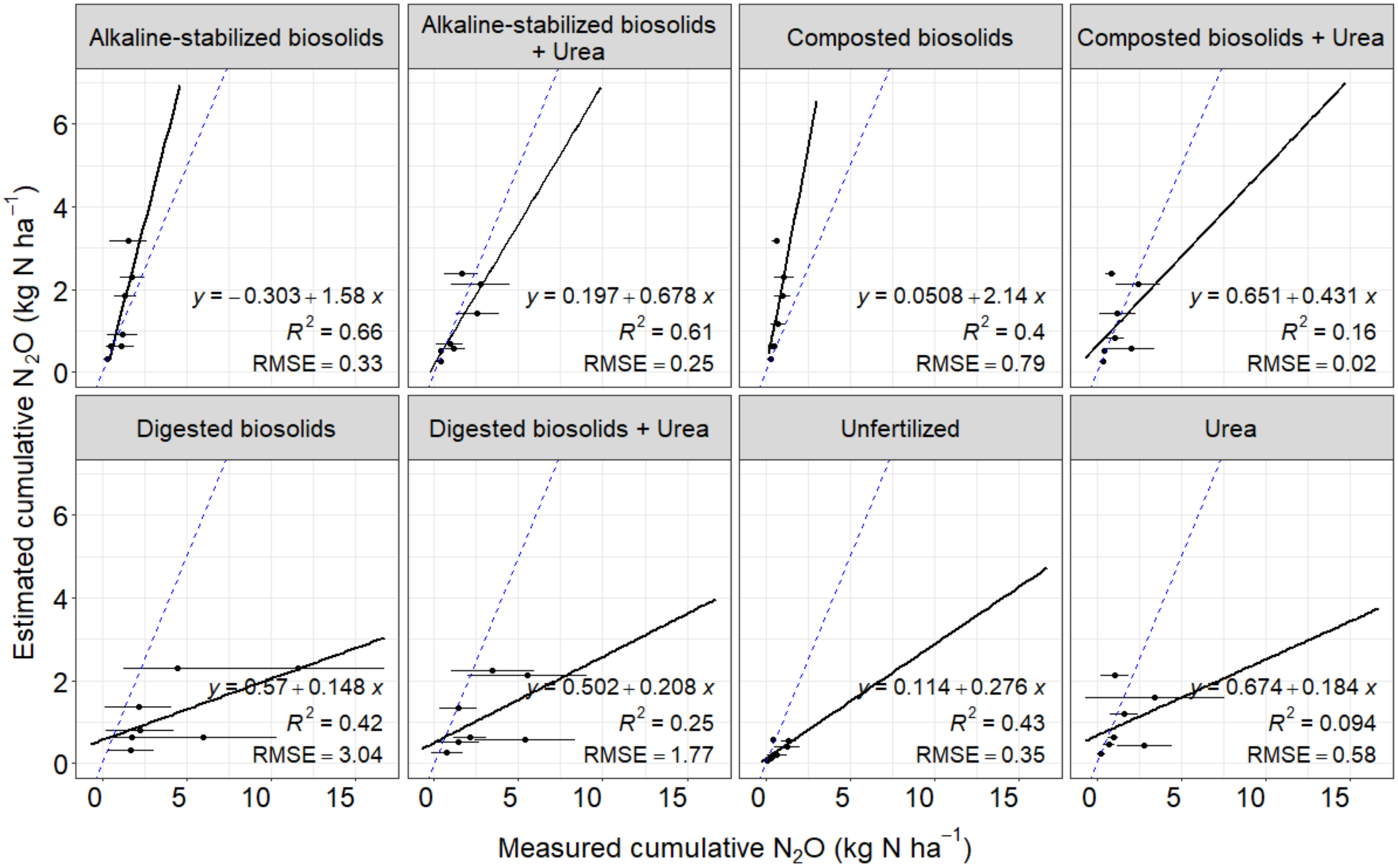

Figure A 5.6. Comparison between measured mean and standard deviation (n=4) values (X-axis) and IPCC Tier 2 (2018)-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from all treatments across fields in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

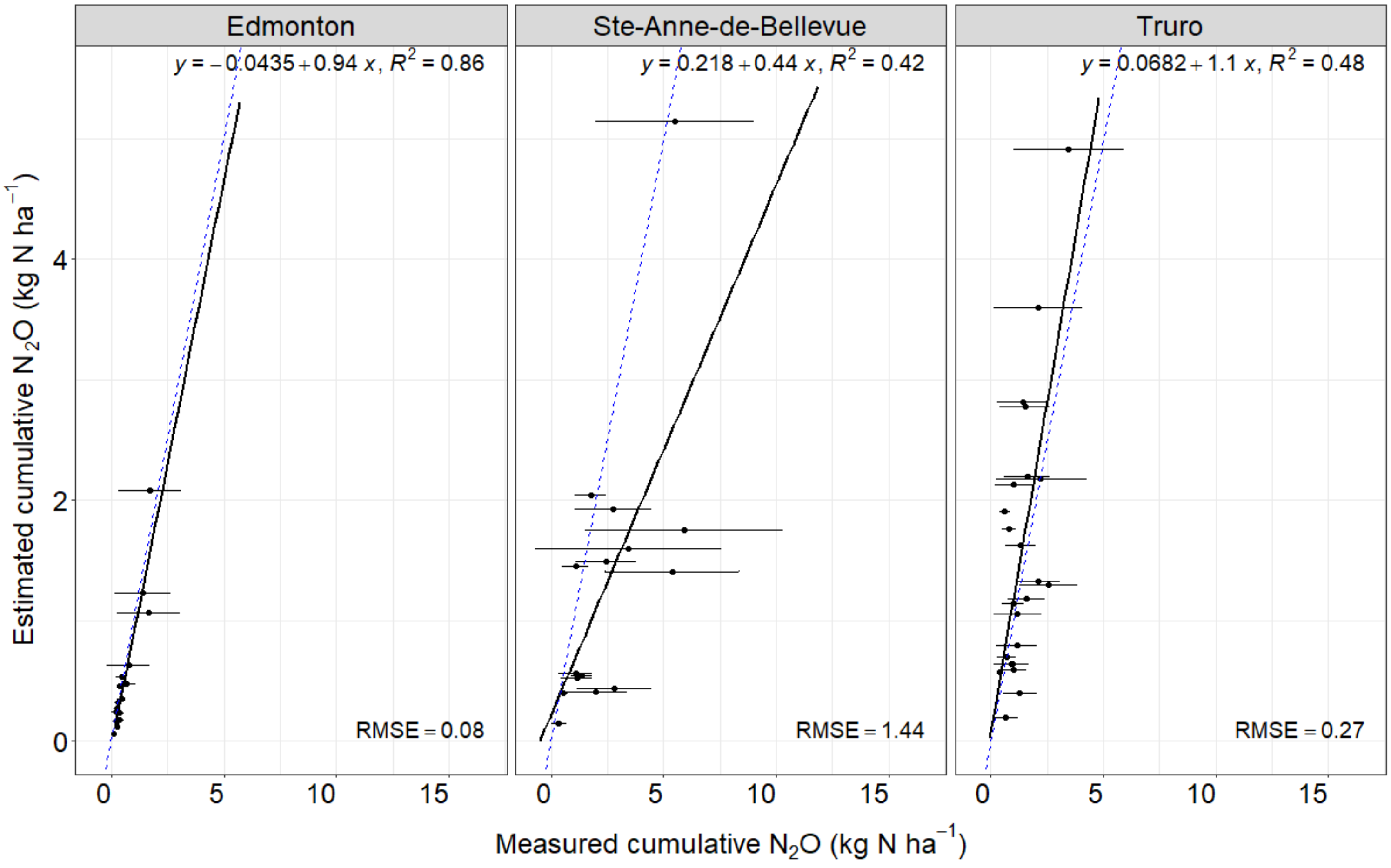

Figure A 5.7. Comparison between measured mean and standard deviation (n=4) values (X-axis) and biosolids-corrected IPCC Tier 2 (2018)-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from a field in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

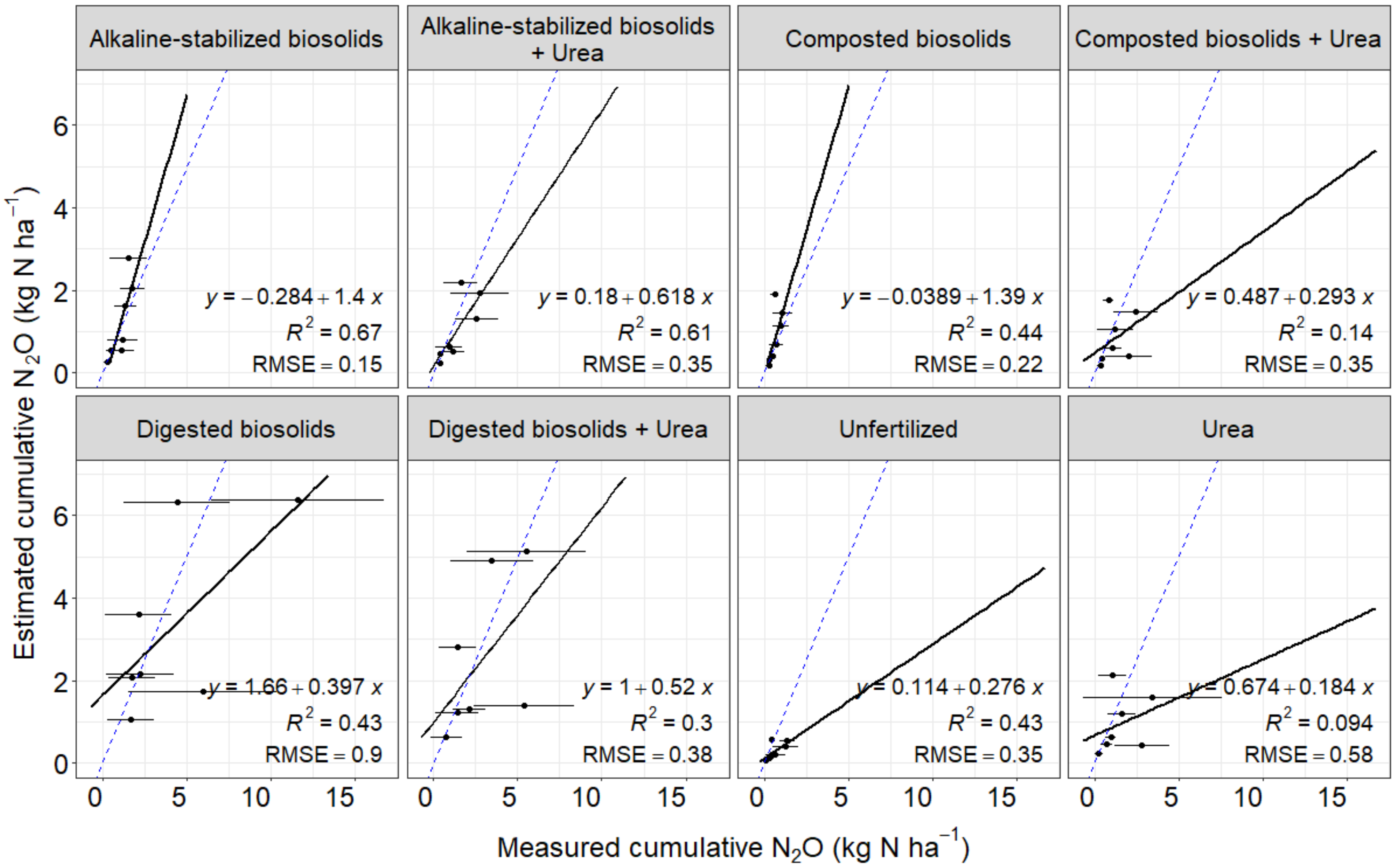

Figure A 5.8. Comparison between measured mean and standard deviation (n=4) values (X-axis) and biosolids-corrected IPCC Tier 2 (2018)-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from all treatments across fields in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

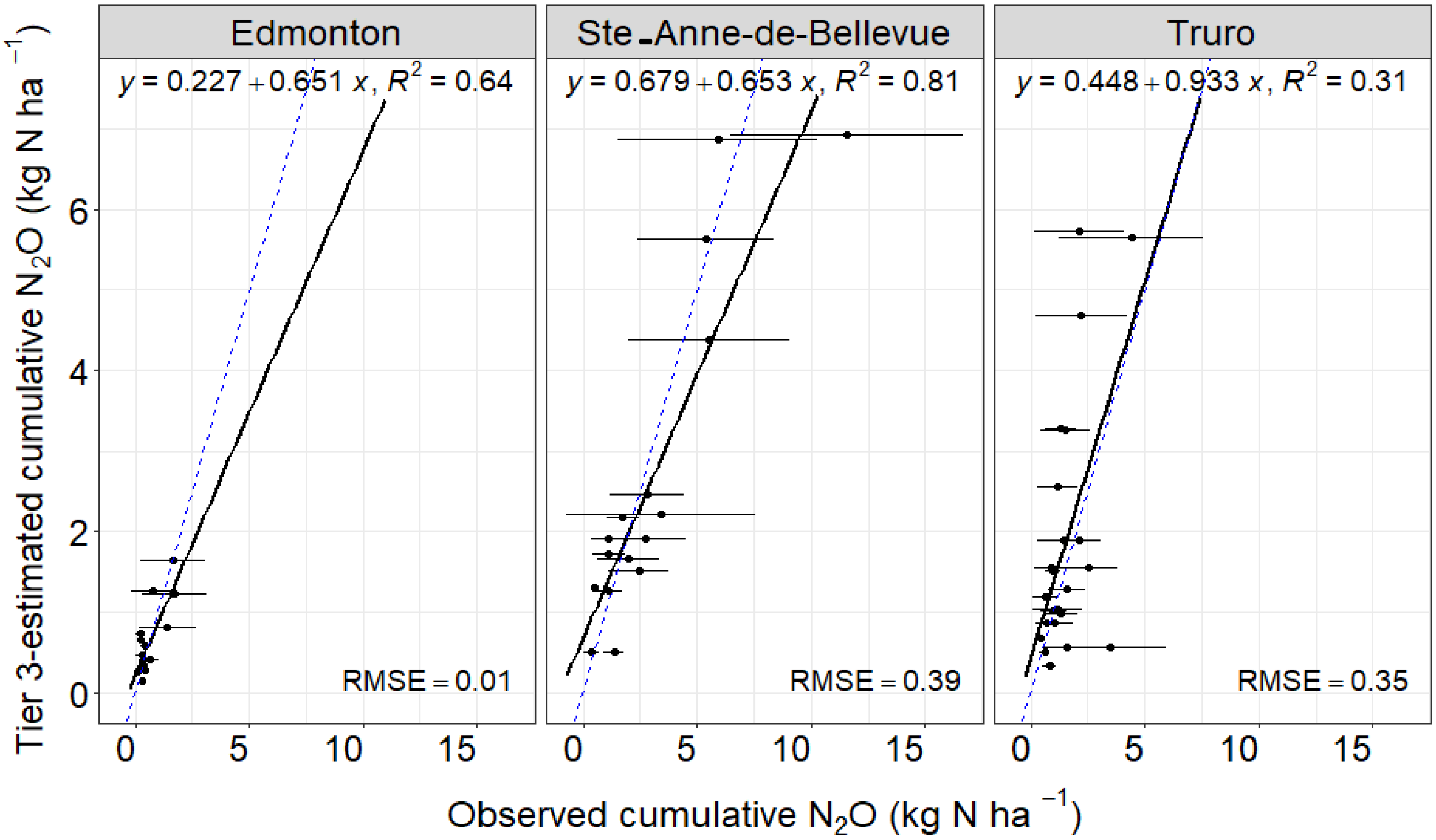

Figure A 5.9. Comparison between measured mean and standard deviation (n=4) values (X-axis) and IPCC Tier 3 (DNDC)-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from a field in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

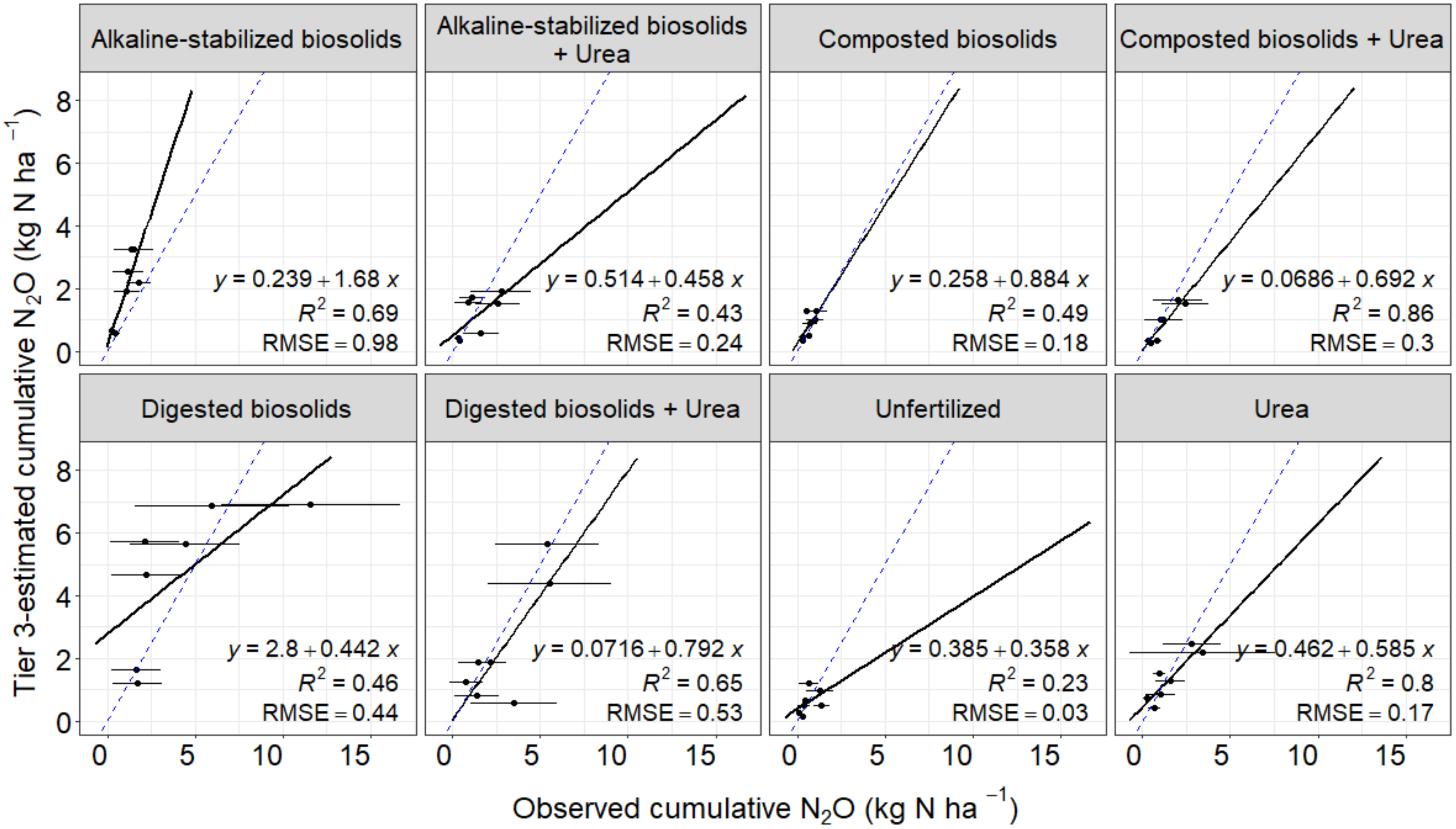

Figure A 5.10. Comparison between measured mean and standard deviation (n=4) values (X-axis) and IPCC Tier 3 (DNDC)-estimated mean values (Y-axis) of nitrous oxide emissions during the growing season from all treatments across fields in Edmonton, Ste-Anne-de-Bellevue, and Truro amended with biosolids and/or urea between 2017 and 2019. The black lines represent the trend lines, while the blue dashed lines represent the 1:1 line.

Chapter 6. Summary and Conclusions

6.1. Summary

The overarching goal of this research was to measure emissions, generate emissions factors, and refine models of biosolids-induced GHG emissions through laboratory incubation and field studies, to improve the federal government's accounting and reporting of greenhouse gas (GHG) emissions associated with the agricultural use of municipal biosolids. With more stringent regulations on municipal organic waste disposal, including bans on landfilling, and increasing quantities of biosolids generated in the last decade, a greater number of farmers use this material as a source of nutrients for crop production. A preliminary literature review indicated that there was limited empirical data on the contributions to national GHG emissions from the agricultural use of municipal biosolids. This lack of data made it difficult to generate needed national estimates of biosolids-induced GHG emissions. My research identified three problems associated with the lack of concise estimates as follows: (1) current methods for estimating C and N dynamics resulting from land-application of biosolids are based on simplified linear models, which do not represent the complex biochemical reactions and interactions with soil moisture, nutrients, and plant growth; (2) a lack of empirical data to understand C and N dynamics in cropping systems amended with municipal biosolids under specific management practices in major Canadian agricultural regions; and (3) a lack of country-specific or regional activity data and emission factors for land-applied biosolids for use in compiling a national GHG inventory.

A complete C and N budget for biosolids-amended soils should include the relevant GHG emissions. Compiling a complete and accurate GHG national inventory therefore involves a system-level C and N budget for all biosolids-amended agroecosystems across Canada, using hourly or daily time increments throughout the growing season of each year. However, owing to the practical challenges (technical, labour, and economic) associated with a detailed accounting of the entire C and N flows in such agroecosystems, my thesis combined a laboratory study and three-year field experiments in three locations to parameterize mathematical models that were used to quantify the relevant agricultural GHG emissions. The mathematical models used in this thesis follow a three-tier protocol as recommended in the guidelines of the Intergovernmental Panel on Climate Change (IPCC) for accounting and reporting national GHG fluxes to the United Nations Framework Convention on Climate Change. Briefly, estimating N_2O emissions involves multiplying an emission factor, which represents a fraction of the applied fertilizer N lost as N_2O, by the activity data, which is the anthropogenic activity during a given period. The quality and spatial resolution of the data used to derive these emission factors increases from Tier 1 to 3 as follows: Tier 1 uses aggregated, internationally-derived emission factors for estimating national and subnational N_2O emissions, neglecting management practices other than applied N amount; Tier 2 uses region- or country-specific emission factors to estimate disaggregated GHG emissions; and Tier 3 uses site-specific data and/or process-based models to estimate disaggregated GHG emissions. The data generated using the IPCC Tier 2 or 3 approaches in this research will help to improve the quality of the national GHG emissions inventory by Environment and Climate Change Canada (ECCC).

The Tier 2 approach used in this research was adapted with correction factors to improve its accuracy when used to estimate biosolids-induced soil N_2O emissions. Precipitation was the main environmental variable responsible for the differences in N_2O emissions among the sites. The physico-chemical characteristics of the different N sources were not considered as most of the commonly reported fertilizer parameters (e.g., pH and NO_3^- content) do not exert as much influence on N_2O emissions as the amount of N applied. Also, using additional model parameters requires additional data to develop and use the Tier 2 approach (e.g., the physico-chemical characteristics of each type of biosolids), especially when it is deployed on the ecodistrict scale. The simplicity of the Tier 2 methodology makes it more amenable to Canada's current GHG inventory framework than Tier 3 methods, however, it is underparameterized for evaluating the effects of N_2O mitigation strategies.

The Tier 3 approach is generally more accurate than the Tier 2 approach but is more complex. Tier 3 approaches involving process-based models like the Denitrification and Decomposition model (DNDC) are data intensive, require expertise to deploy for national GHG emissions estimates, and are computationally expensive. However, process-based models can be validated using data from- or combined with chamber, eddy covariance, and other empirical methods to improve estimates of sub-daily, daily, and even multi-year GHG emissions on field, landscape, or even regional and national scales. Despite the limitations of these modelling approaches, these tools are generally useful for estimating GHG emissions. The knowledge and tools described in this thesis have improved the baseline estimates of GHG emissions from biosolids-amended agricultural soils in Canada.

Beyond providing an approach to estimate biosolids-induced emissions, this research provides other useful information. Chapter 3 of this thesis provides an understanding of biosolids degradation kinetics and nitrogen release in a laboratory incubation study which lasted for 92 days. This study is important as biosolids application rates and provincial regulations depend, in part, on the C and N mineralization rates which are highly variable and depend on the pH and proportions of C and N in the different type of organic compounds in biosolids. Meanwhile, the pH, labile C and N pools, and C/N ratio of the biosolids depend on the treatment methods used in their production. For example, anaerobic digestion of sewage sludge to produce biosolids mineralizes some organic N but cannot support nitrification processes; composting increases the C/N ratio because of the addition of carbonaceous materials and the volatilization of nitrogen; and alkaline stabilization increases the pH of biosolids due to the addition of alkaline material and reduces N content due its volatilization under thermal treatment. Therefore, setting similar regulations for the use of all biosolids types, using a specific emission factor for all types of biosolids, or using the same emission factor for biosolids as for urea or manure misrepresents the characteristics of each type of biosolids and the attendant consequences of their application to soils.

The estimated kinetic parameters associated with biosolids degradation also aid the parameterization of DNDC to simulate C and N cycling in biosolids-amended soils. DNDC models the decomposition process using first-order kinetics, where the rate constants depend primarily on C and N supply, moisture, and temperature. As such, DNDC can be tested beyond the scope of this work to explore the effects of different agronomic practices and climatic conditions. However, given the current discrepancies between the observed emissions and those simulated with DNDC, it is evident that DNDC should be improved, as the uncertainties in the simulated data could compound over spatial and temporal scales.

The empirical data generated by this research also provide additional useful information to compute the life-cycle environmental impacts associated with the use of each type of biosolids. The empirical studies conducted across the three ecozones included in this project showed that soils amended with mesophilic anaerobically digested biosolids emitted the most N_2O, while composted biosolids sequestered the most carbon in soils. This work provides some of the information needed to calculate the overall environmental impacts, including the potential GHG offsets if biosolids were to be used instead of fertilizer as a source of plant nutrients.

Farm profit is an important factor which should be considered when assessing the suitability of biosolids as a source of organic nutrients. That is, since biosolids are often inexpensive or free, how will yields and net profit be affected over the long and short terms if biosolids are used instead of other fertilizers? Due to the lower N content by dry mass of biosolids (N ranges from 1 to 71 g kg^{-1}) compared to urea and anhydrous ammonia, between 6.5 to over 460 times more biosolids must be applied to equal the N content of urea (46-0-0) and 11.5 to 820 times for Anhydrous NH_3, which contains 82% N. This means additional transport, storage, and application cost, as well as time duration of land-application. However, there are numerous agronomic benefits associated with the use of biosolids. Improving soil pH, SOC, and soil biota are few of the benefits while also recycling nutrients. The use of biosolids is a way of recycling nutrients as opposed, for example, to the mining and depletion of non-renewable global phosphorus reserves to produce mineral fertilizers. Understandably, the wage of farm workers is associated to the time and effort required to apply the biosolids compared to mineral fertilizers. However, the time and effort required to apply biosolids depend on the nature of the biosolids and the equipment used. For instance, when dewatered, mesophilic anaerobically digested biosolids are more difficult to handle using conventional manure spreaders in comparison to alkaline-stabilized or composted biosolids, or even mineral fertilizers. As such, specialized machinery may be required to spread the biosolids, and the attendant capital expenses must be considered. A well-informed choice between biosolids versus mineral fertilizers should also consider the broader environmental and social impacts associated with their production and use, both on and off-farm, such as GHG emissions and the distortion of natural landscape during phosphate and potash mining.

In summary, farmers may adopt management practices that are convenient and secure the highest profit margin without necessarily considering their broader environmental and social costs. While some farmers will consider long-term strategies that preserve soil quality, others may adopt practices that maximize short-term profits. Either way, the implications of intensive N application, whether as mineral fertilizers or organic amendments, require policies that guarantee decent profits for farmers using biosolids, while also ensuring minimal adverse effect on the environment. Therefore, a quantitative analysis of the agronomic and economic costs of using different types of biosolids as compared to conventional nutrient sources is required to inform farmers and policymakers when considering these choices. This factor, the holistic impact on the economy, environment, and society, is the key determinant of the future of biosolids in Canadian agriculture.

6.2. Conclusion

Canada intends to improve its GHG emissions inventory, including using higher-tier IPCC methodologies (e.g., Tiers 2 and 3) and reporting biosolids-induced N_2O emissions, which were previously unaccounted for due to scarcity of data. In this thesis, N_2O emissions were measured using non-steady-state manual chambers from land application of mesophilic anaerobically digested, alkaline-stabilized, and composted biosolids in three ecozones (Atlantic maritime, mixedwood plains, and prairie) to generate Tier 2 and 3 emission factors. In addition to the 2019-refined Tier 1 method, Canada’s current (2008) and updated (2018) Tier 2 methods (called uncorrected Canada-specific Tier 2 (2008 and 2018) methods in this study) and the Tier 3 method (using DNDC) were compared with measured GHG emissions from biosolids-amended soils. While all three principal GHGs were present in the field measurements, only N_2O emissions were analyzed across the three sites because CH_4 emissions were not significant, and (biogenic) CO_2

emissions are not reported in GHG inventories. Results from this study showed that N_2O emissions varied with biosolids type and site-specific factors such as precipitation and soil texture, pH, and organic carbon. Mean N_2O emissions from land-applied mesophilic anaerobically digested biosolids were higher than those of composted and alkaline-stabilized biosolids across the three sites.

Three objectives were addressed in order to generate the GHG emission factors associated with agricultural use of municipal biosolids and thereby improve the federal government's accounting for and reporting GHG emissions. The first objective was to assess the kinetics of C decomposition and N mineralization in a loam soil amended with three biosolids and incubated under different soil moisture conditions. To achieve this objective, an incubation experiment was conducted to assess the rate of C and N mineralization in biosolids-amended soil under either sub-optimal or optimal moisture conditions. It was found that moisture deficiency limited organic carbon decomposition and that the biosolids decomposed at different rates: mesophilic anaerobically digested and alkaline-stabilized biosolids decomposed more rapidly than composted biosolids. Four fitted models estimated different rates of C degradation but were consistent in the amounts of mineralizable C and N predicted under both moisture conditions. We concluded that (1) soil moisture influenced GHG emissions from biosolids-amended soil but biosolids type did not, and (2) any of the four models that were evaluated can be used to simulate biosolids degradation in the loam soil used in the study. This study provided rate constants associated with the degradation of biosolids which can be used to parameterize DNDC to accurately simulate C and N dynamics in a loam soil amended with these three types of biosolids.

The second objective was to evaluate the capability of the DNDC model to simulate C and N dynamics in a Canadian agroecosystem amended with municipal biosolids. To achieve this objective, DNDC was calibrated and validated using daily and cumulative GHG emissions, crop yield, soil organic C, and soil mineral N data from three consecutive growing seasons in Ste-Anne-de-Bellevue, Quebec. The DNDC model accurately represented C and N transformations in the soil relative to the measured values. Daily and cumulative CO_2 and N_2O emissions over the growing season, as well as above-ground corn biomass yields, were more variable with composted biosolids, which decompose more slowly than the alkaline-stabilized and mesophilic anaerobically digested biosolids. We concluded that the DNDC model is suitable for estimating N_2O emissions following biosolids application and recommended that future model improvements consider the disaggregation of decomposition processes between biosolids and soils to improve the simulation of CO_2 emissions.

The third objective was to compare estimates of N_2O fluxes from agricultural soils amended with biosolids in Canada’s mixedwood plains (humid continental climate), Atlantic maritime (maritime climate), and prairies (semi-arid climate) ecozones using Tier 1, Tier 2 (Canadian), and Tier 3 (DNDC) methodologies. Then, we intended to recommend the most amendable and accurate approach for the accounting of N_2O emissions from land-applied biosolids in the national GHG inventory. To achieve this objective, estimates of growing season N_2O emissions from IPCC Tier 1, 2, and 3 approaches were compared to measurements from biosolids-amended soils in Quebec (mixedwood plains), Nova Scotia (Atlantic maritime), and Alberta (prairies). The RMSE and R^2 values between the observed and estimated N_2O emissions showed that the Tier 1 and uncorrected Canada-specific Tier 2 (2008 and 2018) approaches produced larger errors than the Tier 3 (DNDC) approach. However, owing to the required data and expertise, the Tier 3 method was considered impractical for GHG inventory purposes in the near term (2 to 3 years). To this end, the Tier 2 (2018) method was successfully adapted to estimate biosolids-induced N_2O emissions using specific correction factors, resulting in the so-called biosolids-corrected Tier 2 (2018) method described in this study. We conclude that the biosolids-corrected Tier 2 (2018) method could be used in the near term to estimate nationwide biosolids-induced N_2O emissions until the Tier 3 approach is fully developed and integrated into the Canadian GHG inventory framework. This study helps to highlight the mitigation potential of composted biosolids towards reducing N_2O emissions and evaluates practical approaches for generally estimating these emissions from Canadian farmlands given the data limitations.

This research makes original contributions to knowledge (see Pages ix to x) as follows:

- provides a suite of empirical data on GHG emissions from land-application of municipal biosolids generated across Canada;
- differentiates the N_2O mitigation potential of land-applied composted biosolids relative to the mesophilic anaerobically digested and alkaline-stabilized biosolids;
- tests DNDC for simulating C and N dynamics in biosolids-amended agroecosystems in three different Canadian ecozones; and
- develops IPCC Tier 2 correction factors to report nationwide emissions of N_2O from land-application of biosolids from 1990 to date.

6.3. Recommendations for future research

The data produced from this research provide a baseline to quantify and advance the scientific understanding of biosolids-related GHG emissions within the Canadian context. However, there is room for future research.

1. Validate the biosolids-corrected Tier 2 (2018) method for estimating biosolids-induced N_2O emissions in the national inventory.

2. Improve SOC modelling for biosolids-amended soils by disaggregating soil and biosolids organic carbon decomposition into two separate but interlinked mechanisms.
3. Calibrate and validate DNDC to estimate C and N dynamics in soils amended with biosolids in the Pacific Maritime ecozone of Canada.
4. Use the calibrated and validated DNDC to simulate the effects of projected climate change scenarios on N_2O emissions and crop yields. Scenarios of interest across the three test sites include: a) +1.5 to 3°C increase in mean temperature during the typical growing season, b) ±10% changes in mean annual precipitation, c) drought conditions over short or extended periods, and d) flooding conditions.
5. Conduct a life-cycle assessment of the three biosolids from the production of sludge at a municipal WWTP to land-application of the biosolids and all the associated impacts.
6. Quantitative analysis of the sustainability of using each of the biosolids on Canadian farmlands. The scope should encompass a holistic analysis using urea and livestock manure as references to conduct a relative: (1) cost-benefit analysis, (2) social implications to farmer and consumers, and (3) environmental impact.

Chapter 7. General References

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