CHAPTER ONE

Novel Practices and Smart Technologies to Maximize the Nitrogen Fertilizer Value of Manure for Crop Production in Cold Humid Temperate Regions

Joann K. Whalen^{*,1}, Ben W. Thomas[†], Mehdi Sharifi[‡]

*Department of Natural Resource Sciences, Macdonald Campus of McGill University, Ste-Anne-de-Bellevue, QC, Canada

[†]Agriculture and Agri-Food Canada, Agassiz Research and Development Centre, Agassiz, BC, Canada [‡]Agriculture and Agri-Food Canada, Summerland Research and Development Centre, Summerland, BC, Canada

¹Corresponding author: e-mail address: joann.whalen@mcgill.ca

Contents

1.	. Introduction	2
2.	Nitrogen Composition of Manure	8
	2.1 Physico-Chemical Characteristics of Manure	8
	2.2 Nitrogen Content of Manure	9
3.	. Soil Conditions and Agronomic Practices Influencing the Nitrogen Fertilizer	
	Value of Manure in Cold Humid Temperate Regions	16
	3.1 Soil Conditions Affecting the Plant-Available N Concentration	
	in Manure-Amended Soil	19
	3.2 Agronomic Practices Affecting the Plant-Available N Concentration in	
	Manure-Amended Soil	31
4.	. Methods to Predict the Nitrogen Fertilizer Value of Manure in Cold Humid	
	Temperate Regions	43
	4.1 Laboratory-Based Soil Tests to Estimate the N Fertilizer Value of Manure	43
	4.2 Field-Based Soil Tests to Estimate the N Fertilizer Value of Manure	50
	4.3 Plant-Based Tests to Estimate the N Fertilizer Value of Manure	54
	4.4 Models to Estimate the N Fertilizer Value of Manure	59
5.	. Smart Systems to Conserve the Nitrogen Fertilizer Value of Manure in Cold	
	Humid Temperate Regions	60
	5.1 Smart Technologies for Conserving N Fertilizer Value During Manure	
	Storage	61
	5.2 Smart Systems for Maximizing N Fertilizer Value of Field-Applied Manur	e 66

1

58
,0
59
59
35

Abstract

Manure applications support crop production, maintain soil fertility, and recycle locally available nutrients in cold humid temperate regions, consistent with the principles of sustainable agriculture. Manure may be an excellent nitrogen (N) fertilizer for crops if it provides plant-available N as ammonium (NH₄⁺) and from organic N mineralization in synchrony with crop N demands. The objective of this review was to describe the N fertilizer value of manure based on its physico-chemical characteristics, its transformation into plant-available N as modulated by soil abiotic and biotic conditions, and agronomic practices related to manure handling, storage, and land application. Methods of measuring the plant-available N released from manure and estimating its N fertilizer value are presented. Finally, we discuss how sensor networks can be used to optimize the N fertilizer value of manure. Our concept includes (1) a smart approach to conserve manure N in livestock production facilities and storages and (2) a smart system for precise spatio-temporal application of manure to deliver plant-available N in synchrony with crop N demands. Sensor networks that monitor real-time changes in ammonia (NH₃) and oxygen concentrations should help to minimize losses of plant-available N during manure storage. On-the-go technologies for variable rate manure application will be linked with multispectral crop data and geospatial soil inputs to make a smart decision system that can maximize the N fertilizer value of manure in cold humid temperate regions.

1. INTRODUCTION

Manure from livestock production operations is an inexpensive, locally available N fertilizer that is typically recycled when applied to agricultural land. Globally, the 92 Tg of N from animal manure that was applied to farmland in 2000 was similar to the 83 Tg of N input from inorganic fertilizers $(1 \text{ Tg} = 10^{12} \text{ g}; \text{ Bouwman et al., 2013})$. There is an excess of manure in many regions around the world, and the amount of manure available for land application is increasing. Rising global demand for livestock products, coupled with a trend to include more protein-rich grain in the diets of ruminant and monogastric animals, will supply agricultural land with approximately 130–153 Tg of N from animal manure by 2050, whereas the N input from inorganic fertilizers is estimated at 83–109 Tg of N in the same period (Bouwman et al., 2013). There is a pressing need to improve manure handling, storage, and land application practices to ensure that future N inputs from animal manure will support crop production efficiently, to reduce our reliance on inorganic N fertilizers.

Since animal manure tends to be wet, odorous, and bulky, it is expensive to transport and is generally applied to agricultural soils within 20–30 km of the livestock production facility (Whalen and Chang, 2001). Soil receiving repeated manure applications generally have high fertility, however repeated application of excess manure in the long-term can build up the soil N supply in excess of crop N requirements, and may exceed the capacity of soil to retain manure N (Sharifi et al., 2011). At this point, the manure-amended soil is likely to release excess nutrients into the environment, with undesirable consequences for adjacent ecosystems. Declining water quality in coastal and inland water bodies is reported in areas where animal manure was discharged from livestock production facilities to rivers (Strokal et al., 2016) and in watersheds where farmland has high or excessively high soil test phosphorus levels due to long-term, repeated manure applications (Sharpley, 2016; Sharpley et al., 2011).

In cold humid temperate regions, the phosphorus legacy of farms is a particular concern because (1) higher precipitation than evapotranspiration means that a significant amount of water and soluble ions, including orthophosphate, are lost from fields through drainage, and (2) the water discharge pattern includes peak events related to snowmelt and heavy rainfall events, which releases high water volumes with sufficient energy to dislodge phosphorus-rich sediments and transport them via overland flow and subsurface drainage into streams and rivers. Furthermore, the growing season in cold humid temperate regions is limited to warmer months (generally from May to October) and vegetative growth slows or stops during colder periods in the spring, fall, and winter. Low biological demand for phosphorus during colder months, especially in annually cropped soils that are bare of vegetation, increases the risk that orthophosphate released continually through chemical solubilization and biological mineralization reactions will be lost from soil.

Nitrogen loss from manure-amended soils in cold humid temperate regions is responsible for water and air pollution. In Canada, approximately 80% of the total N load in surface water is attributed to agriculture, and reactive N species such as NH_4^+ , nitrite (NO_2^-) , NO_3^- , and dissolved organic N compounds contribute to the eutrophication of aquatic systems (Chambers et al., 2001). Runoff and subsurface drainage water from manured soils and livestock production facilities contain an appreciable total N load, and NO_3^- leaching through the vadose zone to aquifers that supply drinking water has

well-documented consequences for public health (Rasouli et al., 2014). Considerable amounts of manure N are lost in the gaseous N products: NH₃ (g), nitrous oxide (N₂O), and dinitrogen (N₂). For example, a regional analysis of manure N stocks in Canada reported that 26% of total manure N, on average, was volatilized as NH₃ (g) during storage and land application (Yang et al., 2011). On mixed livestock farms in central Scotland, the mean N₂O (g) fluxes from animal barns (5038 μ g N₂O-N m⁻² h⁻¹), manure heaps (10,828 μ g N₂O-N m⁻² h⁻¹), and feeding areas (2539 μ g N₂O-N m⁻² h⁻¹) were orders of magnitude higher than the 0–160 μ g N₂O-N m⁻² h⁻¹ emitted from arable land and pastures (Levy et al., 2017).

Guidelines and regulations can be enacted to reduce the environmental risks associated with N surpluses from manure applications in cold humid temperate regions. In some jurisdictions, environmental legislation set limits on the permissible manure application rates and restricts the spreading period when manure can be applied during the year (e.g., between April 1 and October 1 in Quebec, Canada; Government of Quebec, 2017). In addition, the distribution of technical factsheets promoting better management practices, voluntary environmental farm plans, and agricultural subsidies for modernizing farm operations are examples of government-led and producer-led incentives to control N pollution from livestock manure (Rasouli et al., 2014). The recommendations of these programs are guided by science-based evidence that manure is a valuable N source and should be applied as part of an integrated nutrient management program to support crop production (Fig. 1).

Nitrogen fertilizer recommendations are estimated from the relationship between inorganic N fertilizer inputs and crop yield response. Inorganic N fertilizers increase the mineral N (NH_4^+ and NO_3^-) concentration in soil



How much crop N is acquired from each source?

N fertilizer value of manure = % of crop N needs met by manure N input

Fig. 1 A rational manure application program considers manure as one of several sources of plant-available N for crop production.

solution due to chemical reactions (e.g., anhydrous ammonia (NH₃) reaction with H⁺, dissolution of soluble calcium ammonium nitrate) and biological reactions (e.g., urea solubilization and hydrolysis to NH4 ⁺ and carbon dioxide, CO₂). Furthermore, NH₄⁺ is subject to biological transformations by ammonia oxidizers and nitrifiers, which produces NO₃⁻, an ion that is susceptible to loss through abiotic and biotic pathways. The NH4 + and NO₃⁻ forms represent the plant-available N that can be absorbed by crop roots. Soil reactions and climate conditions modulating the plant-available N supply to crops are determined in field-based fertilizer trials located in multiple site-years (Nelson et al., 1985). This information is required to develop crop-specific N fertilizer recommendations that consider the N use efficiency of inorganic N fertilizers, based on the proportion of added N that was recovered in the crop. In addition, fertilizer trials provide insight into the appropriate source, rate, placement, and application time for inorganic N fertilizer. These principles for rational use of inorganic N fertilizers, further described by the International Plant Nutrition Institute (2012), are designed to achieve high N use efficiency and meet crop yield targets.

Since N fertilizer recommendations were developed for inorganic N fertilizers, it is necessary to estimate the N fertilizer value for manure, by predicting its contribution to the plant-available N supply for crops. There are several challenges to determine the N fertilizer value of manure. Manure has diverse physico-chemical characteristics, since it may be solid (e.g., animal excreta mixed with plant-based bedding, referred to as farmyard manure), semi-solid material that contains 25% total solids (wet basis), a slurry with 10-12% total solids (wet basis) or liquid (e.g., liquid pig manure contains >90% water; NRSC, 2008). The chemical composition of manure depends on factors such as the animal diet and additives (i.e., salt blocks, vitamins), the amount of bedding and water mixed with the manure, and nutrient loss occurring during manure storage and land application (Gagnon et al., 1999). Furthermore, manure contains NH₄⁺, which enters the plant-available N pool in manure-amended soil, and organic N compounds that must undergo biochemical transformation (i.e., mineralization) to release plant-available N for crops. The NH4⁺ content of manure can vary from 7% to 79% of total manure N (Table 1), with higher proportions of NH4⁺ in liquid manure and slurries, and is assumed to be equivalent to the NH4⁺ input from an inorganic fertilizer (CRAAQ, 2010). Manure also contains organic N, a mixture of proteinaceous compounds, purines, nucleic acids, uric acid, urea, and other N-containing compounds that become available to crops after enzymatic hydrolysis to

Animal Storage	Ave. DM	Total N	$\rm NH_4$	Org. N	Р	к		
System	kg Mg ⁻¹ Fresh Weight Basis					_ Sample #	Reference	
Pig								
Liquid	36	3.9	2.6	1.3	1.2	1.9	2202	OMAFRA (2009)
Liquid	ND	2.8	2.2	0.5	ND	ND	1	Clark et al. (2009)
Liquid	57	4.5	2.9	1.6	ND	ND	8	Chadwick et al. (2001)
Dairy cattle	•							
Liquid	86	3.9	1.6	2.3	0.9	2.5	2449	OMAFRA (2009)
Liquid	56	2.9	1.5	1.4	0.8	2.4	4	Zebarth et al. (1996)
Liquid	100	3.2	1.5	1.7	1.3	2.8	2	Carter et al. (2010)
Liquid	94	2.5	0.7	1.8	ND	ND	9	Griffin et al. (2005)
Semi-solid	212	6.9	1.6	5.3	2.0	6.0	278	OMAFRA (2009)
Solid	410	8.2	1.1	7.1	2.1	6.6	86	OMAFRA (2009)
Beef cattle								
Semi-solid	241	7.0	1.4	5.6	2.2	5.5	416	OMAFRA (2009)
Semi-solid	179	3.9	1.1	2.8	ND	ND	10	Sharifi et al. (2011)
Solid	393	11.7	2.2	9.4	4.4	8.0	360	OMAFRA (2009)
Solid	704	8.3	0.6	7.8	2.4	ND	4	Eghball (2000)
Solid	672	10.7	0.9	9.8	4.1	ND	>25	Whalen et al. (2001)
Poultry (Br	oiler)							
Solid	712	41.4	2.6	38.8	ND	ND	15	Gordillo and Cabrera (1997)
Solid	661	31.2	6.6	24.6	14.1	17.9	193	OMAFRA (2009)
Solid	563	24.9	4.6	20.3	ND	ND	6	Chadwick et al. (2001)

 Table 1 Dry Matter (DM) and Nutrient Content of Manure Is Affected by the Type of

 Livestock and Storage System

ND, value was not determined.

Table 2 Estimated N Fertilizer Value (in kg Nha⁻¹) During the GrowingSeason From Various Manure Sources, Applied in Spring at a Rate of 100 kgOrganic Nha⁻¹ in a Cold Humid Temperate Region

Manure Source	N Fertilizer Value (kg Nha ⁻¹)
Liquid—poultry	30
Liquid—all others	20
Slurry (liquid plus solids)	30
Solid—poultry	30
Solid—pig	25
Solid with <50% dry matter content	15
Solid with >50% dry matter content	5

Adapted from Ontario Ministry of Agriculture Food and Rural Affairs (OMAFRA), 2009. Agronomy Guide for Field Crops. OMAFRA Publication 811, Toronto, Ontario. [Online] Available: http://www.omafra.gov.on.ca/english/crops/pub811/9manure.htm [10 October 2017].

 $\rm NH_4$ ⁺. The N fertilizer value of the organic N compounds in manure varies and may be from 5 to 30 kg N ha⁻¹ in the year of application (Table 2). Mineralization of organic N in manure-amended soil may supply NH₄⁺ to crops in the current growing season or in a future growing season, depending on the mineralization rate. The timing and amount of organic N mineralized from manure is difficult to predict because it is affected by the manure physico-chemical characteristics, previous manuring history, management practices such as the method, time, and uniformity of manure application, soil properties, and climatic conditions (Beauchamp, 1986; Sharifi et al., 2011). Even when manure is judged to have a high N fertilizer value, this may not translate into high crop yields unless the plant-available N is released from manure in synchrony with crop N demands (Crews and Peoples, 2005).

This review describes how the N fertilizer value of manure, relative to inorganic N fertilizer, is affected by manure characteristics, the NH_4 -N concentration and the mineralization of organic N in manure-amended soils. We also discuss how the N fertilizer value of manure is influenced by soil conditions and agronomic practices, and describe methods for measuring and monitoring the N fertilizer value of manure. Finally, we explain how smart agricultural systems may conserve the N fertilizer value of manure during storage and handling, and improve the N fertilizer value in manure applied to agricultural fields, leading to greater N use efficiency by crops in cold humid temperate regions.

2. NITROGEN COMPOSITION OF MANURE

2.1 Physico-Chemical Characteristics of Manure

Manure is a heterogeneous material collected from livestock raising facilities. In the cold humid temperate regions, manure is generally collected, stockpiled, and stored for months to years before it is applied to agricultural soils. Manure collection may occur daily, at the end of the livestock raising period when barns are cleaned and disinfected (e.g., after broiler chickens and turkeys are sent to market) or every 1 + years (e.g., when outdoor pens housing beef cattle are cleaned after animals are moved to pasture or sent to the slaughterhouse). Manure may be liquid containing up to 95% water if collected from pig barns that are cleaned with water (Zebarth et al., 1996), a slurry in dairy cattle facilities where the milkhouse wastewater is added to the manure storage (Tenuta et al., 2001), semi-solid when excreted by poultry (NRSC, 2008) or solid when animal excreta is mixed with straw or woodchip bedding (Qian and Schoenau, 2002). The physical and chemical properties of manure are therefore specific to each facility and depend on animal species, type of production (e.g., broilers vs. laying hens), animal diet, characteristics of the livestock rearing facility, the manure storage system, and the climate (Eghball, 2000). The physico-chemical properties of manure must be determined before applying manure to agricultural soils, since the physical form (liquid, slurry, semi-solid, or solid) and the chemical composition determines the NH4⁺ concentration and organic N content of the manure (Chadwick et al., 2001).

The physical form of manure is determined by farm practices and storage conditions. Typically, pig manure is collected by washing the barn with water and dairy manure is mixed with milkhouse wastewater. Both practices generate liquids or slurries that are stored in concrete holding tanks or lagoons, and applied as liquid or slurry manures. Beef cattle and poultry manure are commonly stored on large concrete paddocks and contain lignocellulosic bedding material (e.g., straw or woodchips) with dry matter contents ranging from 21–70% to 56–71%, respectively (Table 1). Variation in the dry matter content is related to the amount of water entering the manure storage from spilled drinking water, barn cleaning, rain, and snow-fall. Chemical composition of manure is also altered by the amount of bedding and other materials (wasted feed, soil, salts) that are mixed with animal manure. Although dairy cattle feces taken directly from the rectum contained $281-288 \text{ mgg}^{-1}$ cellulose (Jost et al., 2013a), the bedding material

associated with solid manure increases the cellulose and fiber content and carbon (C):N ratio, compared to liquid manures (Morvan and Nicolardot, 2009). The lignin content of solid beef and solid poultry manure ranged from 29–53 to 54–86 $g kg^{-1}$ manure (dry weight basis), respectively, while liquid dairy and pig manures had 2.5–6.6 g lignin kg⁻¹ manure (Chadwick et al., 2001). Liquid, semi-solid, and solid dairy manures analyzed by Van Kessel and Reeves (2002) contained 1.4-38.6% dry matter with lignin representing 25% of total C, on average, in 107 samples. Finally, manure contains macroand micro-nutrients that are essential for crop growth, and trace metals. Besides N, the most important nutrients for crops are phosphorous (P) and potassium (K). The P content of liquid manure ranges from 0.8 to 1.3 kg PMg⁻¹ and higher values are reported for solid manure obtained from beef (up to 4.4 kg PMg⁻¹) and poultry (14–25 kg PMg⁻¹) raising facilities (Table 1). The manure K content is from $0.9-1.9 \text{ kg K Mg}^{-1}$ in liquid pig manure to $16-18 \text{ kg K Mg}^{-1}$ in solid poultry manure (Table 1), which reflects differences in animal physiology, feeding practices, and manure management.

2.2 Nitrogen Content of Manure

Animal diets are composed of protein, fiber, lipids, trace minerals, and other essential substances necessary to maintain or optimize the nutritional wellbeing of livestock that produce meat, milk, eggs, and other products. Diet affects the amount of NH_4^+ excreted in the urine and undigested protein (organic N) defecated in feces. In poultry, the excretion of NH_4^+ , uric acid, and undigested protein can be reduced significantly by maintaining an ideal protein ratio (Chalova et al., 2016). Reducing the dietary crude protein and adding synthetic amino acids was effective at reducing total N excretion by 27% in a 6-week broiler study (Blair et al., 1999), while a 1.3% reduction in dietary crude protein resulted in 21% less N excretion in laying hens (Meluzzi et al., 2010). Liquid pig manure contains the highest proportion of NH_4^+ (approximately two-thirds of total N; Table 1) and cattle manure has more organic N than pig manure, due to less efficient digestion of crude protein by ruminants vs non-ruminants (Keys et al., 1969).

According to Powell and Broderick (2011), there are two macro-pools of N in ruminant manure. The first pool is endogenous N originating from byproducts of microbial activity in the rumen, small intestine, hind gut, and the digestive tract. Endogenous N is principally urea and NH_4^+ (7–52% of total N in ruminant manure), and the urea fraction is readily hydrolyzed to

 $\rm NH_4^+$ in manure storages and in soil, after manure is applied to agricultural land. The second pool is organic N-containing undigested protein and protein byproducts that are degraded by proteolytic enzymes of microbial origin over a period of months to years. Reducing the dietary protein intake of beef cattle alters the proportion of endogenous N and organic N in manure, which affects transformations of manure N in the environment. For example, there was 42% less NH₃ (g) volatilization per unit of N intake when finishing cattle consumed a barley-based concentrate diet with 12.6% crude protein compared with a 14% crude protein diet (Koenig et al., 2013), while steers fed a diet with 10% crude protein had 37% lower daily NH₃ (g) emissions than steers fed a 13% crude protein diet (Chiavegato et al., 2015). However, the N₂O (g) emissions from beef cattle manure tended to be greater with a low crude protein diet that was more digestable and increased the NH₄⁺ concentration in excreta (Chiavegato et al., 2015), or were unaffected by the crude protein content of the diet (Borhan et al., 2013).

2.2.1 Transformations of NH₄-N Contained in Manure

Since NH4⁺ contained in manure is plant-available, it needs to be conserved to get the greatest N fertilizer value from manure. This requires that (1) manure storage systems are designed to limit NH_4^+ conversion to NH_3 (g) and (2) the manure application method will maximize retention of NH4⁺ in the soil-plant system, such that minimal NH₃ (g) losses occur. Furthermore, the manure needs to be applied during a period of active crop growth, to ensure that most of the NH4⁺ input from manure is absorbed by the crop. In cold humid temperate regions, the NH4⁺ concentration of manure-amended soil increases briefly after manure application, but it returned to baseline levels (<10mg NH_4 - Nkg^{-1} soil) within about 1 week of manuring in the spring (Chantigny et al., 2001; Paul and Beauchamp, 1994). This reflects the fact that soluble NH4⁺ contained in manure is subject to chemical reactions in soil solution (i.e., NH₃ (g) lost through volatilization) and on soil surfaces (e.g., NH_4^+ adsorption to cation exchange sites, NH_4^+ fixation in clays), as well as biological transformations (e.g., crop N uptake, ammonia oxidation that can subsequently lead to nitrification and denitrification reactions) and possibly leaching in sandy soils with low cation exchange capacity.

Volatilization of NH₃ (g) reduces the N fertilizer value of manure substantially. Liquid manure storages are particularly susceptible to NH₃ (g) losses, although the difference in NH₃ (g) fluxes between baseline and peak events can vary by as much as two orders of magnitude. High fluxes of $>7200 \mu$ g NH₃-Nm⁻² min⁻¹ were reported from anaerobic pig slurry treatment lagoons in the spring (Lim et al., 2003), although other anaerobic lagoons containing pig slurry emitted $10-406 \mu g \text{ NH}_3-\text{Nm}^{-2} \min^{-1}$ in the spring (Viguria et al., 2015). Seasonal variation in NH3 emission factors from anaerobic lagoons ranged from <2 kg N animal unit⁻¹ year⁻¹ in January to >40 kg N animal unit⁻¹ year⁻¹ in June (Blunden and Aneja, 2008). This is consistent with Emerson et al. (1975), who noted more volatilization of NH_3 (g) as the temperature increased and found that higher moisture content favored the dissociation of NH₄⁺ to NH₃ (g), resulting in greater NH₃ (g) loss from liquid manure storages than solid manure piles. For instance, Külling et al. (2001) reported more NH₃ (g) loss from dairy slurries (17-36% of total N lost as NH₃ (g) after 7 weeks storage) than solid dairy manure (9-13% of total N lost as NH₃ (g) after 7 weeks storage). Ammonia losses from manure piles were: 2% of total N for poultry manure on a conveyor belt that was being dried during transport to a pelletizing facility, 15% of total N for cattle farmyard manure, and 31% of total N for pig farmyard manure (Webb et al., 2011). Manure accumulating on concrete surfaces, such as in dairy free-stall barns and beef cattle feedlots, is vulnerable to NH_3 (g) loss, with average flux rates of $1.03 \text{ g NH}_3 \text{ m}^{-2} \text{ h}^{-1}$ on dairy farms and 0.174 g NH_3 $m^{-2} h^{-1}$ in beef feedlots reported by Hristov et al. (2011). Overall, NH₃ (g) losses represent 25–50% of the total N excreted by dairy and beef cattle in such facilities.

In storages containing liquid, slurry, semi-solid, and solid manure, the reactions that lead to volatilization of NH_3 (g) are:

$$(NH_2)_2CO + H_2O \rightarrow NH_2COOH + NH_3(g)$$
(1)

$$NH_2COOH \rightarrow NH_3(g) + CO_2(g)$$
 (2)

Animal urine is the source of urea, $(NH_2)_2CO$, in manure. Urease (produced by fecal bacteria) catalyzes the reaction in Eq. (1), while carbamate (NH₂COOH) is degraded by spontaneous hydrolysis (Eq. 2). Consequently, a peak in NH₃ (g) loss occurs within 2–10 h of mixing urine and feces with soil (Huijsmans et al., 2003). Higher pH values increase the NH₃ (g) concentration, while urea hydrolysis increases pH in the solution because it can generate CO_3^- and HCO_3^- , so the reaction is limited by substrates (urea and NH₄⁺), as illustrated below:

$$(NH_2)_2 CO + 2H_2 O \to NH_2 COOH + (NH_4)^+ + H_2 O \to 2(NH_4)^+ + (CO_3)^- \to (NH_4)^+ + NH_3 (g) + (HCO_3)^-$$
(3)

Gaseous NH₃ is also released when the solid and liquid fractions of manure are mixed, such as when liquid storages are emptied or solid manure piles are turned. Stirring may bring dissolved NH₃ (aq) to the surface, where it diffuses to the atmosphere as NH₃ (g). In addition, stirring increases the contact between solid and liquid components, which enhances urease hydrolysis. Solid-liquid separation, originally conceived as a technology for odor control and methane (CH₄) capture from the C-rich solid fraction of manure, is also effective at reducing NH₃ (g) loss from liquid manure and slurries. Szogi et al. (2006) described a system to remove solids from pig slurry before pumping the liquid fraction into an anaerobic lagoon, which reduced the NH4⁺ concentration of the wastewater by 10-fold and emitted approximately 1311kg NH₃-N ha⁻¹ year⁻¹, an order of magnitude lower than the 13,633 kg NH₃-Nha⁻¹ year⁻¹ emitted from the conventional practice of pumping untreated pig slurry into an anaerobic lagoon. Finally, wind speed affects the NH3 (g) loss from uncovered manure storages (Fig. 2A). The chemical equilibrium between NH_4^+ (aq) and NH_3 (g) species in a manure storage can be maintained by covering the manure storage, which should reduce NH₃ (g) loss and thus preserve the N fertilizer value of manure.





Other approaches to minimize NH_3 (g) loss from manure storages involve chemical treatments to inhibit urea hydrolysis or acidify the manure. Although the urease inhibitor N-(n-butyl) thiophosphoric triamide proved ineffective in reducing urea hydrolysis, acidification of manure is a promising method to reduce NH_3 (g) loss because the NH_4^+ concentration did not increase with storage time in hydrochloric acid-treated pig slurry (Panetta et al., 2005). Continuous in-house acidification of pig slurry proved effective at reducing the NH_3 (g) loss from treated slurry to <10% of the NH_3 (g) emissions from untreated slurry, which attests to the practicality of this technology at the farm-scale (Kai et al., 2008).

The reaction shown in Fig. 2A, where soluble NH_4^+ becomes deprotonated to produce the NH₃ (aq) and NH₃ (g) species, also occurs during manure transport and land spreading. Once manure is incorporated in the soil, it is likely that NH_3 (aq) will react with excess H^+ ions present in soil and be protonated to NH_4^+ (aq), which is biologically available for plants and microorganisms and also reacts with soil minerals through adsorption and fixation reactions (Fig. 2B). Therefore, best practices for manure application dictate that manure be incorporated as soon as possible to enhance NH_3 (aq) protonation with H^+ and thereby retain NH_4^+ in the soil-plant system (Sommer and Hutchings, 1995). Ammonia volatilization was responsible for the loss of 24–33% of NH4⁺ from liquid dairy cattle manure applied to the soil surface and unincorporated, after 6-7 days (Beauchamp et al., 1982). Similarly, between 35% and 40% of applied NH4⁺ was volatilized after 2 days, with an additional 5% of applied NH_4^+ volatilized after 9 days, when liquid pig manure was surface applied (unincorporated) on a bare loamy soil (Chantigny et al., 2004). The N fertilizer value of manure is greater with rapid incorporation or direct injection of liquid and slurry manures in the cold humid temperate region of Quebec, Canada, particularly when manure is applied in the autumn/postharvest period (Table 3). Although relatively small amounts of NH₃ (g) are lost from unincorporated solid manure in the first 1–2 days, the fact that solid manure remains on the soil surface makes it to susceptible to continual volatilization as it dries, compared to surface-applied liquid manure or slurry that gradually seep into the soil profile (Meisinger and Jokela, 2000). Overall, Webb et al. (2014) found that immediate incorporation of solid cattle, pig, and poultry manure reduced NH3 (g) loss by 90% when incorporated by plow, and by 60% when incorporated by disc or tine harrow, compared to leaving manure on the soil surface.

	••					
Application Method	Spring	Growing Season	Autumn/Postharvest			
	Annual crops					
Injection	10	0	40			
Low-ramp spraying an	d incorporat	ion within				
<3h	15	15	55			
3–24 h	30	35	60			
>24 h	35	45	70			
Drop pipe (dribble bar) and incorp	oration within				
<3h	10	5	50			
3–24 h	25	25	55			
>24 h	30	35	65			
	Hayfields					
Injection	0	0	20			
Low-ramp spraying	35	45	55			
Low-ramp spraying wi	ith dribble ba	ar				
without regrowth	25	30	40			
with regrowth	15	25	30			

	Manure Application Time	
Manure	and Slurries Having a Ratio of NH ₄ -N:Total $N \ge$ 0.50 Due to NH ₃ (g) Volat	ilization
Table 3	Estimated Reduction of N Fertilizer Value (% of the Total N Applied) o	f Liquid

Losses vary among cropping systems (annual crops vs. hayfields), application methods, and application times (spring, during the growing season and autumn/postharvest periods) in a cold humid temperate region.

Adapted from Centre de référence en Agriculture et Agroalimentaire du Québec (CRAAQ), 2010. Guide de référence en fertilisation, second ed. (in French). Centre de référence en Agriculture et Agroalimentaire du Québec, Québec, Canada, p. 519.

2.2.2 Transformations of Organic N Contained in Manure

Livestock consume a plant-based diet that is ground and fragmented through mastication before undergoing chemical and enzymatic degradation in the digestive tract. Fecal material containing undigested protein and protein byproducts is defecated along with fibrous plant residues and mixed with urine, which contains NH₄⁺, urea and other N-containing metabolic byproducts. Organic N represents 18–94% of the total N in manure (Table 1), consistent with other reports of the organic N content (14–99% of total N) in poultry

manure, cattle, and pig manure (50 solid and slurry samples; Chadwick et al., 2000). Cattle and pig manure contain organic N that is proteinaceous in nature, derived from microorganisms in the animal gut, intestinal wall secretions and from undigested plant cell components (Chadwick et al., 2000), reflecting the digestion efficiency of crude protein (Eghball, 2000). In poultry manure, uric acid represents 56–79% of the organic N accumulated under caged laying hens without bedding (Groot Koerkamp, 1994; Pan et al., 2009) and from 12% to 14% of the organic N in broiler and layer manure mixed with bedding (Chadwick et al., 2000). As well, uric acid may be synthesized by endogenous bacteria in manure storages when sufficient water is present (Mowrer et al., 2014). Uric acid is not always reported as a component of the organic N in manure due to its rapid hydrolysis during storage and after application to agricultural soils, but the fact that it requires enzymatic degradation to be transformed to urea and subsequently to NH_4^+ warrants its inclusion in the organic N pool.

Organic N may be transformed into NH_4^+ in manure storages, particularly when the manure is moist, well-aerated, the temperature is conducive to microbial activity and microorganisms have an ample supply of soluble C substrates for metabolic processes. Pig rearing facilities are generally cleaned with water, which stimulates the microbial metabolism of volatile fatty acids, a group of C_2 – C_6 compounds that represent about 30% of the organic C in liquid pig manure (Angers et al., 2007), in the first 7 days following manure application (Chantigny et al., 2001). Similarly, mixing milkhouse wastewater with dairy manure creates a semi-solid mixture (slurry) with soluble organic substrates that are susceptible to enzymatic hydrolysis. In contrast, solid manure is drier, as the feces are mixed with bedding that also absorbs excess moisture from urine, drinking water spills and other sources. Faster mineralization of organic N may contribute to the higher NH_4 :total N ratio in liquid and slurry manures than in solid manure (Table 1).

Another reason that solid manure has a lower NH_4^+ concentration than liquid and slurry manures is because the solid components of the feces and bedding material must be decomposed before organic N compounds are mineralized to release NH_4^+ . The first step in decomposition is the physical fragmentation of larger particles to increase the surface area for microbial colonization. Agricultural producers can mechanically reduce the particle size of solid manure by turning, chopping, and screening the organic materials. As well, detritivorous animals such as voles, lizards, snails, slugs, and earthworms are responsible for shredding and fragmenting the organic materials in solid manure piles. The second step is to solubilize the carbonaceous and proteinaceous compounds present in the pile, exposing these compounds to hydrolytic enzymes of microbial origin (Whalen, 2014). The C-rich compounds present in bedding materials stimulate microbial growth, but the relatively low and constant molar ratio of C:N in microbial cells (e.g., C:N ratio from 7 to 8.5 in microbial biomass; Griffiths et al., 2012) means that microorganisms will immobilize NH₄⁺ to maintain the homeostatic balance in their C:N ratio. Gradual loss of C-rich compounds through microbial respiration (i.e., CO₂ from the manure pile) depletes the C substrates available for microbial metabolism, resulting in turnover of microbial biomass that increases the manure NH₄⁺ concentration. Consequently, solid manure with a C:N ratio < 10 has a greater N fertilizer value than solid manure with a C:N ratio of 15–25 (Table 4). This is the reason that solid manure with C-rich bedding is stockpiled and left to decompose, sometimes with periodic turning, for 1–2 years before it is applied to agricultural soils.

3. SOIL CONDITIONS AND AGRONOMIC PRACTICES INFLUENCING THE NITROGEN FERTILIZER VALUE OF MANURE IN COLD HUMID TEMPERATE REGIONS

The N fertilizer value of manure reflects its ability to supply plantavailable N (NH4⁺ and NO3⁻) to a crop. Judicious use of manure implies that most of the N applied is taken up by the crop, allowing farmers to achieve high N use efficiency, and meet crop yield targets while minimizing N losses to the environment. Consequently, the N fertilizer value of manure represents the ability of manure-amended soil to support net N mineralization during periods when crop N demands are high, after the plant-available N pool is depleted (Fig. 3A). Ideally, net N mineralization will occur in synchrony with the crop N uptake pattern and switch to net immobilization when crop growth ceases. In reality, applying the recommended agronomic rate of manure with a high NH₄⁺ concentration or containing a large proportion of labile organic N compounds could supply most of the plant-available N in the early part of the growing season, but provide insufficient plant-available N to meet crop needs during late vegetative growth and at the onset of flowering (Fig. 3B), thus reducing the crop yield potential. Solid manure containing a large amount of C-rich compounds could immobilize plantavailable N in the early part of the growing season, causing a N deficiency in the crop. Net N mineralization late in the growing season (i.e., when the crop has reached the grain filling stage or in the postharvest period) is also problematic because it releases plant-available N during a period of low

Table 4 Estimated N Fertilizer Value (in kg Nha ⁻¹) to Crops When Soil Receives an	
Application Rate of 100 kg Total N ha ⁻¹ From Solid Manure	
Manure Application Time	

Manure C:N Ratio	Soil Type	Spring/Summer	Autumn/Postharvest	
		Annual crops		
C:N <10	Clay	75	65	
C:N 10–12	Clay	65	45	
C:N 13–15	Clay	50	25	
C:N 15–25	Clay	45	20	
C:N <10	Sand and loam	85	70	
C:N 10–12	Sand and loam	75	55	
C:N 13–15	Sand and loam	55	35	
C:N 15–25	Sand and loam	50	30	
		Hayfields		
C:N <10	Clay	85	75	
C:N 10–12	Clay	65	45	
C:N 13–15	Clay	40	30	
C:N 15–25	Clay	20	10	
C:N <10	Sand and loam	90	80	
C:N 10–12	Sand and loam	75	55	
C:N 13–15	Sand and loam	45	20	
C:N 15–25	Sand and loam	30	15	

The N fertilizer value depends on the C:N ratio of the manure, soil texture, the cropping system (annual crops vs. hayfields), and the application time (spring/summer vs. autumn/postharvest periods) in a cold humid temperate region. Manure applied in the autumn/postharvest period is assumed to be a source of inorganic N to crops in the next growing season.

Adapted from Centre de référence en Agriculture et Agroalimentaire du Québec (CRAAQ), 2010. Guide de référence en fertilisation, second ed. (in French). Centre de référence en Agriculture et Agroalimentaire du Québec, Québec, Canada, p. 519.

crop N demand (Fig. 3C), increasing the risk of N loss to the environment. The chemical composition of manure should provide some insight into its potential to supply plant-available N, but its N fertilizer value will be modulated by site-specific soil conditions and agronomic practices related to manure handling and land application. These considerations are presented in the next sections.



Fig. 3 The N fertilizer value of manure for corn (*Zea mays* L.) production is greatest when (A) plant-available N is released from manure in synchrony with the crop N uptake and diminishes when (B) most of the plant-available N is released from manure in the early part of the growing season or (C) in the later part of the growing season. The illustrations in (B) and (C) represent an asynchrony between N supply from manure and corn N demands.

3.1 Soil Conditions Affecting the Plant-Available N Concentration in Manure-Amended Soil

The plant-available N concentration in a manure-amended soil is dynamic and influenced by processes that deplete or add NH_4^+ and NO_3^- ions to soil solution. Biological uptake by plants and microorganisms (including immobilization and denitrification) remove plant-available N from the soil solution, as do physico-chemical reactions like volatilization, adsorption, and leaching. The plant-available N pool is replenished by the soluble NH₄⁺ and NO3⁻ contained in manure, as well as N mineralization, ammonia oxidation, and nitrification reactions. The nature and magnitude of these reactions are strongly dependent on climatic conditions. Cold humid temperate regions are characterized by warm summers (e.g., air temperature exceeding 30 °C in July) with irregular rainfall events that cause soil wetting and drying cycles. Winters are cold (e.g., as low as -30 °C in January), but temperature fluctuations may result in soil thawing and re-freezing during the winter, with more frequent freezing and thawing cycles in early spring (March-April) when snowmelt occurs. Climatic conditions affect the soil physicochemical properties that regulate the soil biological activity, as illustrated in Fig. 4. The next sections explain how manure applications affect the physical, chemical, and biological properties of soil, which influences the plant-available N concentration in manure-amended soils of cold humid temperate regions.

3.1.1 Soil Physico-Chemical Properties in Manure-Amended Soil

Solid manure applications alter soil physical properties rapidly because the addition of organic matter combined with tillage operations that mix manure in topsoil creates a friable structure with lower bulk density than unamended soil (Haynes and Naidu, 1998). Macropore development and water infiltration improve following the addition of solid manure, such that the saturated hydraulic conductivity (K-sat) reached 110% after five annual applications of solid pig manure due to macropore development, but liquid pig manure applied to this Orthic Black Chernozem had no effect on soil bulk density, K-sat, water retention, or aggregation (Adesanya et al., 2016). Similarly, 12 annual applications of solid beef cattle manure (30–180 Mgha⁻¹) increased the soil water holding capacity compared to unamended soils (Sommerfeldt and Chang, 1985). Solid manure promotes aggregate formation and increases the proportion of macroaggregates in soils of cold temperate regions (Courtier-Murias et al., 2013; Jiao et al., 2006;



Fig. 4 Manure is a source of plant-available N (NH_4^+ and NO_3^-) for crop production because it contains soluble NH_4^+ that enters the plant-available N pool, as well as organic N that is transformed by soil biota through mineralization-immobilization-turnover (M-I-T) reactions into plant-available N. Agronomic practices related to manure storage, handling, and land application methods determine the quantity of NH_4^+ and organic N that enters the soil. Soil biotic activity is affected by climate conditions as well as soil physico-chemical properties. Plant-available NH_4^+ and NO_3^- are lost through abiotic and biotic reactions. The N fertilizer value of manure reflects the proportion of plant-available N that was taken up by the crop, relative to the manure N input.

Miller et al., 2012; Whalen and Chang, 2002; Yan et al., 2012). Macroaggregates were enriched with organic C and N in soils amended with $>30 \text{ Mg} ha^{-1} \text{ year}^{-1}$ of beef cattle manure (Whalen and Chang, 2002), although Miller et al. (2012) found that macroaggregates <0.47 mm contained the most mineralizable N after 11 repeated applications of beef cattle manure (77 Mg ha⁻¹ year⁻¹).

On the other hand, the high water content of liquid and slurry manures can temporarily saturate the soil. Solids present in pig manure slurry blocked water infiltration in a gravely clay soil (Fares et al., 2008), suggesting that high slurry applications are to be avoided on fine-textured soils. In saturated soil, the high NH_4^+ :total N ratio plus the labile C substrates (e.g., volatile fatty acids) in liquid manure makes it susceptible to denitrification. Liquid dairy manure application increased the magnitude of N_2O (g) emissions from a clay loam soil during thawing events, with peak emissions at soil moisture contents of 40–70% water-filled pore space, probably because the C-rich and N-rich substrates in manure stimulated nitrifier-denitrification and denitrification in anaerobic microsites, and thawing removed barriers to N₂O (g) diffusion from soil (Singurindy et al., 2009). Consequently, it is not recommended to apply liquid and slurry manures during period of low crop growth or on bare soils due to the risk of N₂O emissions.

Solid manure often buffers the pH of acidic soil because it provides base cations that replace H⁺ ions on exchange sites as well as negatively charged ions (OH⁻, HCO₃⁻) that neutralize the acidity of exchangeable and soluble H⁺ ions. For example, Whalen et al. (2000a) found the addition of cattle manure with pH 6.8 rapidly increased the soil pH of two silt loams from 4.8–6.0 to 5.5–6.3, respectively, and this effect persisted during an 8-week laboratory incubation. Solid poultry manure tends to be alkaline, with pH>8 often reported (Gordillo and Cabrera, 1997; Sims, 1986; Thomas et al., 2016) because hydrolysis of uric acid and its reaction products releases CO_3^- and HCO_3^- . The high pH of poultry manure favors NH₃ (g) volatilization. However, there was no net change the pH of an acidic soil (pH 5.8) after applying poultry manure (pH 7.7), possibly due to the soil buffering capacity and the relatively low application rate (4Mgha⁻¹) of poultry manure (Rees et al., 2014).

The pH of slurries is generally near-neutral, with Sommer and Hutchings (2001) reporting pH 6.7 in pig slurry and pH 7.2 in cattle slurry. However, Sørensen (1998) applied an anaerobically stored dairy cattle slurry with pH 8.4 to a sandy soil and noted that soil pH increased from 6.8 to 8.6 for 2 days, and declined thereafter. Similarly, surface application (unincorporated) of anaerobically stored liquid pig manure (pH 7.7) to a loamy soil (pH 5.9) increased soil pH 8 in the top 2 cm for 2 days, but it declined to pH 7 in the top 5 cm within 9 days of manure application (Chantigny et al., 2004). The alkaline nature of anaerobically stored slurries is attributed to a high concentration of volatile fatty acids, which are degraded within days of manure application, leading to a decline in the soil pH of slurry-amended soil (Sørensen, 1998). Soil acidification in slurry-amended soils may be attributed to the production of H⁺ ions, since NH₃ (g) loss generates 1 mol of H⁺ for every mole of N converted from NH₄⁺ to NO₃⁻ (Havlin et al., 2005).

Physico-chemical changes in manure-amended soils will affect soil biota responsible for organic N mineralization to plant-available N because:

1. Manure-amended soils tend to have more organic matter and are darker than non-manured soils, and thus retain more radiative energy.

Warmer soil conditions favor soil enzyme and biological activities that contribute to N mineralization, which exhibit a Q_{10} temperature response (Griffin and Honeycutt, 2000).

- 2. The formation of stable macroaggregates and well-connected macropores in manure-amended soil supports greater water infiltration and more air exchange with the atmosphere. This is expected to favor aerobic biological processes such as ammonia oxidization and nitrification that require oxygen to oxidize NH₄⁺ to NO₃⁻. As well, porosity affects water flow to plants, which rely on transpiration to acquire plant-available N through mass flow (NO₃⁻), diffusion and root interception (NH₄⁺) processes.
- 3. Well-structured soils develop after manure application and possess more aerobic microsites and organic substrates from the manure. However, organic N compounds that bind to mineral surfaces (Gillespie et al., 2014) may be protected from hydrolytic enzymes, so the physico-chemical matrix controls microbial access to substrates for decomposition and N mineralization.
- 4. Changes in soil pH and buffering capacity, as well as the ionic strength of the soil solution, affects enzyme and microbial activities involved in N mineralization. Bacteria and most extracellular enzymes have an optimal pH range of about 6–7.5 (Burns et al., 2013), whereas fungi are more abundant in acidic soils. Nitrification rates are the highest at pH 6.5 and the reaction rate declines with increasing acidity (Dancer et al., 1973). Soil buffering capacity increases in manure-amended soils because the organic matter adds more negatively charged surfaces that maintain chemical equilibria (Haynes and Naidu, 1998). Ions that inhibit or stimulate the activity of extracellular enzymes (i.e., as co-factors) are present in manure-amended soil.

Finally, the soil physico-chemical matrix may possess an inherent capacity for NH_4^+ fixation that affects the plant-available N concentration in manure-amended soils. Temporary NH_4^+ fixation by clays will preserve NH_4^+ in soil-plant system because it reduces the NO_3^- production through ammonia oxidation and nitrification (Nieder et al., 2011). Clay mineralogy affects the NH_4^+ fixation capacity, with higher NH_4^+ fixation in 2:1 vermiculite and illite clay minerals, and negligible fixed NH_4^+ in 1:1 kaolinite clay, and higher clay content increases NH_4^+ fixation. Clay soil fixed 34% of NH_4^+ contained in pig slurry while a sandy loam fixed 11% of NH_4^+ from the same slurry within 6 h of application (Chantigny et al., 2004). The clay soil exhibited a gradual increase in NH_4^+ fixation for 14 days, thereafter declining to 20% of applied NH_4^+ after 96 days, while the sandy loam released a significant amount of NH_4^+ to the soil solution throughout the study, so that only 2% of applied NH_4^+ remained fixed after 96 days (Chantigny et al., 2004).

3.1.2 Soil Biological Activity in Manure-Amended Soil

Biological activity in manure-amended soil determines the rate at which organic N compounds are converted to NH4⁺, which may be relatively fast (days to weeks) or slow (months to years), depending on the manure source and other abiotic factors (e.g., soil physico-chemical properties, agronomic practices) in the cold humid temperate region (Eghball, 2000; Powell and Broderick, 2011). Manure, like other organic materials, contains C substrates and nutrients that support the metabolic processes, growth, and reproduction of organisms in the soil foodweb (Whalen et al., 2013). Soil macro- and meso-fauna such as earthworms and collembola ingest and reduce the particle size of solid manure, increasing the surface area for colonization by microfauna and microorganisms. Saprophytic bacteria and fungi produce extracellular enzymes that degrade complex polymers (e.g., protein, cellulose) in the manure, releasing soluble substrates (e.g., amino acids, celliobiose) that are absorbed by microbial cells. There, intracellular enzymes hydrolyze these compounds to release energy and substrates for cellular processes (e.g., NH4⁺ for protein metabolism). Microbial biomass is an important sink for NH4⁺ and other N compounds, which are released through cell lysis. Degradation of microbial cell membranes may be the result of natural aging, substrate limitation, exposure to toxic substrates, abiotic processes (e.g., wetting-drying, freezing-thawing), or biotic interactions (e.g., viral infection, predation).

In cold humid temperate regions, fluctuations in soil temperature and moisture conditions are responsible for wetting-drying and freezingthawing cycles that disrupt and damage microbial cells. Drying a soil amended with poultry slurry increased the NH_4^+ concentration, possibly because (1) osmotic stress caused cell lysis and NH_4^+ release, (2) NH_4^+ did not diffuse to microsites where ammonia oxidizers and nitrifiers were active, or (3) there was limited water for enzymatic hydrolysis and other biological reactions (Sims, 1986). Rewetting a dry soil fills the pore space with water and re-establishes the connection between substrates, extracellular enzymes, and microorganisms. This is generally accompanied by a pulse of CO_2 associated with rapid microbial growth (e.g., on lysed substrates that accumulated during the drying phase; Blazewicz et al., 2013), which may temporarily immobilize NH_4^+ in the microbial biomass.

Freeze-thaw events occur in late autumn when air temperatures fall below 0° C at night and warm to $>0^{\circ}$ C in daytime, during thaws in winter months, and in the spring when the snowpack melts. Freezing causes cell lysis due to physical abrasion from soil minerals that expand when water freezes and ice crystal formation within cells. When the soil thaws, new microbial growth can increase C and N mineralization two- to threefold (DeLuca et al., 1992; Herrmann and Witter, 2002). Chantigny et al. (2014) applied ¹⁵Nlabeled liquid pig manure in spring and found 60-65% of total N applied was in organic N or clay fixed forms by harvest, with <5% of the mineral N applied present in the soil mineral N pool by the end of the growing season. Between 20 and 32.5 kg Nha⁻¹ was lost during the non-growing season due to frequent freeze-thaw cycles, probably through gaseous emissions. Pelster et al. (2013) reported greater NO3⁻ concentrations and higher N2O (g) emissions during freeze-thaw cycles than when soil was maintained at a constant 1 °C. Adding crop residues with high C:N ratio (C:N=75 for soybean, C:N=130 for corn) increased microbial activity but reduced N₂O (g) emissions, suggesting that the substrate-induced N immobilization reduced the risk of gaseous N emissions from the soil surface during freeze-thaw cycles.

Biotic interactions that cause turnover of soil microbial biomass affect the plant-available N concentration. Soil viruses may be important, given that bacteriophages are responsible for the death through cell lysis of approximately 80% of the prokaryotes found in marine sediments and control the N turnover from sediment-dwelling microbial biomass (Weinbauer, 2004). Soil microbial populations also exhibit a high level of viral infection, based on the observation that 22-68% of the cultivable soil bacteria in temperate soil samples contained genetic material from bacteriophages (Williamson et al., 2007) and mycoviruses are found in all phyla of the true fungi: Chytridiomycota, Zygomycota, Ascomycota, and Basidiomycota (Son et al., 2015). However, Williamson et al. (2007) suggested that most soil bacteriophages exhibit a lysogenic rather than a lytic lifestyle and thus probably have little impact on N release from microbial biomass. Still, virulent soil phages are often tested as biocontrol agents due to their ability to lyse pathogenic soil-borne prokaryotes (e.g., Yordpratum et al., 2010). Most mycoviruses are latent and infected fungi remain asymptomatic, although some soil mycoviruses alter the growth and sexual reproduction of their host, and hypovirulence has potential to control plant pathogenic fungi in agricultural soils (Son et al., 2015). Overall, the lysis and N turnover from soil microorganisms due to viral infection remains largely unknown. On the other hand, predation of microbial cells contributes to N turnover

when bacteria and fungi are grazed by a number of specialized predators (e.g., soil protists, bacterivorous, and fungivorous nematodes). In temperate soils, predation contributes about 30% of the annual NH_4^+ turnover from microbial biomass (Verhoef and Brussaard, 1990), depending upon soil foodweb interactions and the population density of microorganisms and soil fauna. If manuring increases soil microbial biomass, it may be expected to stimulate predation and cause greater NH_4^+ turnover in manured soil than non-manured soil, but this remains to be confirmed.

3.1.2.1 Soil Fauna

Manure applications generally increase the abundance of soil fauna. At the DOK trial in Therwil, Switzerland, the continuous application of farmyard manure for 27 years resulted in larger populations of bacterivorous, herbivorous and omnivorous nematodes, enchytraeids, earthworms, fly larvae (Diptera, Brachycera), whereas protists, euedaphic collembola, and chilipoda populations were similar in plots that received farmyard manure and inorganic fertilizers (Birkhofer et al., 2008). Although moderate applications of cattle and pig slurry increased the population of hemiedaphic Collembola (Bolger and Curry, 1984), soils receiving solid farmyard manure and inorganic fertilizer were equally favorable for soil microarthropods, including collembola, various soil mites (Mesostigmata, Oribatida, Acaridae, Prostigmata) and thysanoptera (Kautz et al., 2006). Soil macrofauna use manure as a food source, while also benefiting from greater primary production and microbial biomass in manured soils. As well, the improvement in soil structure (i.e., aggregation and porosity), water retention capacity, and water balance following manure applications could be positive for soil biota.

Earthworm populations are generally larger in manure-amended soil than in soils receiving NPK fertilizer or no fertilizer. There were more earthworms in corn agroecosystems with straw-packed dairy cow manure application than NPK fertilizer on 8 of the 14 sampling dates during a 2-year period (Whalen et al., 1998) and they contributed an estimated 12–25 kg Nha⁻¹ toward silage corn production in manure-amended plots (Whalen and Parmelee, 2000). The ability of earthworms to fragment, redistribute, and mix solid manure in the soil profile means that they contribute to macroaggregate and macropore formation, and they accelerate manure decomposition and N mineralization (Whalen, 2014). Liquid manure and slurries are detrimental to earthworms if their application causes temporary saturation of soil pores, increases the concentrations of NH₄⁺ and trace metals to toxic levels, or contributes to soil acidification (Bogomolov et al., 1996; Ma et al., 1990).

3.1.2.2 Soil Microorganisms

After manure is physically fragmented and degraded by extracellular enzymes to release soluble substrates, it is a source of energy and nutrients for microbial metabolism. Consequently, manuring increases the soil microbial biomass, particularly when solid manure is applied (Birkhofer et al., 2008; Jost et al., 2013b; McGill et al., 1986; Rochette and Gregorich, 1998). Soil receiving dairy manure slurry had greater bacterial biomass and lower fungal biomass (Bittman et al., 2005), probably because the NH_4^+ contained in manure slurry was a preferred substrate for bacterial growth and gave them a competitive advantage over fungi. The NH_4^+ input could explain the sevenfold increase in ammonifier populations in the 0-15 cm soil layer and the fivefold increase in nitrifiers in the 15-30 cm soil layer of a silt loam that received $60 \text{ m}^3 \text{ ha}^{-1}$ liquid pig manure annually for 18 years (Lalonde et al., 2000). Manure applications that increase the biomass of heterotrophic microorganisms involved in decomposition and N mineralization processes, together with larger populations of ammonia oxidizers and nitrifiers, are expected to increase the plant-available N concentration in soil. Consequently, greater N mineralization and higher crop N uptake was observed in soil receiving composted dairy manure than in the unamended control (Paul and Beauchamp, 1996).

3.1.2.2.1 Extracellular Enzymes Involved in N Mineralization Physical fragmentation of manure by tillage and the action of soil macrofauna reduces the size of manure solids, increasing their susceptibility to enzymatic hydrolysis. Extracellular enzyme activity represents a control point in the decomposition and N mineralization processes because it is responsible for the depolymerization of C-rich and N-rich polymers (Kemmit et al., 2008; Schimel and Bennet, 2004). For example, extracellular cellulase of fungal and bacterial origin acts on cellulose, the most abundant C compound in the primary cell wall and a component of the lignocellulosic-rich secondary cell wall of plants. The product of cellulose hydrolysis is cellulobiose, a two subunit compound of glucose bound by 1–4 β linkages, that is transported through the cell membrane or further hydrolyzed by cellulobiase before glucose enters the microbial cell (Himmel et al., 2007). Cellulobiose and glucose support microbial growth and respiration, which releases CO_2 (Fig. 5). Organic N in manure is proteinaceous in nature, although poultry manure contains appreciable quantities of uric acid, both of which are hydrolyzed by extracellular enzymes of microbial origin. Protein depolymerization is mediated by proteolytic enzymes

Depolymerization of organic C to CO₂



Hydrolysis of organic N to NH4⁺

Fig. 5 Concurrent carbon and nitrogen mineralization in poultry manure is the result of enzymatic depolymerization that successively cleaves complex substrates, yielding molecules that can be absorbed by microbial cells. The carbon degradation pathway provides carbon for microbial metabolism and growth, and the microbial nitrogen requirement is met by assimilating small molecules (e.g., urea) or NH₄⁺ via the mineralization-immobilization-turnover (M-I-T) process. Poultry manure contains NH₄⁺ that directly enters the NH₄⁺ pool, and most of the organic N is in the form of uric acid, which is degraded within a few days of manure application. Protein hydrolysis occurs over a longer period (weeks to months). *Amounts of N-containing compounds are expressed per kg of dry matter in manure, based on data from Pan, J., Fadel, J.G., Zhang, R., El-Mashad, H.M., Ying, Y., Rumsey T., 2009. Evaluation of sample preservation methods for poultry manure. Poult. Sci. 88, 1528–1535.* (proteases and peptidases) that release amino acids, which are absorbed by microbial cells and subsequently cleaved by intracellular enzymes to produce NH_4^+ for *de novo* protein synthesis (Kirchmann and Witter, 1992; Fig. 5). Uric acid is rapidly hydrolyzed to urea and NH_4^+ in the soil solution within 3–14 days of applying solid poultry manure to soil (Bitzer and Sims, 1988; Gordillo and Cabrera, 1997; Sharifi et al., 2009). The first step involves the hydrolysis of uric acid to allantoin by uricase (Schefferle, 1965). Next, allantoin is degraded by allantoinase to allantoic acid, and then hydrolyzed by allantoicase to urea, which is hydrolyzed by urease to produce NH_4^+ (Groot Koerkamp, 1994). Soluble NH_4^+ produced from uric acid degradation may be adsorbed to clay minerals, immobilized in microbial cells or remain in the soil solution, as part of the plant-available N pool (Fig. 5) prior to undergoing ammonia oxidation and nitrifying reactions.

The activity of soil proteolytic enzymes is affected by the substrate concentration and the amount of extracellular proteases and peptidases present (Brzostek and Finzi, 2011; Schimel and Weintraub, 2003). However, proteolytic enzyme activity is not directly related to microbial biomass (Henry, 2012) because abiotically stabilized extracellular enzymes are able to catalyze reactions, independent of microbial demands for metabolizable C and N monomers (Burns et al., 2013). Greater extracellular enzyme activity is often reported in manure-amended soil, likely due to the substrates supplied by manure (Bowles et al., 2014; Fauci and Dick, 1994; Giacometti et al., 2013; Lalonde et al., 2000), which stimulated the activity of N cycling (aspartase, L-asparaginase, urease) and C cycling (α -galactosidase, β -glucosidase) enzymes in soil with a history of poultry manure applications (Bowles et al., 2014). Long-term application of solid cattle manure increased the activity of protease, β -glucosidase, histidase, and urease enzymes in soil, compared to soils and soils receiving inorganic N fertilizer, no fertilizer (Fauci and Dick, 1994) or an equivalent amount of crop residue (Giacometti et al., 2013). The application of $90 \text{ m}^3 \text{ ha}^{-1}$ liquid pig manure to a silt loam soil increased acid phosphatase, alkaline phosphatase, arylsulfatase, urease, and dehydrogenase activities in the 0-15 cm soil layer after 28 days, compared with inorganically fertilized and unamended soils (Lalonde et al., 2000). The activity of the extracellular protolytic enzymes is not well correlated to N mineralization, perhaps because they are involved in protein depolymerization and peptide hydrolysis, and the reaction products are not small enough to be adsorbed into microbial cells where NH4 + is produced. Bacterial and fungal cells produce the extracellular lysosomal enzyme N-acetyl-β-D-glucosaminidase, which breaks chemical bonds in glycosides and amino

sugars (Hussain et al., 1992; Silva et al., 2004) and this enzyme was strongly correlated (P < 0.001) with N mineralization in soil incubated under aerobic conditions at 20 °C (r=0.87) and at 30 °C (r=0.95) for 20 weeks (Tabatabai et al., 2010). However, soils tested by Tabatabai et al. (2010) did not have a history of manure application, so it is not known if manuring affects the production of *N*-acetyl- β -D-glucosaminidase and its ability to release NH₄⁺ in manure-amended soil.

Another reason that extracellular enzyme activity is not always related to plant-available N concentrations is that biotic and abiotic conditions control the NH_4^+ production and consumption in microbial cells, as well as NH_4^+ released through cell lysis, referred to as mineralization-immobilizationturnover (M-I-T; Schimel and Bennet, 2004). Stoichiometric homeostasis in the C:N ratio of microbial cells suggests that C availability regulates NH_4^+ retention or excretion from microbial cells (Geisseler et al., 2010). If C and N mineralization occurs concurrently (Fig. 5), the C:N ratio of manure may be a better indicator of N mineralization and immobilization rates than the extracellular enzyme activity in manure-amended soil. Typically, a manure with C:N ratio [>]15 results in N immobilization (Beauchamp and Paul, 1989; Chadwick et al., 2000; Qian and Schoenau, 2002; Webb et al., 2013), although practical recommendations suggest that manure with a C:N ratio of 10-25 will be mineralized during the growing season in the cold humid temperate region of Quebec, Canada (Table 3; CRAAQ, 2010). In principal, the C:N ratio of manure should be a good indicator of N mineralization in soils when C and N mineralization reactions proceed at similar rates. This assumption is probably appropriate for solid manure that contains C-rich polymers from primary and secondary cell walls of plant materials, which must be decomposed to expose the intracellular proteinaceous compounds to enzymatic hydrolysis. These sequential reactions may take weeks, months, or years to occur, depending on the particle size of the manure, soil physico-chemical properties, and climatic conditions.

In liquid and slurry manures, the plant-available N concentration is not related to the extracellular enzyme activity or the C:N ratio of the manure because C and N mineralization processes are uncoupled. Liquid and slurry manures contain labile C substrates that are not associated with proteins contained in undigested plant cells, such as volatile fatty acids. The concentration of volatile fatty acids fell to a non-detectable level within 6 days of pig slurry application and was likely a substrate for microbial metabolism since soluble NH_4^+ and NO_3^- were immobilized in the first 3 days after slurry application to meet microbial N demands (Kirchmann and Lundvall, 1993).

Likewise, Sørensen and Amato (2002) observed short-term N immobilization for 14 days after liquid pig manure was applied. The high concentrations of dissolved organic C in six dairy lagoon effluents (containing from 27 to 80 mg dissolved organic C L⁻¹) also caused N immobilization during the first 7 days after soil was amended with liquid dairy effluent (Heinrich and Pettygrove, 2012). Manure-derived sterols comprise 10-13% of colloidal C in liquid pig manure (Dinel et al., 1998) and may temporarily stop N mineralization, based on a report that β -sitosterol, the main sterol of higher plants, inhibited N mineralization for up to 14 days in a sandy soil (Heumann et al., 2013). After labile C substrates are depleted, NH4⁺ production will soon exceed NH4 ⁺ consumption to maintain homeostasis in the C:N ratio of microbial cells. Although the initial rate of plant-available N release is not easy to predict in liquid and slurry manures, in practice these manures can be considered a good source of NH4 + with a higher N fertilizer value due to their higher NH4⁺:total N ratio (0.35–0.74; Zebarth et al., 1996; Thomas et al., 2015) than the NH4⁺:total N ratio of 0.02–0.25 in solid manure (Hao et al., 2016; Thomas et al., 2017a) during the growing season in cold humid temperate regions (Table 2; OMAFRA, 2009).

3.1.2.2.2 Ammonia Oxidation and Nitrification Reactions Plantavailable N in manure-amended soil includes the NH4 ⁺ contained in the manure, the NH₄⁺ mineralized from organic N, and the NO₃⁻ produced from ammonia oxidation and nitrification reactions. Ammonia oxidation is carried out by ammonia oxidizing archaea (AOA), mostly in the phylum Thaumarachaeota, and ammonia oxidizing bacteria (AOB) of the betaproteobacteria and gammaproteobacteria groups. Both AOA and AOB possess the amoA gene that encodes ammonia monooxygenase, an intracellular enzyme found in the membrane and cytoplasm that is responsible for NH_4^+ oxidation (Prosser and Nicol, 2012). The Thaumarchaeota are more abundant in soil amended with dairy cattle manure and other organic materials, and populations are lower when NPK fertilizer is added (Chan et al., 2013; Levičnik-Höfferle et al., 2012). This implies that manure with a high NH4⁺ concentration could support larger populations of AOB, whereas manure with relatively more organic N should favor AOA populations, although population size should not be confused with biological activity. Sterngren et al. (2015) reported larger AOA populations in microcosms of grassland soil amended with an amino acid mixture, but gross nitrification rates were related to AOB activity. More research is needed to understand the contribution of AOA and AOB to ammonia oxidation and the

consequences for nitrification. However, the rapid conversion of NH_4^+ to NO_3^- after manure application (Griffin, 2007) results in NO_3^- being the dominant form of plant-available N in most manure-amended soils (Chantigny et al., 2001; Paul and Beauchamp, 1994).

3.2 Agronomic Practices Affecting the Plant-Available N Concentration in Manure-Amended Soil

Organic N mineralization in manure-amended soil is highly variable under field conditions, even when the same manure source is considered. For example, 0-50% of the organic N contained in solid cattle manure is mineralized in the first year after its application (Chae and Tabatabai, 1986; Chescheir et al., 1986; Kirchmann and Lundvall, 1993; Paul and Beauchamp, 1994; Serna and Pomares, 1991). Similarly, Van Kessel and Reeves (2002) found net N mineralization over a 56 day period ranged from -29% to 55% of the applied organic N in 107 dairy manures from Maryland, Pennsylvania, Virginia, New York, and Connecticut, USA. Negative values indicate that net immobilization exceeded net N mineralization during the study. This variation can be attributed, in part, to differences in manure physico-chemical characteristics and soil conditions. Agronomic decisions that affect the N fertilizer value of manure include: the manure storage system, the application rate, method, placement and timing of manure applications, and the prior history of manuring on agricultural fields. The next sections discuss how these agronomic practices can be optimized to increase the N fertilizer value of manure.

3.2.1 Manure Storage Systems

In cold humid temperate regions, farmers transfer the manure generated from livestock raising facilities into a storage system that is designed to prevent nutrient losses into the environment. The manure storage system must be large enough to accommodate the animal wastes produced on the farm, depending on the barn cleaning method (i.e., whether the barn will be cleaned with water, or the animal waste will be mixed with bedding) and account for additional wastes that are mixed with the manure (e.g., runoff from the barnyard, wastewater from the milkhouse). The capacity of the manure storage is based on the volume of waste that will be generated, how long it will be retained before the storage is emptied, and whether precipitation will enter the storage (Hillborn, 2010).

Liquid and slurry manure storages include lagoons, in-ground, and aboveground concrete tanks. These storages may be open to the atmosphere or covered with materials that are permeable (e.g., straw, geotextile, foam) or impermeable (e.g., inflatable plastic, floating plastic, wood/steel, concrete) (Bluteau et al., 2009; English and Fleming, 2006). Emissions of NH₃ (g) and greenhouse gases from liquid manure storages are affected by the surface covering. In a storage with liquid pig slurry, a layer of chopped straw (5-15 cm deep, floating on the surface) reduced the volatilization of NH₃ (g) by about 80%, while swelled clay (i.e., 10 cm layer of Pegülit M perlite) reduced NH₃ (g) emissions by 91%, compared to an uncovered storage (Hornig et al., 1999). These permeable materials were less effective than an impermeable floating film, which reduced NH_3 (g) loss by 99% and virtually eliminated odors. Emissions of N2O and CH4 are greater when liquid manure storages are covered with straw than left uncovered, likely because labile C compounds in the straw stimulated denitrification and methanogenesis, and the straw cover created anaerobic conditions by limiting O2 diffusion into the storage (Amon et al., 2006). The lowest greenhouse gas emissions from dairy cattle slurry were achieved by converting the storage into an anaerobic digester (Amon et al., 2006), with the added benefit that anaerobic digestion of slurry produced biogas for on-farm use. However, anaerobic digestion for biogas production leads to several changes in manure properties such as the NH4⁺ concentration, pH, and C:N ratio, all of which alter the N fertilizer value of the digestate. A study comparing pig slurry and four types of anaerobic digestates as fertilizer for wheat production showed that pig slurry was a better source of NH4⁺ with greater N mineralization potential, but similar ammonium oxidation rates, as anaerobic digestate (Abubaker et al., 2012). The N fertilizer value of anaerobic digestate is similar to that of liquid and slurry manures. Sieling et al. (2013) found that crops had an apparent N recovery of 54-70% from anaerobic digestate, which was comparable to the apparent N recovery of 51–70% from cattle slurry and liquid pig manure under the same growing conditions. Variation in the apparent N recovery from these manure sources was related to the crop rotation and field conditions.

Solid manure is generally stored on a concrete pad with runoff collection and may be uncovered or covered. Both permeable and impermeable materials are used to cover solid manure. Kopke (1995) reported that covering manure heaps with clay or stone meal possessing high exchange capacity, or with a layer of organic residues having a high C content, were effective in reducing NH₃ (g) emissions. Hansen et al. (2006) noted a 12% reduction in NH₃ (g), 99% less N₂O, and 88% lower CH₄ emissions from a pile of solid pig manure covered with an airtight 0.15 mm polyethylene sheet, compared to an uncovered pig manure pile. Some jurisdictions allow temporary storage of uncovered solid manure in fields where it is to be applied. For example, straw-bedded manure or woodchip-bedded poultry manure from broiler facilities may be stored in agricultural fields in Quebec, Canada, although the pile may not contain >2000 kg P₂O₅, and must be spread on a nearby cultivated parcel by the next growing season; also, it must be placed in a location where there is minimal risk of nutrient runoff from the pile to surface water bodies (Government of Quebec, 2017). The N fertilizer value of solid manure depends on its C:N ratio at the time of application, soil texture, and the cropping system where it is applied in the cold humid temperate region of Quebec, Canada (Table 4). Alternatively, the N fertilizer value may be estimated from its organic N content. In New York, 35% of organic N applied in solid cattle manure and 55% of organic N in solid poultry manure are considered to be plant-available N in the application year (Ketterings et al., 2005).

3.2.2 Modification of Manure During the Storage Period

Manure may be modified during the storage period through physical, chemical, and biological processes. Drying and pelletizing manure causes a physical change, reducing the moisture content, and changing the geometry of the excreta. Commercial poultry operations often transform manure from laying hens and broilers into a dry pellet, known as pelletized poultry manure, to reduce the manure volume and odor. Pelletized poultry manure contains from 3% to 7% N (Adeli et al., 2015; Acti-Sol, 2017), suggesting that the process conserves the N excreted by poultry, consistent with the estimated loss of 2% of total N as NH₃ (g) during pelletization (Webb et al., 2014).

The physical separation of solids from the liquid fraction of manure is another strategy to improve handling and conserve the N fertilizer value of the manure. Liquid and slurry manures typically contain <25% solids (Table 1), which settle in the storage (e.g., earthen tank, concrete tank, lagoon). Removal of these sediments often entails mixing and re-suspending the solid fraction before the material is pumped into a tanker truck for transport and land application. Since mixing of solid and liquid fractions stimulates NH₃ (g) loss (Amon et al., 2006), it should be done infrequently. Solid separation from liquid manure relies on physical principles, such as settling basins where manure solids are collected after a period of time, or mechanical approaches with inclined or vibrating screens, screw presses, and centrifuges (Hjorth et al., 2010). The addition of bentonite clay or polyacrylamide polymers to enhance flocculation and sedimentation of the solids is recommended to enhance physical separation (Henriksen et al., 1998; Hjorth et al., 2010). Mechanical separation involves the addition of polyacrylamide polymers and multivalent ions (e.g., aluminum sulfate, ferric chloride) to coagulate solids and precipitate phosphorus compounds from the liquid fraction (Hjorth et al., 2008; Oh et al., 2005). Solid recovery on a 1 mm screen was 90-94% of total suspended solids when pig slurry was treated with cationic polyacrylamide polymers having a moderate-charge density (20%), whereas only 5-14% of the suspended solids were recovered from untreated pig slurry (Vanotti and Hunt, 1999). Separated solids may be applied directly to farmland, composted, or undergo anaerobic digestion to generate biogas, before the digestate is land applied. The separated liquid fraction can be reused for barn cleaning, purified with ion exchange materials (e.g., zeolites) to remove nutrients before water is released to the environment (Henriksen et al., 1998) or applied to cropland as nutrient-rich irrigation water (Béline et al., 2004). The separated liquid fraction of dairy slurry was a good fertilizer for perennial grassland (tall fescue, Festuca arundinacea Schreb.), and resulted in a yield gain of >2 Mg dry matter ha^{-1} and an extra 75 kg N ha^{-1} uptake, compared to untreated dairy slurry (Bittman et al., 2011).

Solid separation is an effective means of reducing volatilization of NH₃ (g) from liquid and slurry manures. Stevens et al. (1992) demonstrated that the solid fraction of mechanically separated slurry (<0.4 mm) had about 50% lower NH₃ (g) emissions than untreated cattle slurry, and that volatilization of NH_3 (g) could be virtually eliminated by acidifying the slurry to pH 6.5 before the mechanical separation process. Solids separated from liquid manure are rich in N. Solids separated from pig slurry contained 2.7–3.2kg NH₄-NMg⁻¹ and 7.3–8.2kg total N Mg⁻¹, while the liquid fraction had $0.01-0.12 \text{ kg NH}_4-\text{NMg}^{-1}$ and $0.08-0.37 \text{ kg total NMg}^{-1}$, depending on the separation procedure and farm characteristics (Béline et al., 2004). Similarly, Chantigny et al. (2007) reported that solids separated from pig slurry contained 2.3-3.5 kg NH₄-Nm⁻³, slightly lower than the $3.76 \text{ kg NH}_4\text{-Nm}^{-3}$ in untreated pig slurry, with 3.0--5.1 kg total N m⁻³ in the separated solids and 5.5 kg total Nm^{-3} in the untreated pig slurry. Although the separated solid fraction of pig slurry was not as effective as an equivalent amount of mineral N fertilizer, its application resulted in greater dry matter and N uptake by timothy (Phleum pretense L., a perennial forage grass) on loam and sandy loam soils than untreated pig slurry (Chantigny et al., 2007). They concluded that the solid fraction of pig slurry had a greater N fertilizer value than untreated pig slurry, based on the forage N uptake and reduction in NH_3 (g) loss measured after solid separation.

3.2.2.1 Composting

Composting is the passive or active decomposition that occurs naturally due to the action of saprophytic microorganisms and other soil biota present in solid manure that is mixed with straw, wood, paper, and other fibrous materials. Passive composting occurs when manure is stockpiled, covered, and left to decay for an extended period (i.e., months to years) before the manure pile is loaded into a spreader and applied to an agricultural field. Passive composting tends to be a slow decomposition process because uneven aeration and limited oxygen diffusion through the pile mean that some C-rich substrates are fermented to CH₄, organic acids, and alcohols. Better aeration and moisture control in active composting systems should favor aerobic decomposition, which produces CO2 and water, and stimulates N mineralization (Linn and Doran, 1984). Larney et al. (2000) demonstrated a greater volumetric reduction of beef cattle manure mixed with barley straw bedding when it was composted in summer with regular turning (72% volume lost) compared to passive aeration composting (55% volume lost). Composting during winter months resulted in greater volumetric loss from active (51%) than passive (34%) processes, even when the air temperature was as low as -30 °C (Larney et al., 2000).

Active composting may occur in animal pens or in a designated area outside the barn. A compost bedded pack barn is a free-stall building where cattle walk about and rest on a 0.3–0.5 m deep layer of bedding, normally dry wood shavings or sawdust (Barberg et al., 2007). Fresh shavings or sawdust are added when the bedding pack becomes wet and sticks to the animals. The bedding is regularly aerated to a depth of 20-25 cm, as often as twice a day in dairy cattle barns, which removes excess humidity, enhances aerobic decomposition, and provides a fresh surface for cows to lie on when they return from the milking parlor or feeding area (Barberg et al., 2007). Active composting also occurs when beef cattle are placed in winter housing with a solid bedding pack. Kapuinen (2001) reported an indoor housing system where beef cows and their calves enter pens with a shallow litter layer (0.1–0.2 m deep, of straw alone or straw mixed with peat and woodchips). About 4-5 mm of litter is added each day, resulting in an accumulation of 1.1–1.4 m of litter after 8 months. The trampling action of cattle hooves causes physical fragmentation of the bedding and mixes fresh manure with older bedding and feces. As a result, the bedding pack is composted and maximum temperatures of 50–55 °C were recorded at a depth of 15–25 cm below the surface of the straw bedding pack (Kapuinen, 2001). Composting was confirmed by mass loss of 23-38%, total N loss of 2-20%, and NH₄-N loss of

Physico-Chemical Properties	Top Layer (0–30 cm)	Middle Layer (30–60 cm)	Bottom Layer (60–90 cm)
Dry matter (gkg ⁻¹)	337	334	314
pH	9.3	9.4	9.7
Electrical conductivity (dSm^{-1})	2.9	2.7	2.5
Total C (gkg^{-1} dry matter)	451	466	458
Total N (gkg ⁻¹ dry matter)	12	14	16
NH ₄ -N	2	5	4
Р	1.8	3.7	3.7
К	18	17	18

 Table 5
 Selected Physical and Chemical Properties of Beef Manure Compost Generated

 From a 90 cm Deep In-barn Compost Bedded Pack System

Data from Pagliari, P.H., Laboski, C.A.M., 2013. Dairy manure treatment effects on manure phosphorus fractionation and changes in soil test phosphorus. Biol. Fertil. Soils 49, 987–999.

53–76% during the 8-month study (Kapuinen, 2001). Composted bedding pack contains 12–16 kg total NMg^{-1} and 2–5 kg NH_4 - NMg^{-1} (Table 5), similar to other solid cattle manures (Table 1). Active composting also occurs when outdoor beef cattle pens accumulate a bedding pack, although the composting process may slow or cease temporarily if the bedding pack freezes or becomes saturated with water.

Bedding, urine, and feces removed from animal pens can undergo active composting when the manure is piled in windrows and aerated by regular mixing. Turning the pile with a front-end loader or a windrow turner will fragment the manure and simulate saprophytic microbial activity. Active composting is also facilitated by adding water if the pile is too dry, mixing a bulking agent with the pile to facilitate air flow and adsorb excess moisture, installing a plenum to increase aeration, inoculating the pile with desirable microflora and fauna, and by adding C-rich or nutrient-rich substrates to optimize microbial action (Poincelot, 1975). The progress of active decomposition is monitored by measuring the temperature of the pile regularly, since composting is characterized by the length of the thermophilic and mesophilic phases, followed by the maturation (curing) phase. The length of each phase is dependent on the physico-chemical characteristics of the starting material, temperature and moisture conditions that control biological activity in the pile.
Considerable mass loss from water evaporation, CO2 and nutrient emissions occur during active composting. Eghball et al. (1997) found 15-20% mass loss from beef cattle feedlot manure after 110 days of active windrow composting, and the compost had 45-62% less total C, 19-43% lower total N, and 7–16% less total K with negligible changes in total P, Ca, and Mg. In a comparable study, Adams et al. (2004) reported that 25-62% of N was lost from beef cattle manure following active composting. During a 280-331 day period, stockpiled manure lost 23% N and composted manure lost 46% N, compared to fresh beef cattle feedlot manure (Larney et al., 2006). The reduction in N content was attributed to gaseous N losses (NH₃ (g), N2O, and N2), since runoff N represented a negligible loss pathway in the cold semi-arid temperate climate where this study occurred. In the early thermophilic stage, NH_3 (g) losses predominate because NH_4^+ from urea hydrolysis and N mineralization is susceptible to volatilization, depending on the pH, porosity, and air movement within the windrow (Larney and Hao, 2007). Composting of beef cattle manure produced about 23% of farm-level NH₃ (g) emissions, and the rest of the farm-level NH₃ (g) losses was emitted from housing (feedlots, barns) and pastures on beef farms in Alberta, Canada (Chai et al., 2014). Ammonia oxidation and nitrification reactions predominate in the mesophilic phase of composting, leading to a decline in the NH_4^+ concentration and accumulation of NO_3^- . For example, the NH4⁺ concentration decreased from 2270 to 500 mg $NH_4 kg^{-1}$ and there was an increase of $6-550 mg NO_3 kg^{-1}$ during active composting of beef cattle manure (Larney and Hao, 2007). The NH4⁺ and NO3⁻ in compost are susceptible to gaseous loss through nitrification and denitrification reactions. During a 3-month summer storage period, more N_2O was lost from composted dairy manure (0.58 g N_2O kg⁻¹ dry matter) than stockpiled dairy manure $(0.40 \text{ g N}_2 \text{O} \text{ kg}^{-1} \text{ dry matter})$ and slurry $(0.10 \text{ g N}_2 \text{ O kg}^{-1} \text{ dry matter})$, whereas beef cattle manure emitted 0.16 g $N_2O \text{ kg}^{-1}$ dry matter when composted, $0.03 \text{ g} N_2O \text{ kg}^{-1}$ dry matter when stockpiled and $0.02 \text{ g N}_2 \text{O kg}^{-1}$ dry matter when stored as a slurry (Pattey et al., 2005). Chemical changes in composted and stockpiled manure indicate that N2O emissions were the result of nitrification during the initial decomposition phase, with a low level of denitrification throughout the storage period.

Since relatively more C than N is lost during the composting process, compost often has a lower C:N ratio than fresh manure. Sharifi et al. (2014) reported that fresh beef cattle manure on straw and woodchip bedding had C:N ratios of 15 and 22, respectively, which was higher than the composted manure with straw bedding (C:N ratio = 12) and composted manure with woodchip bedding (C:N ratio = 18). Based on the relatively low C:N ratio, high NO₃⁻ concentration and its physical characteristics (e.g., small particle size compared to undecomposed manure), composted manure is considered to be a good source of plant-available N. Although Loecke et al. (2004) reported 10% greater corn grain yield and greater soil NO₃⁻ concentration with composted pig manure than fresh pig manure, Wilkinson (1997) found lower N use efficiency of bermudagrass fertilized with composted broiler litter (7% N use efficiency) than fresh broiler litter (15% N use efficiency), and these manures were poor N fertilizers compared to mineral fertilizer (58% N use efficiency). Thus, composting does not guarantee an improvement in the N fertilizer value of manure. The benefits obtained from composting (e.g., less water content, greater plant-available nutrient concentration) must be balanced against the economic costs and nutrient losses that occur during composting. It can be expensive to establish and maintain a farm-scale composting facility, and the appreciable NH₃ (g) and N₂O losses that occur during composting can be avoided by applying fresh manure directly to farmland.

3.2.3 Manure Application Rate, Method, Placement, and Timing

Nutrient management programs stress the importance of applying manure as a fertilizer to meet crop yield targets. Therefore, manure application rates are calculated to provide some of the N required by the crop, particularly in jurisdictions where manure applications are limited by soil test P levels or the soil P index (Daniel et al., 1998; Kuipers and Mandersloot, 1999; Mallarino et al., 2002). A good nutrient management program should not apply manure at rates that exceed the agronomic nutrient requirements. When the N input from manure exceeds crop N demands, there is a risk of N loss to the environment (Ninh et al., 2015; Qian and Schoenau, 2002; Sharifi et al., 2011). However, low application rates of manure may not sustain crop production, requiring the application of supplemental N sources (e.g., legume residues, inorganic N fertilizer) to support crop N needs. Sharifi et al. (2011) found that soil mineralizable N pools did not increase proportionally when greater N inputs from semi-solid cattle manure were applied, suggesting that there was a limit to the ability of soil to retain organic N from manure. The plant-available N losses increased exponentially when the manure application rates exceeded this limit (Sharifi et al., 2011).

Once the right manure application rate is known, it is important to calibrate the application equipment to ensure that manure is applied uniformly across the field, since high spatial variability in manure applications reduces crop yield across fields (Eghball et al., 2000). The application method and time of manure spreading are selected to minimize NH3 (g) losses. In general, fresh manure spread on the soil surface should be incorporated as soon as possible to reduce the NH_3 (g) loss (Table 3). Lauer et al. (1976) described NH₃ (g) emissions from surface-applied manure in field plots as a three-stage process characterized by a (1) rapid peak in NH₃ (g) loss within the first 24h due to high partial pressure of NH_3 (g) in the manure, followed by (2) moderate NH₃ (g) loss as manure dried in the next 2-4 days, and (3) lower, sustained NH₃ (g) emissions from urea hydrolysis up to 7 days. Solid dairy manure applied to the soil surface of field plots in New York in January lost as much as 85% of the NH_4^+ , while applying the same manure source in April led to a 61-85% decline in NH4⁺ concentration in 6 days before the plots were cultivated for corn planting (Lauer et al., 1976). Ammonia losses represented 24-33% of the NH4⁺ in liquid dairy cattle manure that was left on the soil surface of fields in Ontario for 6-7 days in May (Beauchamp et al., 1982). Liquid manure should be injected into the soil and surface-applied solid manure must be incorporated with tillage equip-

ment as soon as possible after application, to conserve the N fertilizer value of these manures (Table 3; Webb et al., 2014). Increasing the depth of manure injection or incorporation from 5 to 10 cm can be considered for further abatement of NH_3 (g) and N_2O (g) emissions, since deeper burial of manure increases the diffusion path to the soil surface of these reactive N gases while promoting the biological reduction of N_2O to N_2 (Webb et al., 2010).

Direct injection is also suitable for grasslands. Thompson et al. (1987) found that injecting dairy cattle slurry in a perennial ryegrass sward reduced NH₃ (g) losses to about 2 kg NH_3 -Nha⁻¹, whereas 77 kg NH_3 -Nha⁻¹ was lost from slurry applied to the sward in winter and 53 kg NH_3 -Nha⁻¹ was lost from spring-applied slurry. More denitrification occurred in swards receiving winter-applied slurry than spring-applied slurry, and the N uptake by ryegrass was 12–27% greater with spring-applied slurry (Thompson et al., 1987). Agricultural producers are advised to apply manure during the growing season, rather than in the autumn when crop growth slows or ceases. Manure spreading in winter is strongly discouraged or forbidden by nutrient management legislation (Government of Quebec, 2017).

Although manure spreading during the growing season (spring-summer) should result in higher N use efficiency and support higher crop yields (Tables 3 and 4), it is not always possible. Producers in the cold humid temperate regions cite logistics as the reason for spreading manure in the autumn/postharvest period. For example, they may have more time in autumn than spring to complete the work, drier soil conditions in autumn lessen the risk of soil compaction from manure tankers in the field, and the producer may need to empty their manure storage before winter when it is impossible to enter fields due to snow and frozen/wet soil conditions. In Canada, between 15% and 54% of manure is applied in the autumn/ postharvest period (Yang et al., 2011). This contributes to a pool of soil residual NO₃⁻ that is susceptible to leaching and denitrification during the winter (Zebarth et al., 2005, 2009). Using the NCSOIL model, Burger and Venterea (2008) predicted N availability from solid dairy manure, turkey litter, and liquid hog manure and found no difference in the N fertilizer value of manure applied in late autumn and spring but there was higher NO3⁻ leaching potential from the autumn-applied manure in the U.S. Midwest. Clark et al. (2009) predicted more NO₃⁻ loss when pig slurry was applied in autumn than spring to clay soils, due to the higher N mineralization and nitrification rates in clay versus loamy soils in Quebec, Canada. As well, organic N from manure is mineralized and nitrified during the winter months, albeit slowly, and the accumulated NH_4^+ and $NO_3^$ pools are susceptible to denitrification in the spring thaw period when soils are temporarily saturated following snowmelt in cold humid temperate regions (Chantigny et al., 2002, 2014).

Applying manure in autumn is proposed to increase N mineralization, particularly from manure containing straw or woodchip bedding with a high C:N ratio, thus liberating plant-available N for the subsequent growing season. However, Thomsen (2004) reported no difference in the N fertilizer value of poultry manure without bedding, with straw bedding, and with woodchip bedding when these materials were applied in autumn to a loamy sand in Denmark. The N use efficiency of the autumn-applied manures was about 15% for the spring barley crop, and this increased to 33–43% when the same manure source was applied in spring before planting the barley. This is consistent with the observation that manure with C:N ratio <10–25 has lower N fertilizer value when applied in autumn than in the spring/summer period (Table 4).

3.2.4 Manuring History

Long-term (\geq 8 year), repeated manure applications increase the soil organic N concentration, and some of this organic N is potentially mineralizable

(Mallory and Griffin, 2007; Sharifi et al., 2011, 2014; Whalen et al., 2001). Decay series are a method to estimate the organic N mineralization from soil with a history of manure applications. For beef cattle manure, Pratt et al. (1973) estimated the decay series was 0.35, 0.10, 0.05, and 0.02, meaning that 35% of total N in manure was plant-available in the first year and 10%, 5%, and 2% of the total N applied was plant-available in the second, third, and fourth year after application, respectively. In contrast, 90% of the total N in poultry manure was plant-available in the first growing season while 75%, 4%, and 1% of the total N in pig manure was plant-available in the first, second, and third growing seasons (Pratt et al., 1973). According to Gilbertson et al. (1979), approximately 90% of the total N in poultry manure (laying hens) and pig manure is plant-available in the first growing season, whereas solid dairy and beef feedlot manure continues to be a source of plant-available N in the second, third, and fourth growing seasons. In New York state, a 3-year decay series was used to estimate the proportion of organic N that was released as plant-available N in the first year of application and in subsequent growing seasons. Depending on the manure source, 25–55% of the organic N became plant-available in the first year, with the greatest residual N obtained from poultry manure. In the second and third growing seasons, an estimated 12% and 5% of the organic N from manure was transformed into plant-available N, regardless of the manure source (Ketterings et al., 2005). However, the ¹⁵N recovery in perennial ryegrass (Lolium perenne L.) from ¹⁵N-labeled poultry manure was only 6% and 2% in the second and third years after application, indicating low residual N from poultry manure relative to crop demands (Thomsen, 2004). Therefore, predictions of N availability from decay series should be validated with site-specific measurements of organic N mineralization and crop N uptake

Another way to evaluate the residual N is to measure the soil N supply, a measure of the NH_4^+ and NO_3^- concentrations plus plant N uptake in manure-amended soil. Mallory and Griffin (2007) found that soil with a 13-year history of beef manure applications supplied approximately 173 kg N ha⁻¹ more than unamended (control) soil. The residual N from previous manuring represents a supply of 150–300 kg N ha⁻¹ during the current growing season (Lynch et al., 2004), which is consistent with the 60–228 kg N ha⁻¹ supplied following 10 years of semi-solid beef cattle manure in eastern Canada (Sharifi et al., 2011). Variation in the soil N supply is expected due to differences in manure sources, as well as site-specific edaphic and climatic factors. Sharifi et al. (2014) noted significantly higher crop N uptake in

(Haney et al., 2001).

long-term (8-year) plots that received beef cattle manure with straw-based bedding than beef cattle manure containing wood-based bedding. Bedding material affected the decomposition and N mineralization processes, and also altered the soil N supply in these manure-amended soils.

Manuring history needs to be documented on farms because the incremental increase in soil organic N from manure is a reserve of plant-available N that counts as an "N credit" when calculating the N application rate for crops. It is challenging to assign an N credit from historical manuring due to the difficulty in predicting N mineralization based on manure composition (Van Kessel and Reeves, 2002), and uncertainties about site-specific mineralization rates, considering variation in cropping practices, agronomic management, soil, and climatic conditions (Mallory et al., 2010; Nyiraneza et al., 2012). While fertilizer guidebooks often attribute an N credit to manure applied in the previous growing season (e.g., Table 6), there is no widelyaccepted method to verify the N credit from historical manure applications. Field-based soil tests that document the soil NH_4^+ and NO_3^- concentrations in spring or early summer cannot predict the rates of NH_4^+ and NO_3^-

Manure Source	Crop This Year	Nitrogen Credit (kg Nha ⁻¹)
Liquid pig manure	Cereal	4
	Corn	4
	Hayfield	5
Dairy slurry	Cereal	11
	Corn	8
	Hayfield	18
Solid dairy manure	Cereal	20
	Corn	10
	Hayfield	29

Table 6 Nitrogen Credit (in kg Nha⁻¹) Attributed to the Application of 100 kg Total Nha⁻¹ in the Previous Growing Season, According to the Manure Source and Crop That Will Be Grown This Year

The N credit can be adjusted according to site-specific factors such as soil texture and the C:N ratio of the manure source.

Adapted from Centre de référence en Agriculture et Agroalimentaire du Québec (CRAAQ), 2010. Guide de référence en fertilisation, second ed. (in French). Centre de référence en Agriculture et Agroalimentaire du Québec, Québec, Canada, p. 519.

production later in the growing season, during growth stages that are critical for the development of crop yield. In-season N mineralization of solid dairy manure often peaks between mid-August and early September in the cold, semi-arid temperate climate of Idaho, according to Lehrsch et al. (2016). In the cold humid temperate region, winter- and spring-sown cereals are normally harvested by early to mid-August, so late-season N mineralization is unlikely to contribute to yield improvements. However, long-season grasses, corn, and other crops that are harvested in late September to October may benefit from N mineralization at this time. Techniques to assess the N credits from historical manure applications need to be developed to improve N fertilizer management and increase N use efficiency of crops growing in manure-amended soils.

4. METHODS TO PREDICT THE NITROGEN FERTILIZER VALUE OF MANURE IN COLD HUMID TEMPERATE REGIONS

The N fertilizer value of manure is the sum of the plant-available N, mostly $\rm NH_4^+$, in the manure applied this year, plus the $\rm NH_4^+$ and $\rm NO_3^-$ released from organic N mineralization and nitrification of this year's manure and historical manure applications. Several approaches are used to assess the N fertilizer value of manure, including soil testing in the laboratory and field, plant testing in controlled and field environments, and simulation models.

4.1 Laboratory-Based Soil Tests to Estimate the N Fertilizer Value of Manure

The NH₄⁺ in manure at the time of application can be considered equivalent to an ammonium-based inorganic N fertilizer because the soluble NH₄⁺ is biologically available. Organic N present in manure must be mineralized to release NH₄⁺, and may be estimated in the laboratory. The potentially mineralizable N method developed by Stanford and Smith (1972) is a 20-week aerobic soil incubation evaluates NH₄⁺ and NO₃⁻ released from N mineralization and nitrification reactions in a well-aerated soil at 35 °C. Sharifi et al. (2011) extended the incubation period to 44 weeks and lowered the incubation temperature to 25 °C for manure-amended soils from a cold humid temperate region because they found that

more time was needed to reach a plateau in the cumulative $NH_4^+ + NO_3^-$ concentration. The potentially mineralizable N is then calculated with a first order kinetic model:

$$N_{\min} = N_0 \left(1 - \mathrm{e}^{-kt} \right) \tag{4}$$

where N_{\min} is the cumulative N mineralized at time *t*, N_0 is potentially mineralizable N, and *k* is the mineralization rate constant (Curtin and Campbell, 2008). Other calculation methods include (1) a first order and logistic equation called FLOG, developed by Gillis and Price (2011), (2) a combined zero order and first order model (Bernal and Kirchmann, 1991; Dessureault-Rompré et al., 2013), and (3) a double exponential model (Cabrera and Kissel, 1988; Wang et al., 2004). Net N mineralization (net N_{\min}) is the mineral N (NH₄⁺ plus NO₃⁻) accumulated during the incubation period:

net
$$N_{\min} = (NH_4^+ + NO_3^-)_t - (NH_4^+ + NO_3^-)_{t0}$$
 (5)

where t_0 is the initial time and t is the end of the incubation period. Positive values indicate that mineral N production exceeds its consumption, while negative values suggest that N immobilization occurred, assuming no gaseous or soluble N losses during the incubation.

In manure-amended soils, potentially mineralizable N is generally described with more complex kinetic models because these soils contain multiple forms of organic N with varying degrees of susceptibility to decomposition and N mineralization. Sharifi et al. (2007, 2011) explained that potentially mineralizable N is derived from three distinct pools in manure-amended soils. Pool I contains labile organic N that is transformed into $NH_4^+ + NO_3^-$ following soil rewetting in the first 2 weeks of the aerobic incubation at 25 °C, and it is not included in the calculation of N_0 . Manure characteristics and application rates have more influence on Pool I than the other two pools (Nyiraneza et al., 2012; Sharifi et al., 2011). Pool II is the cumulative N mineralized between 2 and 44 weeks, representing an intermediate pool of mineralizable organic N. Pool III is the difference between N_0 , predicted by the kinetic model, and Pool II. The assumption is that stable organic N in Pool III could mineralize if the incubation period extended beyond 44 weeks (Sharifi et al., 2007, 2011). Aerobic soil incubations are considered a good estimate of the plant-available N supply, but they are too long for routine soil test analysis. Considerable effort has focused on identifying one or more parameters related to the potentially mineralizable N that may be used as a quick indicator of the plant-available N supply in manure-amended soils.

4.1.1 Manure Properties Related to the Potentially Mineralizable N in Manure-Amended Soils

Physico-chemical properties of manure are expected to influence the mineralization of organic N, and the C:N ratio of solid manure is often used as indicator of its N fertilizer value (e.g., Table 4). Qian and Schoenau (2002) found the organic C:total N ratio of various animal manures, with and without bedding, was negatively correlated to the potentially mineralizable N and more strongly in a sandy loam soil (r=-0.71) than a clay loam soil (r=-0.51). Similarly, Morvan et al. (2006) found that N mineralized from a variety of non-composted and composted manures during a 224 day aerobic incubation at 15 °C was inversely correlated with the C:N ratio of the amendment (r=-0.74). This is consistent with the expectation that manure with a lower C:N ratio releases more mineral N than manure with a high C:N ratio.

In contrast, an investigation of 107 liquid, semi-solid, and solid dairy manures by Van Kessel and Reeves (2002) revealed that organic C:organic N and organic C:total N ratios were not correlated with net N mineralization during 56 days of aerobic incubation in a sandy loam soil, but significant relationships were found between net N mineralization and the acid detergent fiber:total N ratio (r=0.351), the cellulose:total N ratio (r=0.344) and the lignin:total N ratio (r=0.239). This suggests that N mineralization depended more on the chemical composition of C compounds than the organic C content. Net N mineralization during 199–224 day aerobic incubations was positively correlated with manure properties such as the soluble C extracted by neutral detergent (r=0.73; Morvan et al., 2006) and the organic N concentration (r=0.63-0.68; Chadwick et al., 2000; Morvan et al., 2006). In addition, potentially mineralizable N was strongly related ($R^2=0.87$) to the water-soluble organic N concentration in poultry manure during a 112 day aerobic incubation at 25 °C (Qafoku et al., 2001).

Nitrogen mineralization is related to microbial metabolism of labile organic C compounds in manure, which produces CO_2 under aerobic conditions. Castellanos and Pratt (1981) found that the CO_2 evolved in the first week after manure addition was positively correlated (r=0.92-0.95) with the N mineralization from various manures (pig, poultry, beef, sheep, dairy) in a 10-month aerobic incubation, which is consistent with Gilmour et al. (1985),

who reported that CO₂ evolution was strongly correlated to N mineralization for a variety of crop residues and sewage sludge (r=0.90-0.995). Similarly, Haney et al. (2001) found the CO₂ released during a 24h period was related to N mineralized during a 24 day incubation ($R^2 = 0.78$ and 0.93) and forage N uptake ($R^2 = 0.93$ and 0.91) in two soils amended with dairy cattle manure. In poultry manure-amended soil, the uric acid concentration was the best predictor of the rapidly mineralizable N (r=0.96), while the total C concentration and C:N ratio were the best predictors of the slowly mineralizable N (r = -0.71 and r = -0.73, respectively), based on a two-pool non-linear kinetic model that estimated potentially mineralizable N during a 112 day aerobic incubation (Gordillo and Cabrera, 1997). Amino sugars are also abundant in manure; fresh dairy manure contained the amino sugars glucosamine (2.4 mgg^{-1}) and galactosamine (2.0 mgg^{-1}) and their mineralization would release about 187 and 156 mg Nkg⁻¹ of manure, respectively (Jost et al., 2013b). Although the C:N ratio continues to be a popular indicator of the N fertilizer value of manure, the labile organic C and N concentrations in manure are considered to be better indicators of potentially mineralizable N because these compounds are metabolized readily by microorganisms involved in N mineralization (Cabrera et al., 2005).

4.1.2 Soil Properties Related to the Potentially Mineralizable N in Manure-Amended Soils

After manure is incorporated into soil, organic N is partitioned into several fractions, including the microbial biomass N (MBN), water extractable organic N (WEON), particulate organic matter N (POMN), and light fraction organic matter N (LFOMN) fractions. Collectively, these organic fractions represent about 20% of the total soil N pool (Haynes, 2005). The organic N contained in these fractions is heterogeneous, not mutually exclusive and has variable susceptibility to N mineralization. Given that labile organic N compounds contribute to N mineralization (Ros et al., 2011; St. Luce et al., 2014), these fractions may be indicators of potentially mineralizable N in manure-amended soils.

4.1.2.1 Microbial Biomass

The MBN fraction accounts for 3–5% of total soil N pool (Murphy et al., 2000) and represents the soil's biodiversity and capacity to mediate soil biogeochemical reactions. The metabolic activities of microbial biomass control decomposition and virtually every reaction in the soil N cycle. In addition, microbial biomass contributes to soil organic N formation through the stabilization of necromass and microbial byproducts (Kallenbach et al., 2016; Knicker, 2011). Soil microbial biomass is considered the most labile organic N fraction in soil (Smith and Paul, 1990), and may produce or consume NH_4^+ and NO_3^- (Brookes, 2001). The balance between production (i.e., net N mineralization) and consumption (i.e., net immobilization) depends on substrate availability, abiotic factors such as wetting and drying that affect the size and activity of the microbial biomass, as well as biotic conditions that affect the turnover and size of the standing stock biomass (Geisseler et al., 2010).

Some authors report that manure-amended soils have twofold or more MBN than inorganically fertilized and unfertilized soils (Jost et al., 2013b; McGill et al., 1986; Rochette and Gregorich, 1998), while others report similar MBN concentration in manure-amended and non-manured soils (Jensen et al., 2000; Thomas et al., 2016). A metadata analysis by Kallenbach and Grandy (2011) reported 36% more microbial biomass C and 27% more MBN in organically amended soils than those receiving inorganic fertilizer. Although MBN was suggested as an indicator for plant-available N (Burton and McGill, 1992; Carter and MacLeod, 1987; Deng et al., 2000), this idea has not gained momentum because the dynamic nature and rapid turnover time of the microbial biomass mean that it is constantly renewed and thus it does not show a directional shift as the cumulative $NH_4^+ + NO_3^-$ concentration increases during aerobic incubations. Paul and Beauchamp (1996) confirmed that greater microbial biomass in manured soil did not result in higher net N mineralization than urea fertilizer in soils under corn production, suggesting that MBN is unlikely to be a good indicator of plant-available N.

4.1.2.2 Water-Soluble Organic Matter Fractions

The WEON represents about 0.75% of total soil N (Curtin et al., 2006) and is defined operationally as organic N compounds that were extracted with deionized water and passed through a 0.45 μ m filter (Zsolnay, 2003). The WEON includes dissolved organic N compounds that exist naturally in the soil solution and are extracted with low ionic strength aqueous solution (0.01 *M* CaCl₂) or deionized water at room temperature. The WEON contains soluble organic N compounds that are susceptible to breakdown by hydrolytic enzymes in soil solution, or if sufficiently small, they may be assimilated into microbial cells (Burford and Bremner, 1975; McGill et al., 1986). The biodegradability of WEON will depend on its molecular size, chemical structure, and polarity as well as soil properties and microbial

communities (Marschner and Kalbitz, 2003). The WEON concentration is greater in manure-amended soils (Gregorich et al., 2003) and is related to soil N mineralization (Appel and Mengel, 1998; Murphy et al., 2000; Tian et al., 2010).

Another way to isolate WEON is to extract it with stronger ionic solutions (e.g., 1 M KCl) or hot water. The hot-WEON method involves sequential extraction with deionized water at room temperature, followed by placing a soil-deionized water slurry in a hot water bath (50–80 °C) for 16 h, and finally extracting WEON with 2 M KCl to remove adsorbed NH₄⁺ from the heat induced hydrolysis of organic N (Chantigny, 2003; Ghani et al., 2003; Curtin et al., 2006). The hot water extraction thermally degrades labile organic N, may release clay fixed NH₄⁺ into solution, and likely includes lysed microbial biomass, reflecting M-I-T processes (Chantigny et al., 2010). Hot-WEON was composed of carbohydrates and N-containing compounds (amino-N species and amides) in soil with a long-term history of manure and mineral fertilizer applications (Leinweber et al., 1995).

In laboratory incubation studies, the hot water extractable organic carbon (hot-WEOC) fraction was strongly correlated (r=0.86-0.90) to N mineralization in a wide-range of soils, including soils from sheep and cattle pastures (Ghani et al., 2003; Ros et al., 2011). Curtin et al. (2017) compared the N mineralization during a 14-week aerobic incubation at 25 °C to rapid bioassays such as N mineralization after 2-week aerobic incubation, anaerobically mineralizable N (7 day incubations at 25 and 40 °C) and the CO₂ release after soil rewetting, as well as soil extractable and organic matter pools. In 130 soils from New Zealand, they found the best prediction of N mineralization (N_{\min} in mg Nkg⁻¹) was obtained from the model:

$$N_{\rm min} = a + b_1 \,{\rm Hot} - {\rm WEON} + {\rm LU} + b_2 \,{\rm SUVA} \,R^2 = 0.91$$
 (6)

where *a* is the intercept, b_1 and b_2 are regression coefficients, Hot-WEON concentration is in mg Nkg⁻¹, LU is the land use (pastoral vs. cropped) and SUVA is the specific UV absorbance measured in the hot water (single) extract at 260 nm. Still, it is not clear whether the hot-WEON concentration is a good predictor of N mineralization in manure-amended soils. While the WEON originating from poultry manure was strongly related to N_0 during a 112 day aerobic incubation at 25 °C ($R^2 = 0.87$; Qafoku et al., 2001) and the hot-WEON fraction was the best indicator of potentially mineralizable N in a silty clay soil, the hot-WEON was not a good predictor of N mineralization in a sould be sold to make the al., 2015). Similarly,

the hot-WEON concentration was not a good estimator of the mineral fertilizer equivalent N of 15 organic fertilizers because it did not reflect the readily-mineralizable N concentration of slaughterhouse wastes (i.e., meat meal, bone meal, blood meal, and feather meal powders; Delin et al., 2012). When these products were excluded, the hot-WEON concentration was positively correlated to the inorganic N fertilizer equivalent of excreta and crop residues ($R^2 = 0.62$; Delin et al., 2012). Further investigation of the relationship between hot-WEOC, hot-WEON, and potentially mineralizable N is needed to resolve these contradictions.

4.1.2.3 Physically Uncomplexed Organic Matter

Soil organic matter is composed primarily of solid materials that are associated with soil minerals, occluded within aggregates or exist without strong bonding to soil minerals. The physically uncomplexed organic matter is a possible substrate for N mineralization since it is relatively more accessible for decomposition than mineral-associated organic matter and is derived from animal manure and other sources. Particulate organic matter (POM) is the organic matter (i.e., animal excreta, plant tissues, animal tissues, and microbial cellular debris) that is physically separated by size separation (>53 µm) of sand-sized materials (Baisden et al., 2002; Gregorich and Beare, 2008). Larger, partially decomposed residues that are recovered in a solution with greater density than water (generally $1.6 \,\mathrm{g \, cm^{-3}}$ using sodium polytungstate or sodium iodide; Cerli et al., 2012) are referred to as light fraction organic matter (LFOM; Gregorich et al., 1994). Metadata analysis showed that manure and other organic amendments increased the POM content by 29% and the LFOM by 39% in agricultural soils, due to direct inputs from the organic amendment plus the indirect inputs from the crop, which produced more biomass in amended soils than unfertilized soils (Gosling et al., 2013). In 65 agricultural soils, the average N concentration in the POMN and LFOMN fractions represented 18% and 5% of the total soil N, respectively (Gregorich et al., 2006). Manure applications increased the soil POMN content (Griffin and Porter, 2004; Mallory et al., 2010; Nyiraneza et al., 2010; Sharifi et al., 2011; Spargo et al., 2011) and the soil LFOMN content (Marriott and Wander, 2006; Wu et al., 2005).

The POM has a relatively small physical size and is depleted in carbohydrates and aliphatic compounds, compared to undecomposed organic residues. Aoyama et al. (1999) showed that the POM in soil receiving solid dairy cattle manure had a lower C:N ratio than POM originating from crop residues. Decomposition of POMN is followed by N mineralization (St. Luce et al., 2014) and Sharifi et al. (2008) found the POMN concentration was strongly related ($R^2 = 0.50-0.73$) to field-based indices of the N supply in soils with a 13-year history of organic amendments. Furthermore, Sharifi et al. (2011) found that the POMN concentration increased in proportion to the size of Pool I, the NH₄⁺ + NO₃⁻ concentration measured in the first 2 weeks of the aerobic soil incubation at 25 °C, in manure-amended sandy and clayey soils. In soils receiving N-rich crop residues, the POMN concentration is an indicator of potentially mineralizable N (Spargo et al., 2011; St. Luce et al., 2014; Wilson et al., 2001) and this may also be the case for manure-amended soils, as POMC (r=0.87) and POMN (r=0.83) were strongly correlated to the N supply to wheat in a 42 day incubation study of manure-amended sandy loam and silty clay soils (Thomas et al., 2016).

The LFOM is larger in size and has greater carbohydrate, aliphatic, and lignin content than POM (Gregorich et al., 2006). Ruminant manure contains a large proportion of undigested fibrous plant material from their diet and bedding, hence contributes more organic residues to the soil LFOM fraction than other manures. Due to its size and slight degree of decomposition, the LFOM fraction is unlikely to be a good indicator of N mineralization in manure-amended soils. Whalen et al. (2000b) reported that the LFOM was a sink for N in agricultural and forest soils, regardless of management practices. In fact, the mineral-associated organic matter fraction, not the LFOM, contained the highest organic C and N concentrations in soil amended with cattle manure (Courtier-Murias et al., 2013). The LFOMN fraction is a transient pool that must be fragmented and decomposed into smaller physical size fractions before it is solubilized to water-soluble compounds that undergo N mineralization, so it is unlikely to be a robust indicator of plant-available N in manure-amended soils.

4.2 Field-Based Soil Tests to Estimate the N Fertilizer Value of Manure

Field-based soil tests are an alternative to laboratory evaluation of the potentially mineralizable N concentration in manure-amended soils. These tests require timely collection and analyses of samples collected from the field, and results are used to make interpretations about the $\rm NH_4^+$ and $\rm NO_3^-$ supply to crops during the growing season. Samples may be collected once a year, at a pre-determined time or crop growth stage, or they may be taken at regular intervals throughout the year. The test may measure $\rm NH_4^+$ and NO_3^- , or a mineralizable organic N pool that will be a source of plantavailable N during the growing season.

Field-based soil tests that rely on punctual sampling include the pre-plant soil N test (PPNT) and the pre-sidedress soil N test (PSNT), which measure the soil NO_3^- concentration once during the growing season. The $NO_3^$ concentration is an indicator of the plant-available N level, particularly in fields that received manure or were planted with legumes (Walters, 1995). The PPNT uses composite samples, typically collected from 0–30 to 30–60 cm soil layers in the spring. Soil samples are transported on ice to the laboratory, where they are extracted with 2M KCl (1:5 soil:solution) and analyzed for NO_3^- . The PPNT is done in the spring so the producer can select the appropriate N fertilizer rate before planting corn or adjust the N fertilization of winter wheat at the tillering stage. The PPNT is most successful at predicting the N fertilizer response of the corn or cereal crop in fields where manure was applied (53–61% success rate) in cold temperate regions of the U.S. Midwest (Brouder and Mengel, 2003; Walters, 1995).

The PSNT method follows the same soil sampling and analysis procedures, but the sampling time differs because the PSNT is designed to adjust the sidedress N fertilizer rate for corn. Therefore, the test is done at the V4–V6 growth stage of corn, prior to the sidedress N fertilizer application. The PSNT is responsive to differences in soil NO₃⁻ concentrations due to pre-plant N fertilizer inputs and manure applications, and is suitable to predict the likelihood of N fertilizer response on manure-amended soils (67–85% success rate; Brouder and Mengel, 2003; Heckman et al., 1995; Walters, 1995). The regional N fertilizer rate (i.e., based on yield potential and field management history) is applied when the PSNT (0–30 cm depth) is <10 mg NO₃–Nkg⁻¹, and the N fertilizer rate declines with increasing PSNT values. Generally, no sidedress N fertilizer is recommended when the PSNT level is >25 mg NO₃–Nkg⁻¹, since the soil contains sufficient N to meet corn requirements (Brouder and Mengel, 2003).

The PPNT and PSNT methods are useful to assess the NO_3^- concentration in manure-amended soils, which frequently have ample N to support crop production. These tests are limited in their ability to predict the plant-available N supply during the growing season because the measurement is taken once, prior to planting or in the early crop growth stages (Walters, 1995). Also, the soil NO_3^- concentration is the product of nitrification and is a poor predictor of the potentially mineralizable N. In addition, the soil NO_3^- level cannot reflect the year-to-year variation in crop N demands that depend on the weather and other factors that affect the yield

potential, such as soil moisture, compaction, and pest pressure. While the PPNT method is a fairly robust indicator of plant-available N for manure-amended soils in semi-arid climates (Brouder and Mengel, 2003; Thomas et al., 2017b; Walters, 1995), the spring rainfall pattern in cold humid temperate regions is characterized by frequent, heavy precipitation events that reduce the accuracy of N recommendations based on PPNT and PSNT methods (Sharifi et al., 2007; St. Luce et al., 2011).

An alternative to soil NO₃⁻ testing is the amino sugar test, also known as the Illinois soil N test (ISNT) that analyzes amino sugar N in soil hydrolysates (6 M HCl) from composite soil samples (0-30 cm depth; Mulvaney et al., 2001). Amino sugar N is a potentially mineralizable fraction of soil organic N that is affected by previous legume crops and manuring history. Soils from corn fields in Illinois with $< 200 \,\mathrm{mg \, kg^{-1}}$ of amino sugar N were responsive to N fertilizer applications (Mulvaney et al., 2001). Evaluation of the ISNT method in other regions showed its ability to predict N-responsive corn fields in North Carolina (Wall et al., 2010) but the test had limited predictive ability for corn N requirements in Virginia (Spargo et al., 2009). In the cold humid temperate climate of New York, the ISNT alone was a poor predictor of crop N response, but when both ISNT and SOM content were considered, a response index was developed for sidedress N fertilizer applications on corn silage fields (Klapwyk and Ketterings, 2006). Characterization of the soil hydrolysates extracted with 6 MHCl revealed a high proportion of monomeric amino sugars from bacterial cell walls (95% recovery) and amides (55% recovery) but not alpha amino acids or chitin, an amino sugar polymer from fungal cell walls (Kwon et al., 2009). Consequently, an increase in the ISNT level can be expected when manure-amended soils have more bacterial growth, and this was confirmed in corn fields amended with compost and liquid manure (Klapwyk et al., 2006). The ISNT extracts some of the amino acids and amino sugars present in soil and produced during manure decomposition, so it cannot fully represent the mineralizable organic N pool in manure-amended soils.

4.2.1 In Situ Measurement of Plant-Available N

Regular measurements of the plant-available N concentration may be achieved *in situ* with ion exchange membranes (IEMs). These ion-selective membranes are fabricated from cross-linked copolymers of vinyl monomers and functionalized with positively charged groups such as $-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$, or negatively charged groups (e.g., $-SO_3^-$, $-COO^-$, $-PO_3^{2-}$, $-PO_3H^-$, $-C_6H_4O^-$; Xu, 2005). The functional groups

repels like charges and binds ions with the opposite charge through electrostatic attraction, so IEMs placed in contact with the soil will exchange counter-ions present on the membrane surface with ions from the soil solution. The diffusion gradient created at the membrane surface increases adsorption of ions from the soil solution, until equilibrium is attained between ions in soil solution and on the membrane surface (Bremer et al., 2014). The IEMs represent a sink for ions and reflect the cumulative interception and adsorption of ions through time, analogous to the passive adsorption of ions by roots. Consequently, Qian and Schoenau (1995) reported a stronger relationship ($R^2 = 0.86$) between canola N uptake and the IEM - NO₃ $^{-}$ concentration (i.e., on anion exchange membranes) buried in the soil for 2 weeks than 1 h. Generally, IEMs placed in the same environmental and edaphic conditions as plant roots absorb NH4⁺ and NO₃⁻ in similar proportions as crops, so IEM measurements are correlated with crop N uptake (Cambouris et al., 2014; Nyiraneza et al., 2011; Sharifi et al., 2009; Ziadi et al., 1999). Under field conditions, León Castro and Whalen (2016) reported significant correlations between the IEM-NO₃-N concentration and arugula N uptake in sandy clay loam (r=0.86, p<0.01) and sandy loam (r=0.71, p<0.05) soils amended with pea-oat green manure.

The main advantage of IEMs is that they are an effective surrogate for plant N uptake and reflect the dynamics of plant-available N during the growing season. Researchers may choose to use commercial Plant Root Simulator (PRS®) probes, ion exchange resin membranes held in plastic supports that are easily inserted into soil to measure the ion supply in situ with minimal disturbance, or they can prepare IEMs in another suitable configuration for their experiment. The IEMs may be placed into root exclusion cylinders to measure soil N supply in the absence of root competition in annual crop systems, but this is generally not feasible with established perennial crops. Cumulative N adsorption to IEMs is correlated with plant nutrient uptake during the same period of time. For instance, the canola N uptake was correlated with the available N supply rate estimated from IEMs in soils amended with liquid pig manure and urea (r=0.79-0.96; Qian and Schoenau, 2000) and with 13 types of solid cattle, poultry, and pig manure (r=0.47-0.80; Qian and Schoenau, 2002). The available N supply rate from IEMs was not related to the C:N ratio of solid manure, indicating that factors such as the degree of manure decomposition and manure chemistry were influencing N mineralization (Qian and Schoenau, 2002), but IEMs provide a good indication of the available N supply rate of diverse organic amendments, including poultry manure compost, feather meal, alfalfa meal, and vermicompost (Hammermeister et al., 2006). The dynamics of NH_4^+

and NO_3^- absorption by IEMs at 15 day intervals reflected a change in short-term N immobilization to N mineralization in pots amended with poultry manure on woodchip bedding, which was a poor N fertilizer for wheat (Thomas et al., 2016).

Relationships between IEMs and crop N uptake were generally derived from pot studies, so researchers and practitioners must be aware that IEMs have limited ability to adsorb ions in hot, dry soil conditions. Also, IEMs and plant roots may compete for a limited supply of NH_4^+ and NO_3^- when plant-available N concentrations are low (Qian and Schoenau, 2002). In field experiments, replicate IEMs should be deployed to capture the spatio-temporal variability in NH_4^+ and NO_3^- concentration and provide a good estimate of the *in situ* plant-available N dynamics.

4.3 Plant-Based Tests to Estimate the N Fertilizer Value of Manure

Plant-based tests are the most direct way to determine what proportion of the manure N was acquired by plants in controlled studies or under field conditions. This measurement will account for the uptake of NH_4^+ from manure, as well as the uptake of plant-available N released from organic N mineralization during the growth period. The presence of plants stimulates the N mineralization rate. Unlike aerobic incubations, where plantavailable N accumulates during the study, plant roots continuously remove $\mathrm{NH_4}^+$ and $\mathrm{NO_3}^-$ from the soil solution. This may create competition for NH4⁺ and NO3⁻ with microorganisms, stimulating production of extracellular enzymes for decomposition and N mineralization (German et al., 2011). Carbon-rich root exudates are substrates for heterotrophic microorganisms, which may activate microbially-mediated reactions and support preferential substrate utilization (Kuzyakov, 2002). Thomas et al. (2016) noted that wheat plants stimulated N mineralization from poultry-litteramended soils, resulting in 31-66% more N uptake in the wheat by 45 days after planting than in unplanted soils. The N fertilizer value of manure is determined from plant N uptake in controlled pot studies in growth benches and greenhouses, and in field studies.

4.3.1 Pot Studies of Plant-Available N

Pot studies to determine the N fertilizer value of manure are preferred when researchers wish to compare multiple manure sources and application rates for one or more crops (e.g., Hammermeister et al., 2006; Qian and Schoenau, 2002). Each pot contains a known amount of well-homogenized

soil and is planted with a known number of seeds from the crop of interest. Replicate pots are prepared for each manure treatment, and every manure source is mixed and sieved to produce a uniform amendment. After preparation, pots are placed in a growth bench or greenhouse with controlled or semi-controlled environmental conditions (e.g., temperature, light intensity, photoperiod, relative humidity, soil moisture, CO₂ concentration, and so on). Pot studies must include an unfertilized control, to determine the proportion of plant N uptake that can be attributed to the manure NH4⁺ input plus organic N mineralization. Basal fertilization with P, K, and other nutrients may be added to the unfertilized control and the manure-amended pots to prevent deficiencies of these nutrients, so that comparisons are based solely on the manure N input. A fertilized control containing water-soluble N fertilizer such as calcium ammonium nitrate, urea, or urea ammonium nitrate solution may be included in the experiment. Plant N uptake and N use efficiency are compared in the fertilized control and the manure-amended pots to determine the inorganic N fertilizer equivalent value of manure. Plant biomass and N concentration are measured at least once (i.e., at physiological maturity or a selected growth stage), but can be evaluated repeatedly at regular intervals, preferably by preparing enough replicates that pots are removed from the experiment for destructive sampling to avoid confounding effects associated with subsampling or resampling plant tissues. Other plant growth parameters (e.g., height, leaf area, chlorophyll content, net photosynthesis rate), and relationships between plant growth and soil-based measures of plant-available N, can be compared in the manure-amended and control pots.

The N fertilizer value of manure and other organic amendments is easily determined from pot experiments. Delin et al. (2012) grew perennial ryegrass in pots amended with 15 organic fertilizers, including 5 manure sources, 3 plant-based residues, powders from meat, bone, blood and feathers, sewage sludge, biogas residue, and mussel compost. The inorganic N fertilizer equivalent of each amendment was calculated as the fraction of total N or organic N in the amendment that was adsorbed by ryegrass after 4 and 10 weeks of growth. The inorganic N fertilizer equivalent values were 6–8% of total N in horse manure and mussel compost, about 50% of the total N in chicken manure, dairy slurry and pig slurry, and as high as 70–80% of total N for biogas residue, feather meal, and blood meal powders (Delin et al., 2012). In another pot experiment with perennial ryegrass, Chadwick et al. (2000) found that N mineralization from the organic N fraction of manure supplied 2% of plant N uptake for a dairy cattle slurry, 6% for beef cattle farmyard manure, 37% for pig slurry, and 56% for poultry (layer) manure. Nitrogen mineralization ranged from 1.6% to 55.7% of applied organic N in the manure, indicating that mineralizable organic N depended on the manure type.

Pot studies are a cost-effective, rapid method to quantify the N fertilizer value of manure, but as they are conducted in controlled environments, it is challenging to extrapolate the results to the field-scale. A major limitation of pot studies is that they cannot accurately reflect the priming effect of manure on soil organic matter mineralization, which is may be over-estimated in pots due to restricted root growth, regular watering and higher temperatures in growth benches and greenhouses. As well, it is difficult or impossible for pot studies to simulate the range of application methods and timing of manure application that occurs in agricultural fields. Conclusions about the N fertilizer value of manure need to be validated by quantifying the plant N uptake from manure under field conditions.

4.3.2 Field Studies of Plant-Available N

Field studies rely on agronomically-relevant rates of manure that are applied at specific times during the year with farm-scale equipment. The proportion of manure N that is taken up by the crop during the growing season is measured, as well as the residual soil N that was mineralized during the non-growing season (Jayasundara et al., 2010) or lost from the field through gaseous and leaching losses (Chantigny et al., 2014; Zebarth et al., 2009). The N fertilizer value of manure in field studies may be determined from the soil N supply calculator, by comparing the N use efficiency of manure to inorganically fertilized plots, or through a partial mass balance approach that uses ¹⁵N stable isotopes to track manure N transformations in the soil-plant system, and account for N losses in agricultural drainage and gaseous forms.

The Agriculture and Horticulture Development Board (2017) calculates the soil N supply (SNS, in kg N ha⁻¹) as an indicator of the in-season N fertilizer requirements:

$$SNS = Soil mineral N + Crop N + Mineralizable soil N$$
 (7)

where the soil mineral N (kg N ha⁻¹) is the NH₄⁺ + NO₃⁻ concentration in the potential crop rooting depth, crop N (kg N ha⁻¹) is the total N content of the crop at the time of sampling for soil mineral N, and mineralizable soil N (kg N ha⁻¹) is the estimated amount of N that will be mineralized from organic N compounds from the time of sampling for soil mineral N until the end of the growing season. Conceptually, the SNS approach provides an accurate account of the plant-available N level in the soil and crop at the sampling time (i.e., from planting to early vegetative growth stages) and predicts the plant-available N release from organic N during the rest of the growing season. Practically, there is no universally accepted method to predict the mineralizable soil N concentration, with since the N mineralized during short-term aerobic and anaerobic incubations and its relationship to soil extractable and organic matter fractions varies with land use, crop type, and manuring history (Curtin et al., 2017; Zebarth et al., 2005), although Sharifi et al. (2007) reported good success in relating the Pool I plus soil mineral N concentration at planting to the end-of-season soil N supply.

Nitrogen use efficiency is a plant-based approach that describes the N content in plant biomass (i.e., marketable biomass or total above-ground biomass) relative to the external N inputs, which may include fertilizer, manure, and N_2 fixation. There are several ways to express the result, each of which has advantages and disadvantages (Cassman et al., 2002; Ladha et al., 2005). For example, the apparent N recovery (ANR, in percentage) is calculated as:

$$ANR = (U - U_o)/N_A \tag{8}$$

where the difference in N content of the fertilized crop (U, in kg Nha^{-1} derived from the crop yield (kg dry matter ha^{-1}) × crop N content (kg N kg⁻¹ dry matter)) and the unfertilized control $(U_0, \text{ kg N}ha^{-1})$ is divided by the N applied $(N_A, \text{kg N ha}^{-1})$ (Crasswell and Godwin, 1984). When this calculation is used to estimate the ANR from manure, it assumes that: (1) organic N mineralization rates are the same in the manure-amended and unfertilized control soils, (2) there is no other N input to manure-amended and unfertilized control soils, such as atmospheric deposition or N₂ fixation by endophytic, associative, or symbiotic bacteria, (3) soil physico-chemical properties like moisture, temperature, aggregation, SOM content, and pH are identical in the manure-amended and unfertilized control soils, and (4) there is no difference in plant-induced feedbacks (i.e., priming effects) in the manure-amended and unfertilized control soils. Clearly, the ANR and similar measures of N use efficiency will be hampered by the fact that manuring, particularly in fields that receive manure on a regular (annual) basis, induces changes in soil physico-chemical and biological properties that affect crop N uptake.

Finally, the fertilizer N value of manure can be evaluated with a partial N mass balance. This method tracks the proportion of plant-available

N from manure that is taken up by the crop, plus it accounts for the nonassimilated NH_4^+ and NO_3^- from manure that is retained in the soil, transformed into soil organic N fractions or lost from the agroecosystem via leaching and in gaseous forms. The fate of manure N may be determined by measuring net changes in these N pools in manure-amended and unfertilized control plots, or measured directly with ¹⁵N stable isotope tracers. For example, the transformations of ¹⁵N-labeled liquid pig manure applied at different times (in autumn, pre-plant, at sidedressing stage) to corn agroecosystems were evaluated over a 2-year period in Ontario, Canada by Jayasundara et al. (2010). Manure applied during the growing season supplied more N to corn (46-57% of manure N) than manure application in the autumn (22-28% of manure N). In the second year of corn production, 2-8% of the residual manure N was recovered in the corn crop (Jayasundara et al., 2010). Leaching accounted for 8–15% of applied N from ¹⁵N-labeled pig manure and 16–29% of applied N was lost in gaseous forms, mostly as N₂O and N₂ because NH₃ losses were lower (7% of applied N) (Jayasundara et al., 2010). Similarly, corn N uptake accounted for 26-48% the N applied from ¹⁵N-labeled pig manure (Chantigny et al., 2014), while winter wheat accumulated 32% of the N from ¹⁵N-labeled cattle slurry applied in autumn (Jensen et al., 2000). In these cold humid temperate regions of these field studies, over-winter losses were approximately 20-23% of the applied N (Chantigny et al., 2014; Jensen et al., 2000).

Estimating the partial N mass balance from transformations of ¹⁵Nlabeled manure is a direct way to measure the N fertilizer value of manure, but it is expensive due to the cost of producing the ¹⁵N-labeled manure (i.e., the research team must first grow ¹⁵N-labeled plants that are then fed to an animal to produce the labeled manure) and analyzing plant, soil, leachate, and gas samples for ¹⁵N by mass spectroscopy. Although the results are highly accurate, there are challenges to extrapolate beyond the site-specific soil, crop, and climatic conditions of the study. However, the ¹⁵N data can be used to develop partitioning coefficients for models and calculators that estimate the N fertilizer value of manure across broader geographical regions and over longer time-scales. When it comes to calculating ANR from manure, this is likely the best method, however, it still does not account for the non-amended soils ability to supply N due to microbial scavenging of N (Craine et al., 2007; Hagedorn et al., 2003; Knicker, 2011). Regardless of the method selected, it is hard to estimate the soil N supply in a manureamended soil, especially in comparison with a non-amended soil. This makes it difficult to derive accurate coefficients of the N fertilizer value of manure, and highlights the need for producers to carefully analyze yield responses so that manure applications can be tailored to meet field-specific conditions.

4.4 Models to Estimate the N Fertilizer Value of Manure

Experimental data on plant-available N concentration, in relation to potentially mineralizable N and plant N uptake, provides insight into the biological and physico-chemical mechanisms responsible for the transformations, dynamics and fate of N in manure-amended soils. This knowledge can be integrated into mathematical models that describe the organic N transformations in manure in relationship to crop growth, either under controlled conditions or considering the field-specific edaphic and climatic factors.

Models parameterized with data from controlled studies give insight into the effect of manure characteristics or soil properties on N mineralization rates. Pansu et al. (2003) adapted the dynamic TAO (Transformation des Apports Organiques) model to describe temporal transformations of soil N following addition of organic amendments, including sheep and chicken manures. The biochemical properties of the manure influenced organic N mineralization, and a function describing the first order volatilization kinetics of NH_3 (g) was included for chicken manure. However, soil-based incubations in the absence of a plant are likely to underestimate the N mineralization of manure-amended soils (Delin et al., 2012). Considering the transformations of ¹⁵N-labeled manure and ¹⁵N recovery in ryegrass cover and spring barley crops, Sørensen et al. (2017) developed an empirical model of the estimated net N mineralization from pig and cattle slurry over a 3-year period. While more realistic, this model is limited by the fact that it is based on site-specific soil and climatic conditions. These factors were considered by Dessureault-Rompré et al. (2010), who developed a multiple regression model that predicted soil mineralizable N based on soil organic N, soil texture, and climatic variables at 120 field locations. However, such a model may be difficult to validate under field conditions because mineralizable N pools are actively replenished during the growing season (Dessureault-Rompré et al., 2013) and often estimated from laboratory-incubated soils without plants.

Dynamic models are suitable to account for the concurrent production and consumption of NH_4^+ and NO_3^- in manure-amended soils, which led

Mohanty et al. (2011) to use the SoilN module of the APSIM (Agriculture Production Systems Simulator) model to predict N mineralization from farmyard manure. Their work showed a tendency for the model to underestimate the rate of remineralization from farmyard manure, and appropriate modification to the size and C:N ratios of the fresh organic matter pools could not be determined from manure chemical analysis alone. Cavalli and Bechini (2012) considered the short-term C and N dynamics in dairy slurry-amended soil with CN-SIM, a mechanistic dynamic simulation model for the turnover of soil organic matter, using the CO_2 production and soil inorganic N concentration measured during a 180-day laboratory incubation of five dairy slurries mixed with three soil types. It was not possible to simultaneously optimize the CO₂ respiration and N mineralization, as model parameterization that simulated N remineralization correctly gave too low CO_2 (g) values. Model performance was improved by considering the temporal fluctuations in C use efficiency and the C:N ratio of microbial biomass, and by adding functions to simulate NH4 + fixation to clays and denitrification (Cavalli and Bechini, 2012). The poor estimation of M-I-T processes in the APSIM and CN-SIM models suggests that biological processes are not well described in these models. Rashid et al. (2014) showed that including the N mineralization from bacteria, fungi, protozoa, enchytraeids, and earthworms in the summed production-ecological model explained 98-107% of the N uptake measured in grasslands that were fertilized with organic N-rich slurry manure and solid cattle manure. A holistic view of soil biota involved in organic N mineralization should improve model estimates of the N fertilizer value of manure, although how this should be accomplished remains an open research question.

5. SMART SYSTEMS TO CONSERVE THE NITROGEN FERTILIZER VALUE OF MANURE IN COLD HUMID TEMPERATE REGIONS

The N fertilizer value of manure is affected by multiple factors, as discussed in earlier sections of this review. There is good evidence that some of these factors can be controlled to conserve the $\rm NH_4$ ⁺ content of manure during its collection, storage, and land application. In addition, we can test manure, soil, and monitor crop growth to determine how much plant-available N is delivered to crops in manure-amended soils. Sensor technologies combined with advanced decision-making algorithms hold promise

for improving manure handing and application at the field-scale to maximize the N fertilizer value of manure. The next sections present a conceptual basis for designing "smart systems" that integrate the latest scientific knowledge on manure management in cold humid temperate regions to maximize N retention in agroecosystems and minimize N losses to the environment, consistent with the goals of sustainable agriculture. We present examples of functional prototypes that may prove effective in this regard.

5.1 Smart Technologies for Conserving N Fertilizer Value During Manure Storage

Ammonia volatilization from manure represents about 66% of the 130 million tons year⁻¹ of atmospheric NH₃ (g) emitted by the agricultural sector in Canada (Sheppard and Bittman, 2016). Animal housing, manure storages, and grazing pastures were the source of about 44% of the NH₃ (g) lost from dairy cattle farms in Ontario, Canada, and approximately 63% of the NH₃ (g) from beef cattle operations in Alberta, Canada (Chai et al., 2014, 2016). Ammonia volatilization diminishes the N fertilizer value of manure and the reaction of NH₃ (g) with acidic gases in the atmosphere produce NH₄⁺ that associates with fine respirable particulate matter <2.5 µm, which is detrimental to human health (Sheppard and Bittman, 2016). In addition, atmospheric deposition of particulate and soluble NH₄⁺ in terrestrial and aquatic ecosystems contributes to acidification and eutrophication of the natural environment. Smart systems are needed to conserve as much NH₄⁺ as possible in livestock manure, to reverse the negative consequences of NH₃ (g) losses from livestock operations.

Poultry manure is susceptible to NH_3 (g) loss because 70–90% of the total N is in the uric acid, urea, and NH_4^+ forms (Groot Koerkamp, 1994; Pan et al., 2009). In Canada, about 22% of the NH_3 (g) loss comes from the excreted uric acid and NH_4^+ in poultry barns housing layer hens, broiler chickens, and turkeys, with an additional 2% of the NH (g) loss is attributed to volatilization of these compounds from other manure storages (Sheppard et al., 2009). Pelletization of manure from poultry layer houses, described in Section 3.2.2, could be an effective measure to conserve NH_4^+ in manure, given that <2% of total N in poultry manure is converted to NH_3 (g) in barns with a pelletization facility (Webb et al., 2014). This is due, in part, to the fact that poultry manure does not accumulate in the barn, but is collected on a conveyer belt and subject to aeration/drying as it moves gradually toward the pelletizer, as described by Rao et al. (2007). The smart

system envisioned in Fig. 6A has a humidity detector that turns on drying fans at designated locations along the manure conveyance system, to dry fresh manure to an optimal level prior to pelletizing (i.e., around 10% to achieve a harder, more durable pellet made with a 4.76-mm diameter die; Rao et al., 2007). Installing a NH₃ sensor network in the barn will provide real-time measurements of NH_3 (g) loss from the fresh manure and trigger automated responses depending on the NH₃ (g) concentration. One response would be to increase the drying rate and speed of the conveyor belt to deliver poultry manure to the pelletizer more quickly. Once the dried poultry manure is compressed into pellets, it should be relatively stable during the storage period, assuming that the storage is dry and pellets do not reabsorb water. Another response could be to spray the surface of the fresh poultry excreta with a dilute acid solution to lower the pH and reduce urease activity, which is optimal at pH 6.8-7.6 in feces (Muck, 1982). As the untreated interior of the fresh excreta may remain a hotspot for NH_3 (g) volatilization, it is recommended that the acidified poultry manure be dried to remove excess



Fig. 6 Smart systems to conserve N in manure using sensor-based networks. (A) The NH₃ sensor network will control the conveyer speed and drying rate of the poultry manure as it moves to the pelletizer. The sensor network will trigger the application of additives like dilute H_2SO_4 or alum ($AI_2(SO_4)_3 \cdot 14H_2O$) that can reduce NH₃ volatilization, if necessary. (B) The NH₃ sensor network will regulate the management of liquid manure, which can be acidified or mixed with flocculating agents to prevent NH₃ (g) loss. As well, solid-liquid separation could be initiated and the lagoon cover can be placed or removed in response to the NH₃ sensor data. A complementary in-line NO₃ sensor can support decisions about recirculating wastewater or sending it to the irrigation system.







Fig. 6—Cont'd

humidity. Alternatively, the fresh poultry manure can be treated with aluminum sulfate (alum, $Al_2(SO_4)_3 \cdot 14H_2O$). Alum lowers the pH and inhibits the growth and activity of ureolytic bacteria; as well, the H⁺ released from alum react with NH₃ (aq) to form NH₄⁺, which then reacts with SO₄²⁻ to produce ammonium sulfate, (NH₄)₂SO₄ (Cook et al., 2008). Alum must be dissolved to affect biological and chemical processes, so it will have to be added as a solution and the resulting alum-manure mixture will be dried before it is pelletized.

The lagoon manure storage presented in Fig. 6B illustrates a wireless sensor network of NH₃ detectors to quantify NH₃ (g) emissions at various locations. The smart system could be based on the design of Baskar et al. (2017), which uses a chemiresistive NH₃ nanosensor with high selectivity and sensitivity as the detector and non-linear computational model based on the modified Levenberg-Marquardt algorithm for accurate quantification of the NH₃ (g) concentration. This design has lower power demands than laser spectroscopic sensors and more complex computational models like artificial neural networks, which increases the lifespan of a battery-powered wireless sensor node (Baskar et al., 2017). However, the NH₃ nanosensor must be equipped with a microheater to improve NH₃ (g) detection at temperatures below 20° C, which are expected in unheated liquid manure storages in the cold humid temperate region.

The NH_3 sensor network (Fig. 6B) could trigger several automated responses, such as (1) addition of aluminum chloride, alum, sulfuric acid, or ferric chloride (Fangueiro et al., 2015) to lower the pH of the waste stream as it leaves the barn and (2) mix the waste stream with coagulating, precipitation, or flocculating agents (Hjorth et al., 2008), particularly those with potential to absorb NH_4^+ , like expandable clays, or alter the physicochemical properties of manure to reduce NH_3 (g) losses. Critical levels of NH_3 (g) emissions could initiate (3) mechanical solid-liquid separation, to remove the solid fraction of fecal material that contains urease, or (4) periodic application of additives on the liquid manure surface. Spraying dilute sulfuric acid or adding alum powder to lower the pH of the manure surface (Regueiro et al., 2016) is a possible low-cost alternative to costly, continuous acidification of the waste stream (Kai et al., 2008). The NH_3 sensor network could also (5) activate the placement or removal of a lagoon cover, which could be an impermeable or permeable floating cover (English and Fleming, 2006) and (6) control the mixing and aeration systems within the lagoon. Mixing should generally be avoided, as continuous agitation of the

liquid pig manure by a tractor-driven mixing pump during its removal from a covered concrete storage was responsible for the highest NH_3 (g) emissions $(0.13 \text{ gm}^{-2} \text{ s}^{-1})$ during a 7-month measurement period (Bluteau et al., 2009). If solid separation is performed, a complementary NO_3 sensor network

could be installed to make decisions about how to manage wastewater, which can be reused for barn cleaning, sent for denitrification treatment, or applied to field crops as irrigation water. Commercial ultraviolet photometers are available for similar waste streams and have the capacity to make *in situ*, real-time NO₃⁻ measurements with good accuracy. For example, the Viikinmäki municipal wastewater treatment plant serving a population of 800,000 citizens in Finland relies upon denitrification post-filtration (i.e., after secondary sedimentation) to remove approximately 90% of total N (Haimi et al., 2015). An optical sensor measures the NO₃⁻ concentration within the denitrifier unit and manipulates the wastewater flow rate and methanol addition, the carbon source for denitrifiers, through a feedback loop that is controlled by the optical NO₃⁻ sensor and input-output regression models (Haimi et al., 2015). Similar technologies exist in many municipal sewage sludge and wastewater treatment facilities (Dries, 2016) and could be adapted to the smart system envisioned in Fig. 6B.

Reducing N losses from solid manure piles requires management of the decomposition process, which is well defined for compost piles. Active composting systems are typically instrumented with thermocouples and moisture probes to make decisions about when to turn the pile, add water or incorporate bulking agents/substrates to stimulate the decomposition process. Higher temperature and moisture content in solid manure piles stimulates NH_3 (g) loss and greater N_2O fluxes. For poultry manure composted inside high-rise layer buildings, Koenig et al. (2005) noticed that

 NH_3 (g) losses peaked at 50 °C when manure contained 50–60% moisture. Controlling the moisture content, reducing the manure particle size, and adding alum were effective in reducing NH₃ volatilization. Oxygen sensors should be deployed because they give an instantaneous assessment of the biological oxygen demand, which governs the activity of thermophilic and mesophilic decomposers (Yoshida et al., 2001). Evans et al. (2017) demonstrated that a network of multiple oxygen sensors equipped with data loggers, installed at several depths and locations throughout a compost bedded pack barn, was suitable to measure differences in oxygen concentration at various depths. Monitoring the oxygen concentration will be helpful to determine the degree of aeration within the solid manure pile, which controls decomposition and N transformations like mineralization, ammonia oxidation, nitrification, and denitrification. Smart systems for solid manure will include temperature, moisture, and oxygen monitoring probes at several depths and locations, to account for spatial variability within the manure pile (Fig. 6C).

5.2 Smart Systems for Maximizing N Fertilizer Value of Field-Applied Manure

Manure application rates in the cold humid temperate region are often estimated from fertilizer reference guides (e.g., CRAAQ, 2010; OMAFRA, 2009). However, a smart system for applying manure to maximize its N fertilizer value will rely on precision agriculture technologies. Many farms already possess spatially-explicit data about their soils, drainage, hydrology, crop yields, pest control program, and other management practices, which are represented in maps with geographical coordinates. Crop assessments are carried out regularly during the growing season with in-field testing (i.e., plant tissue sampling on a weekly basis) or remote sensing (e.g., by satellite or drone-based multispectral imagery), and decision support systems are used to make N fertilizer recommendations (Goffart et al., 2011; Soderstrom et al., 2017). Dynamic simulation tools that link soil, crop, and management information with real-time weather data are proving more accurate than traditional calculators at determining optimum N fertilizer application rates (e.g., Adapt-N for maize production; Sela et al., 2017). These developments hold considerable promise to improve the N fertilizer value of manure. We envision that farms will rely on suitable manure sources (i.e., liquid and slurry manures, solid manure with C:N ratio <20) for in-season fertilization of the crop, and apply manure in several small doses at key growth stages. The smart system for field-applied manure will improve N use efficiency by splitting the N application rate and sidedressing manure during the growing season, a practice already proven to improve the agronomic efficiency of inorganic N fertilizers.

In the future, soil-based and plant-based tests will determine the N rate for manure sidedress applications (i.e., manure injection into agroecosystems with annual and perennial crops; manure spreading and incorporation beside the row of annual crops). Schmidt et al. (2009) reported that the relative green normalized difference vegetation index (GNDVI), based on light energy reflectance (590 and 880 nm) was equal to the chlorophyll meter (SPADTM) and PSNT methods in determining the economically optimum N rate for corn grain yield. The GNDVI can be obtained from tractormounted equipment (commercially available as GreenSeekerTM and Crop CircleTM), meaning that real-time assessment of plant greenness will be communicated to the tractor's computer. On-the-go adjustments of the manure volume or mass applied to soil occurs through the variable rate applicator equipment, analogous to the technologies already in use for inorganic N fertilizers (Diacono et al., 2013). Row injection is a practical method of sidedressing liquid pig manure (Coelho et al., 2006) and variable rate applicators can be retrofit onto slurry tankers, a cost-effective way to improve the precision of manure applications (Calcante et al., 2015). Equipment to sidedress or inject solid manure remains to be developed, but may involve placing the manure hopper and applicator between the tractor and an inter-row cultivator. The cultivator can be equipped with a smart design to avoid excessive soil disturbance and prevent physical damage to the crop, as described for mechanical weeders by Cordill and Grift (2011).

Variable rate manure application will account for spatio-temporal variability in the plant-available N concentration, considering within-field and seasonal fluctuations in crop N demands, and should improve manure management decisions. The algorithms that control the metering system must consider the manure $\rm NH_4^+$ plus organic N content, which will meet the crop N demand by providing soluble $\rm NH_4^+$ at sidedressing and organic N mineralization at later growth stages. Optical sensor-based algorithms already developed to estimate inorganic N fertilizer inputs for crops (e.g., Raun et al., 2005) can be modified to consider the readily-available $\rm NH_4^+$ and slowly-released $\rm NH_4^+ + \rm NO_3^-$ derived from organic N in manure. The advantage of using precision agriculture tools to calculate site-specific manure application rates is that the algorithms can also consider the soil test P level, which is documented in the spatially-explicit soil map (Haneklaus et al., 2016). This will allow producers to simultaneously adjust manure



Fig. 7 A smart system to maximize the N fertilizer value of manure applied to agricultural fields will rely on in-season multispectral crop sensing and geospatial soil maps for decision support. On-the-go variable rate adjustment is essential to match manure N inputs to the crop N demands during the pre-plant and sidedressing periods.

N application rates and apply supplemental inorganic N fertilizer as necessary to meet crop N demands, while avoiding further buildup of soil test P through manuring. The strategy presented in Fig. 7 is extremely timely, given the urgent need to control P inputs in areas where historical manure applications have contributed to P legacies that threaten water quality in cold humid temperate regions.

6. CONCLUSIONS

Defining the N fertilizer value of manure remains an elusive but noble goal. The heterogeneous nature of manure makes it challenging to predict how quickly and how much of the applied manure N is transformed into plant-available N during the growing season in the cold humid temperate region. This is exacerbated by the fact that the plant-available N concentration in manure-amended soils is generally evaluated in laboratory-based soil incubations, which are inherently biased because they reflect manure reactions in a plant-free environment that is not representative of field conditions. We still have not identified simple indicators of potentially mineralizable N from manure, probably because the decomposition and N mineralization processes in manure-amended soils involve a broad array of organic C and organic N compounds, none of which can be isolated with a simple test that predicts the plant-available N supply in manure-amended soils. Furthermore, the susceptibility of manure N to losses as NH₃ (g), other N gases and soluble N from barns, storages and soil is another barrier to extrapolate lab-based estimates of plant-available N from the laboratory to the field. The development of real-time, low-cost sensors, coupled with wireless networks for data acquisition and computationally robust software, make it possible to envision smart systems that conserve manure N and deliver it to agroecosystems in response to crop N demands. At the farm-scale, we will deploy sensor networks that provide rapid and proactive solutions to retain N in manure storages and prevent N loss to the environment. The manure removed from these storages will be more N-rich and thus have more N fertilizer value for crops. Manure N application rates must be based on crop N demands, which can be detected by optical sensors and multispectral data, and decision-support algorithms should encourage farmers to split manure applications and adopt in-season manuring practices. We need to promote the use of farm machinery that is capable to inject or incorporate solid manure, especially for sidedress applications. We need to integrate knowledge about manure N transformations into algorithms that support on-the-go variable rate application of manure, for maximum N use efficiency by the crop, environmental protection, and better economic outcomes on farms. Continued investment in sensor-based technologies will guarantee that future manure use on farms will be smarter and more sustainable.

ACKNOWLEDGMENT

Financial support to J.K.W. and M.S. from the Natural Sciences and Engineering Research Council Discovery Grants program is gratefully acknowledged.

REFERENCES

- Abubaker, J., Risberg, K., Pell, M., 2012. Biogas residues as fertilisers—effects on wheat growth and soil microbial activities. Appl. Energy 99, 126–134.
- Acti-Sol, 2017. The Mother Hen Fertilizer. Available products, http://acti-sol.ca/en/available-products/#other.
- Adams, J.R., Farran, T.B., Erickson, G.E., Klopfenstein, T.J., Macken, C.N., Wilson, C.B., 2004. Effect of organic matter addition to the pen surface and pen cleaning frequency on nitrogen mass balance in open feedlots. J. Anim. Sci. 82, 2153–2163.
- Adeli, A., Read, J.J., McCarty, J., Jenkins, J.N., Feng, G., 2015. Soybean yield and nutrient utilization following long-term pelletized broiler litter application to cotton. Agron. J. 107, 1128–1134.
- Adesanya, T., Akinremi, O., Zvomuya, F., 2016. Physical properties of an Orthic Black Chernozem after 5 years of liquid and solid pig manure application to annual and perennial crops. Can. J. Soil Sci. 96, 145–153.
- Agriculture and Horticulture Development Board, 2017. Nutrient Management Guide (RB209). UK Partnership for Crop Nutrient Management, Warwickshire, UK.

- Amon, B., Kryvoruchko, V., Amon, T., Zechmeister-Boltenstern, S., 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agric. Ecosyst. Environ. 112, 153–162.
- Angers, D.A., Rochette, P., Chantigny, M.H., Lapierre, H., 2007. Use of ¹³C abundance to study short-term pig slurry decomposition in the field. Soil Biol. Biochem. 39, 1234–1237.
- Aoyama, M., Angers, D.A., N'Dayegamiye, A., 1999. Particulate and mineral-associated organic matter in water-stable aggregates as affected by mineral fertilizer and manure applications. Can. J. Soil Sci. 79, 295–302.
- Appel, T., Mengel, K., 1998. Prediction of mineralizable nitrogen in soils on the basis of an analysis of extractable organic N. J. Plant Nutr. Soil Sci. 161, 433–452.
- Baisden, W.T., Amundson, R., Cook, A.C., Brenner, D.L., 2002. Turnover and storage of C and N in five density fractions from California annual grassland soils. Global Biogeochem. Cycles 16. 64-1–64-16.
- Barberg, A.E., Endres, M.I., Janni, K.A., 2007. Dairy compost barns in Minnesota: a descriptive study. Appl. Eng. Agric. 23, 231–238.
- Baskar, C., Nesakumar, N., Rayappan, J.B.B., Doraipandian, M., 2017. A low power ammonia sensor node embedded with a light weight non-linear analytics. Sensors Actuators A Phys. 263, 357–362.
- Beauchamp, E.G., 1986. Availability of nitrogen from three manures to corn in the field. Can. J. Soil Sci. 66, 713–720.
- Beauchamp, E.G., Kidd, G.E., Thurtell, G., 1982. Ammonia volatilization from liquid dairycattle manure in the field. Can. J. Soil Sci. 62, 11–19.
- Beauchamp, E.G., Paul, J.W., 1989. A simple model to predict manure N availability to crops in the field. In: Hansen, J.A., Henriksen, K. (Eds.), Nitrogen in Organic Wastes Applied to Soils. Harcourt Brace Jovanovich Publishers, Boston, MA, pp. 140–149.
- Béline, F., Daumer, M.L., Guiziou, F., 2004. Biological aerobic treatment of pig slurry in France: nutrients removal efficiency and separation performances. Trans. ASAE 47, 857–864.
- Bernal, M.P., Kirchmann, H., 1991. Carbon and nitrogen mineralization and ammonia volatilization from fresh, aerobically and anaerobically treated pig manure during incubation with soil. Biol. Fertil. Soils 13, 135–141.
- Birkhofer, K., Bezemer, T.M., Bloem, J., Bonkowski, M., Christensen, S., Dubois, D., Ekelund, F., Fließbach, A., Gunst, L., Hedlund, K., Mäder, P., Mikola, J., Robin, C., Setälä, H., Tatin-Froux, F., Van der Putten, W.H., Scheu, S., 2008. Long-term organic farming fosters below and aboveground biota: implications for soil quality, biological control and productivity. Soil Biol. Biochem. 40, 2297–2308.
- Bittman, S., Forge, T.A., Kowalenko, C.G., 2005. Responses of the bacterial and fungal biomass in a grassland soil to multi-year applications of dairy manure slurry and fertilizer. Soil Biol. Biochem. 37, 613–623.
- Bittman, S., Hunt, D.E., Kowalenko, C.G., Chantigny, M., Buckley, K., Bounaix, F., 2011. Removing solids improves response of grass to surface-banded dairy manure slurry: a multiyear study. J. Environ. Qual. 40, 393–401.
- Bitzer, C.C., Sims, J.T., 1988. Estimating the availability of nitrogen in poultry manure through laboratory and field studies. J. Environ. Qual. 17, 47–54.
- Blair, R., Jacob, J.P., Ibrahim, S., Wang, P., 1999. A quantitative assessment of reduced protein diets and supplements to improve nitrogen utilisation. J. Appl. Poultry Res. 8, 25–47.
- Blazewicz, S.J., Schwartz, E., Firestone, M.K., 2013. Growth and death of bacteria and fungi underlie rainfall-induced carbon dioxide pulses from seasonally dried soil. Ecology 95, 1162–1172.
- Blunden, J., Aneja, V.P., 2008. Characterizing ammonia and hydrogen sulfide emissions from a pig waste treatment lagoon in North Carolina. Atmos. Environ. 42, 3277–3290.

- Bluteau, C.V., Masse, D.I., Leduc, R., 2009. Ammonia emission rates from covered concrete manure tanks in eastern Canada. Trans. ASABE 52, 1733–1739.
- Bogomolov, D.M., Chen, S.K., Parmelee, R.W., Subler, S., Edwards, C.A., 1996. An ecosystem approach to soil toxicity testing: a study of copper contamination in laboratory soil microcosms. Appl. Soil Ecol. 4, 95–105.
- Bolger, T., Curry, J.P., 1984. Influences of pig slurry on soil microarthropods in grassland. Rev. Écol. Biol. Sol 21, 269–281.
- Borhan, M.S., Gautam, D.P., Engel, C., Anderson, V.L., Rahman, S., 2013. Effects of pen bedding and feeding high crude protein diets on manure composition and greenhouse gas emissions from a feedlot pen surface. J. Air Waste Manage. Assoc. 63, 1457–1468.
- Bouwman, L., Goldewijk, K.K., Van Der Hoek, K.W., Beusen, A.H.W., Van Vuuren, D.P., Willems, J., Rufino, M.C., Stehfest, E., 2013. Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900-2050 period. Proc. Natl. Acad. Sci. 110, 20882–20887.
- Bowles, T.M., Acosta-Martínez, V., Calderón, F., Jackson, L.E., 2014. Soil enzyme activities, microbial communities, and carbon and nitrogen availability in organic agroecosystems across an intensively-managed agricultural landscape. Soil Biol. Biochem. 68, 252–262.
- Bremer, E., Andronak, L., Greer, K., 2014. Use of ion-exchange resin membranes for nutrient management in western Canada. Crop Soils 47, 2–25.
- Brouder, S.M., Mengel, D.B., 2003. The Presidedress Soil Nitrate Test for Improving N Management in Corn. Agronomy Guide. Purdue University Cooperative Extension Service. Publication AY-314-W.
- Brookes, P.C., 2001. The soil microbial biomass: concept, measurement and applications in soil ecosystem research. Microb. Environ. 16, 131–140.
- Brzostek, E.R., Finzi, A.C., 2011. Substrate supply, fine roots and temperature control proteolytic enzyme activity in temperate forest soils. Ecology 92, 892–902.
- Burford, J.R., Bremner, J.M., 1975. Relationship between denitrification capacities of soils and total water soluble and readily decomposable soil organic matter. Soil Biol. Biochem. 7, 389–394.
- Burger, M., Venterea, R.T., 2008. Nitrogen immobilization and mineralization kinetics of cattle, hog, and Turkey manure applied to soil. Soil Sci. Soc. Am. J. 72, 1570–1579.
- Burns, R.G., DeForest, J.L., Marxsen, J., Sinsabaugh, R.L., Stromberger, M.E., Wallenstein, M.D., Weintraub, M.N., Zoppini, A., 2013. Soil enzymes in a changing environment: current knowledge and future directions. Soil Biol. Biochem. 58, 216–234.
- Burton, D.L., McGill, W.B., 1992. Spatial and temporal fluctuation in biomass, nitrogen mineralizing reactions and mineral nitrogen in a soil cropped to barley. Can. J. Soil Sci. 72, 31–42.
- Cabrera, M.L., Kissel, D.E., 1988. Length of incubation time affects the parameter values of the double exponential model of nitrogen mineralization. Soil Sci. Soc. Am. J. 52, 1186–1187.
- Cabrera, M.L., Kissel, D.E., Vigil, M.F., 2005. Nitrogen mineralization from organic residues: research opportunities. J. Environ. Qual. 34, 75–79.
- Calcante, A., Brambilla, M., Oberti, R., Bisaglia, C., 2015. A retrofit variable-rate control system for pressurized slurry tankers. Appl. Eng. Agric. 31, 569–579.
- Cambouris, A.N., St. Luce, M., Ziadi, N., Zebarth, B.J., 2014. Soil- and plant-based indices in potato production in response to polymer-coated urea. Agron. J. 106, 2125–2136.
- Carter, J.E., Jokela, W.E., Bosworth, S.C., 2010. Grass forage response to broadcast or surface-banded liquid dairy manure and nitrogen fertilizer. Agron. J. 102, 1123–1131.
- Carter, M.R., MacLeod, J.A., 1987. Biological properties of some Prince Edward Island soils. Relationship between microbial biomass nitrogen and mineralizable nitrogen. Can. J. Soil Sci. 67, 333–340.

- Cassman, K.G., Dobermann, A., Walters, T., 2002. Agreeoecosystems, nitrogen-use efficiency, and nitrogen management. Ambio 31, 132–140.
- Castellanos, J.Z., Pratt, P.F., 1981. Mineralization of manure nitrogen: correlation with laboratory indexes. Soil Sci. Soc. Am. J. 45, 354–357.
- Cavalli, D., Bechini, L., 2012. Multi-objective optimisation of a model of the decomposition of animal slurry in soil: tradeoffs between simulated C and N dynamics. Soil Biol. Biochem. 48, 113–124.
- Centre de référence en Agriculture et Agroalimentaire du Québec (CRAAQ), 2010. Guide de référence en fertilisation, second ed. Centre de référence en Agriculture et Agroalimentaire du Québec, Québec, Canada, p. 519 (in French).
- Cerli, C., Celi, L., Kalbitz, K., Gugenberger, G., Kaiser, K., 2012. Separation of light and heavy organic matter fractions in soil—testing for proper density cut-off and dispersion level. Geoderma 170, 403–416.
- Chadwick, D.R., John, F., Pain, B.F., Chambers, B.J., Williams, J., 2000. Plant uptake of nitrogen from the organic nitrogen fraction of animal manures: a laboratory experiment. J. Agric. Sci. 134, 159–168.
- Chadwick, D.R., Martinez, J., Marol, C., Béline, F., 2001. Nitrogen transformations and ammonia loss following injection and surface application of pig slurry: a laboratory experiment using slurry labelled with ¹⁵N-ammonium. J. Agric. Sci. 136, 231–240.
- Chae, Y.M., Tabatabai, M.A., 1986. Mineralization of nitrogen in soils amended with organic wastes. J. Environ. Qual. 15, 193–198.
- Chai, L.L., Kroebel, R., Janzen, H.H., Beauchemin, K.A., McGinn, S.M., Bittman, S., Atia, A., Edeogu, I., MacDonald, D., Dong, R., 2014. A regional mass balance model based on total ammoniacal nitrogen for estimating ammonia emissions from beef cattle in Alberta Canada. Atmos. Environ. 92, 292–302.
- Chai, L.L., Kroebel, R., MacDonald, D., Bittman, S., Beauchemin, K.A., Janzen, H.H., McGinn, S.M., Vanderzaag, A., 2016. An ecoregion-specific ammonia emissions inventory of Ontario dairy farming: mitigation potential of diet and manure management practices. Atmos. Environ. 126, 1–14.
- Chalova, V.I., Kim, J.H., Patterson, P.H., Ricke, S.C., Kim, W.K., 2016. Reduction of nitrogen excretion and emissions from poultry: a review for conventional poultry. Worlds Poult. Sci. J. 72, 509–519.
- Chambers, P.A., Guy, M., Roberts, E.S., Charlton, M.N., Kent, R., Gagnon, C., Grove, G., Foster, N., 2001. Nutrients and their Impact on the Canadian Environment. Agriculture and Agri-Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada and Natural Resources Canada, Ottawa, Ontario, Canada, p. 241.
- Chan, Y.K., McCormick, W.A., Ma, B.L., 2013. Effects of inorganic fertilizer and manure on soil archaeal abundance at two experimental farms during three consecutive rotationcropping seasons. Appl. Soil Ecol. 68, 26–35.
- Chantigny, M.H., 2003. Dissolved and water-extractable organic matter in soils: a review on the influence of land use and management practices. Geoderma 113, 357–380.
- Chantigny, M.H., Angers, D.A., Rochette, P., 2002. Fate of carbon and nitrogen from animal manure and crop residues in wet and cold soils. Soil Biol. Biochem. 34, 509–517.
- Chantigny, M.H., Angers, D.A., Rochette, P., Belanger, G., Massé, D., Côté, D., 2007. Gaseous nitrogen emissions and forage nitrogen uptake on soils fertilized with raw and treated pig manure. J. Environ. Qual. 36, 1864–1872.
- Chantigny, M.H., Angers, D.A., Rochette, P., Pomar, C., Pelster, D.E., 2014. Evidencing overwinter loss of residual organic and clay-fixed nitrogen from spring-applied, ¹⁵Nlabelled pig slurry. Can. J. Soil Sci. 94 (1), 18.
- Chantigny, M.H., Curtin, D., Beare, M.H., Greenfield, L.G., 2010. Influence of temperature on water-extractable organic matter and ammonium production in mineral soils. Soil Sci. Soc. Am. J. 74, 517–524.
- Chantigny, M.H., Rochette, P., Angers, D., 2001. Short-term C and N dynamics in a soil amended with pig slurry and barley straw: a field experiment. Can. J. Soil Sci. 81, 131–137.
- Chantigny, M.H., Rochette, P., Angers, D.A., Massé, D., Côté, D., 2004. Ammonia volatilization and selected soil characteristics following application of anaerobically digested pig slurry. Soil Sci. Soc. Am. J. 68, 306–312.
- Chescheir, G.M.I.I.I., Westerman, P.W., Safley, L.M.J., 1986. Laboratory methods for estimating available nitrogen in manure and sludge. Agric. Wastes 18, 175–195.
- Chiavegato, M.B., Powers, W., Palumbo, N., 2015. Ammonia and greenhouse gas emissions from housed Holstein steers fed different levels of diet crude protein. J. Anim. Sci. 93, 395–404.
- Clark, K., Chantigny, M.H., Angers, D.A., Rochette, P., Parent, L.-E., 2009. Nitrogen transformations in cold and frozen agricultural soils following organic amendments. Soil Biol. Biochem. 41, 348–356.
- Coelho, B.R.B., Roy, R.C., Bruin, A.J., 2006. Nitrogen recovery and partitioning with different rates and methods of sidedressed manure. Soil Sci. Soc. Am. J. 70, 464–473.
- Cook, K.L., Rothrock Jr., M.J., Warren, J.G., Sistani, K.R., Moor Jr., P.A., 2008. Effect of alum treatment on the concentration of total and ureolytic microorganisms in poultry litter. J. Environ. Qual. 37, 2360–2367.
- Cordill, C., Grift, T.E., 2011. Design and testing of an intra-row mechanical weeding machine for corn. Biosys. Eng. 110, 247–252.
- Courtier-Murias, D., Simpson, A.J., Marzadori, C., Baldoni, G., Ciavatta, C., Fernández, J.M., López-de-Sá, E.G., Plaza, C., 2013. Unraveling the long-term stabilization mechanisms of organic materials in soils by physical fractionation and NMR spectroscopy. Agric. Ecosyst. Environ. 171, 9–18.
- Crasswell, E.T., Godwin, D.C., 1984. The efficiency of nitrogen fertilizer applied to cereals in different climate. Adv. Plant Nutr. 1, 1–55.
- Craine, J.M., Morrow, C., Fierer, N., 2007. Microbial nitrogen limitation increases decomposition. Ecology 88, 2105–2113.
- Crews, T.E., Peoples, M.B., 2005. Can the synchrony of nitrogen supply and crop demand be improved in legume and fertilizer-based agroecosystems? A review. Nutr. Cycl. Agroecosyst. 72, 101–120.
- Curtin, D., Beare, M.H., Lehto, K., Tregurtha, C., Qiu, W., Tregurtha, R., Peterson, M., 2017. Rapid assays to predict nitrogen mineralization capacity of agricultural soils. Soil Sci. Soc. Am. J. 81, 979–991.
- Curtin, D., Campbell, C.A., 2008. Mineralizable nitrogen. In: Carter, M.R., Gregorich, E.G. (Eds.), Soil Sampling and Methods of Analysis. CRC Press, Boca Raton, FL, pp. 599–606.
- Curtin, D., Wright, C.E., Beare, M.H., McCallum, F.M., 2006. Hot water-extractable nitrogen as an indicator of soil nitrogen availability. Soil Sci. Soc. Am. J. 70, 1512–1521.
- Dancer, W.S., Peterson, L.A., Chesters, G., 1973. Ammonification and nitrification of N as influenced by soil pH and previous N treatments. Soil Sci. Soc. Am. J. 37, 67–69.
- Daniel, T.C., Sharpley, A.N., Lemunyon, J.L., 1998. Agricultural phosphorus and eutrophication: a symposium overview. J. Environ. Qual. 27, 251–257.
- Delin, S., Stenberg, B., Nyberg, A., Brohede, L., 2012. Potential methods for estimating nitrogen fertilizer value of organic residues. Soil Use Manag. 28, 283–291.
- DeLuca, T.H., Keeney, D.R., McCarty, G.W., 1992. Effect of freeze-thaw events on mineralization of soil nitrogen. Biol. Fertil. Soils 14, 116–120.
- Deng, S.P., Moore, J.M., Tabatabai, M.B., 2000. Characterization of active nitrogen pools in soils under different cropping systems. Biol. Fertil. Soils 32, 302–309.
- Dessureault-Rompré, J., Zebarth, B.J., Burton, D.L., Gregorich, E.G., Goyer, C., Georgallas, A., Grant, C.A., 2013. Are soil mineralizable N pools replenished during the growing season in agricultural soils? Soil Sci. Soc. Am. J. 77, 512–524.

- Dessureault-Rompré, J., Zebarth, B.J., Burton, D.L., Sharifi, M., Cooper, J., Grant, C.A., Drury, C.F., 2010. Relationships among mineralizable soil nitrogen, soil properties, and climatic indices. Soil Sci. Soc. Am. J. 74, 1218–1227.
- Diacono, M., Rubino, P., Montemurro, F., 2013. Precision nitrogen management of wheat. A review. Agron. Sustain. Dev. 33, 219–241.
- Dinel, H., Schnitzer, M., Schulten, H.R., 1998. Chemical and spectroscopic characterization of colloidal fractions separated from liquid hog manures. Soil Sci. 163, 665–673.
- Dries, J., 2016. Dynamic control of nutrient-removal from industrial wastewater in a sequencing batch reactor, using common and low-cost online sensors. Water Sci. Technol. 73, 740–745.
- Eghball, B., 2000. Nitrogen mineralization from field-applied beef cattle feedlot manure of compost. Soil Sci. Soc. Am. J. 64, 2024–2030.
- Eghball, B., Hergert, G.W., Lesoing, G.W., Ferguson, R.B., 2000. Fractal analysis of spatial and temporal variability. Dev. Soil Sci. 27, 259–272.
- Eghball, B., Power, J.F., Gilley, J.E., Doran, J.W., 1997. Nutrient, carbon, and mass loss during composting of beef cattle feedlot manure. J. Environ. Qual. 26, 189–193.
- Emerson, K., Russo, R.C., Lund, R.E., Thurston, R.V., 1975. Aqueous ammonia equilibrium calculations: effect of pH and temperature. J. Fish. Res. Board Can. 32, 2379–2383.
- English, S., Fleming, R., 2006. Liquid Manure Storage Covers. University of Guelph Ridgetown Campus, Ridgetown, Ontario, Canada. 18 p, http://www.ridgetownc. uoguelph.ca/research/documents/fleming_liquid_manure_storage_covers.pdf.
- Evans, J.T., Sama, M.P., Taraba, J.L., Day, G.B., 2017. Automated calibration of electrochemical oxygen sensors for use in compost bedded pack barns. Trans. ASABE 60, 957–962.
- Fangueiro, D., Hjorth, M., Gioelli, F., 2015. Acidification of animal slurry—a review. J. Environ. Manage. 149, 46–56.
- Fares, A., Abbas, F., Ahmad, A., Deenik, J.L., Safeeq, M., 2008. Response of selected soil physical and hydrologic properties to manure amendment rates, levels, and types. Soil Sci. 173, 522–533.
- Fauci, M.F., Dick, R.P., 1994. Soil microbial dynamics: short- and long-term effects of inorganic and organic nitrogen. Soil Sci. Soc. Am. J. 58, 801–806.
- Gagnon, B., Robitaille, R., Simard, R.R., 1999. Characterization of several on-farm and industrial composted materials. Can. J. Soil Sci. 79, 201–210.
- Geisseler, D., Horwath, W.R., Joergensen, R.G., Ludwig, B., 2010. Pathways of nitrogen utilization by soil microorganisms—a review. Soil Biol. Biochem. 42, 2058–2067.
- German, D.P., Chacon, S.S., Allison, S.D., 2011. Substrate concentration and enzyme allocation can affect rates of microbial decomposition. Ecology 92, 1471–1480.
- Ghani, A., Dexter, M., Perrott, K.W., 2003. Hot-water extractable carbon in soils: a sensitive measurement for determining impacts of fertilisation, grazing and cultivation. Soil Biol. Biochem. 35, 1231–1243.
- Giacometti, C., Demyan, M.S., Cavani, L., Marzadori, C., Ciavatta, C., Kandeler, E., 2013. Chemical and microbiological soil quality indicators and their potential to differentiate fertilization regimes in temperate agroecosystems. Appl. Soil Ecol. 64, 32–48.
- Gilbertson, C.B., Norstadt, F.A., Mathers, A.C., Holt, R.F., Shuyler, L.R., Barnett, A.P., McCalla, T.M., Onstad, C.A., Young, R.A., Christensen, L.A., Van Dyne, D.L., 1979. Animal waste utilization on cropland and pastureland: a manual for evaluating agronomic and environmental effects. USDA Utilization Research Rep, no. 6, U.S. Gov. Print. Office, Washington, DC.
- Gillespie, A.W., Diochon, A., Ma, B.L., Morrison, M.J., Kellman, L., Walley, F.L., Regier, T.Z., Chevrier, D., Dynes, J.J., Gregorich, E.G., 2014. Nitrogen input quality changes the biochemical composition of soil organic matter stabilized in the fine fraction: a long-term study. Biogeochemistry 117, 337–350.

- Gillis, J.D., Price, G.W., 2011. Comparison of a novel model to three conventional models describing carbon mineralization from soil amended with organic residues. Geoderma 160, 304–310.
- Gilmour, J.T., Clark, M.D., Sigua, G.C., 1985. Estimating net nitrogen mineralization from carbon dioxide evolution. Soil Sci. Soc. Am. J. 49, 1398–1402.
- Goffart, J.P., Olivier, M., Frankinet, M., 2011. Crop nitrogen status assessment tools in a decision support system for nitrogen fertilization management of potato crops. Horttechnology 21, 282–286.
- Gordillo, R.M., Cabrera, M.L., 1997. Mineralizable nitrogen in broiler litter: I. Effect of selected litter chemical characteristics. J. Environ. Qual. 26, 1672–1679.
- Gosling, P., Parsons, N., Bending, G.D., 2013. What are the primary factors controlling the light fraction and particulate soil organic matter content of agricultural soils? Biol. Fertil. Soils 49, 1001–1014.
- Government of Quebec, 2017. Agricultural Operations Regulation, Environment Quality Act. chapter Q-2, r. 26. Ministère de développement durable, de l'environnement et lutte contre les changements climatiques, Quebec, Canada. [Online] Available: http:// legisquebec.gouv.qc.ca/en/ShowDoc/cr/Q-2,%20r.%2026. (Accessed 5 September 2017).
- Gregorich, E.G., Beare, M.H., 2008. Physically uncomplexed organic matter. In: Carter, M.R., Gregorich, E.G. (Eds.), Soil Sampling and Methods of Analysis. CRC Press, Boca Raton, FL, pp. 607–616.
- Gregorich, E.G., Beare, M.H., McKim, U.F., Skjemstad, J.O., 2006. Chemical and biological characteristics of physically uncomplexed organic matter. Soil Sci. Soc. Am. J. 70, 975–985.
- Gregorich, E.G., Beare, M.H., Stoklas, U., St-Georges, P., 2003. Biodegradability of soluble organic matter in maize-cropped soils. Geoderma 113, 237–252.
- Gregorich, E.G., Carter, M.R., Angers, D.A., Monreal, C.M., Ellert, B.H., 1994. Towards a minimum data set to assess soil organic matter in agricultural soils. Can. J. Soil Sci. 74, 367–385.
- Griffin, T.S., 2007. Estimates of gross transformation rates of dairy manure N using ¹⁵N pool dilution. Commun. Soil Sci. Plant Anal. 38, 11–12.
- Griffin, T.S., He, Z., Honeycutt, C.W., 2005. Manure composition affects net transformation of nitrogen from dairy manures. Plant and Soil 273, 29–38.
- Griffin, T.S., Honeycutt, C.W., 2000. Using growing degree days to predict nitrogen availability from livestock manures. Soil Sci. Soc. Am. J. 64, 1876–1882.
- Griffin, T.S., Porter, G.A., 2004. Altering soil carbon and nitrogen stocks in intensively tilled two-year rotations. Biol. Fertil. Soils 39, 366–374.
- Griffiths, B.S., Spilles, A., Bonkowski, M., 2012. C:N:P stoichiometry and nutrient limitation of the soil microbial biomass in a grazed grassland site under experimental P limitation or excess. Ecol. Process. 1, 6. https://doi.org/10.1186/2192-1709-1-6.
- Groot Koerkamp, P.W., 1994. Review on emissions of ammonia from housing systems for laying hens in relation to sources, processes, building design and manure handling. J. Agric. Eng. Res. 59, 73–87.
- Hagedorn, F., Spinnler, D., Siegwolf, R., 2003. Increased N deposition retards mineralization of old soil organic matter. Soil Biol. Biochem. 35, 1683–1692.
- Haimi, H., Corona, F., Mulas, M., Sundell, L., Heinonen, M., Vahala, R., 2015. Shall we use hardware sensor measurements or soft-sensor estimates? Case study in a full-scale WWTP. Environ. Model. Software 72, 215–229.
- Hammermeister, A.M., Astatkie, T., Jeliazkova, E.A., Warman, P.R., Martin, R.C., 2006. Nutrient supply from organic amendments applied to unvegetated soil, lettuce and orchardgrass. Can. J. Soil Sci. 86, 21–33.
- Haneklaus, S., Schick, J., Kratz, S., Ruckamp, D., Schnug, E., 2016. Variable rate application of manure—gain or pain? Landbauforsch. Volk. 66, 11–19.

- Haney, R.L., Hons, F.M., Sanderson, M.A., Franzluebbers, A.J., 2001. A rapid procedure for estimating nitrogen mineralization in manured soil. Biol. Fertil. Soils 33, 100–104.
- Hansen, M.N., Henriksen, K., Sommer, S.G., 2006. Observations of production and emission of greenhouse gases and ammonia during storage of solids separated from pig slurry: effects of covering. Atmos. Environ. 40, 4172–4181.
- Hao, X., Thomas, B.W., Nelson, V., Li, X., 2016. Agronomic values of anaerobically digested cattle manure and the separated solids for barley forage production. Soil Sci. Soc. Am. J. 80, 1572–1584.
- Havlin, J.L., Beaton, J.D., Tisdale, S.L., Nelson, W.L., 2005. Soil Fertility and Fertilizers: An Introduction to Nutrient Management, seventh ed. Pearson Prentice Hall, Upper Saddle River, NJ.
- Haynes, R., 2005. Labile organic matter fractions as central components of the quality of agricultural soils: an overview. Adv. Agron. 85, 221–268.
- Haynes, R.J., Naidu, R., 1998. Influence of lime, fertilizer and manure application on soil organic matter content and soil physical conditions: a review. Nutr. Cycl. Agroecosyst. 51, 123–137.
- Heckman, J.R., Hlubik, W.T., Prostak, D.J., Paterson, J.W., 1995. Pre-sidedress soil nitrate test for sweet corn. HortSci. 30, 1033–1036.
- Heinrich, A.L., Pettygrove, G.S., 2012. Influence of dissolved carbon and nitrogen on mineralization of dilute liquid dairy manure. Soil Sci. Soc. Am. J. 76, 700–709.
- Henriksen, K., Berthelsen, L., Matzen, R., 1998. Separation of liquid pig manure by flocculation and ion exchange—part 1: laboratory experiments. J. Agric. Eng. Res. 69, 115–125.
- Henry, H.A.L., 2012. Soil extracellular enzyme dynamics in a changing climate. Soil Biol. Biochem. 47, 53–59.
- Herrmann, A., Witter, E., 2002. Sources of C and N contributing to the flush of mineralization upon freeze-thaw cycles in soils. Soil Biol. Biochem. 34, 1495–1505.
- Heumann, S., Rimmer, D.L., Schlichting, A., Abbott, G.D., Leinweber, P., Boettcher, J., 2013. Effects of potentially inhibiting substances on C and net N mineralization of a sandy soil—a case study. J. Plant Nutr. Soil Sci. 176, 35–39.
- Hillborn, D., 2010. Storage of liquid manure. Factsheet. Ontario Ministry of Agriculture, Food and Rural Affairs, Toronto, Ontario, Canada.
- Himmel, M.E., Ding, S.Y., Johnson, D.K., Adney, W.S., Nimlos, M.R., Brady, J.W., Foust, T.D., 2007. Biomass recalcitrance: engineering plants and enzymes for biofuels production. Science 315, 804–809.
- Hjorth, M., Christensen, K.V., Christensen, M.L., Sommer, S.G., 2010. Solid-liquid separation of animal slurry in theory and practice. A review. Agron. Sustain. Dev. 30, 153–180.
- Hjorth, M., Christensen, M.L., Christensen, P.V., 2008. Flocculation, coagulation, and precipitation of manure affecting three separation techniques. Bioresour. Technol. 99, 8598–8604.
- Hornig, G., Turk, M., Wanka, U., 1999. Slurry covers to reduce ammonia emission and odour nuisance. J. Agric. Eng. Res. 73, 151–157.
- Hristov, A.N., Hanigan, M., Cole, A., Todd, R., McAllister, T.A., Ndegwa, P., Rotz, A., 2011. Review: ammonia emissions from dairy farms and beef feedlots. Can. J. Anim. Sci. 91, 1–35.
- Huijsmans, J.F.M., Hol, J.M.G., Vermeulen, G.C., 2003. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. Atmos. Environ. 37, 3669–3680.
- Hussain, A.M., Daniel, R.C.W., Frost, A.J., 1992. The bactericidal effect of N-acetyl-β-D-glucosaminidase on bacteria. Vet. Microbiol. 32, 75–80.
- International Plant Nutrition Institute, 2012. 4R Plant Nutrition: A Manual for Improving the Management of Plant Nutrition. International Plant Nutrition Institute, Norcross, GA. p. 130.

- Jayasundara, S., Wagner-Riddle, C., Parkin, G., Lauzon, J., Fan, M.Z., 2010. Transformations and losses of swine manure N-15 as affected by application timing at two contrasting sites. Can. J. Soil Sci. 90, 55–73.
- Jensen, L.S., Pedersen, I.S., Hansen, T.B., Nielsen, N.E., 2000. Turnover and fate of ¹⁵Nlabelled cattle slurry ammonium-N applied in the autumn to winter wheat. Eur. J. Agron. 12, 23–35.
- Jiao, Y., Whalen, J.K., Hendershot, W.H., 2006. No-tillage and manure applications increase aggregation and improve nutrient retention in a sandy-loam soil. Geoderma 134, 24–33.
- Jost, D.I., Aschemann, M., Lebzien, P., Joergensen, R.G., Sundrum, A., 2013a. Microbial biomass in faeces of dairy cows affected by a nitrogen deficient diet. Arch. Anim. Nutr. 67, 104–118.
- Jost, D.I., Joergensen, R.G., Sundrum, A., 2013b. Effect of cattle faeces with different microbial biomass content on soil properties, gaseous emissions and plant growth. Biol. Fertil. Soils 49, 61–70.
- Kai, P., Pedersen, P., Jensen, J.E., Hansen, M.N., Sommer, S.G., 2008. A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. Eur. J. Agron. 28, 148–154.
- Kallenbach, C., Grandy, A.S., 2011. Controls over soil microbial biomass responses to carbon amendments in agricultural systems: a meta-analysis. Agric. Ecosyst. Environ. 144, 241–252.
- Kallenbach, C.M., Frey, S.D., Grandy, S., 2016. Direct evidence for microbial-derived soil organic matter formation and its ecophysiological controls. Nat. Commun. 7, 1–10.
- Kapuinen, P., 2001. Deep litter systems for beef cattle housed in uninsulated barns, part 2: temperatures and nutrients. J. Agric. Eng. Res. 80, 87–97.
- Kautz, T., Lopez-Fando, C., Ellmer, F., 2006. Abundance and biodiversity of soil microarthropods as influenced by different types of organic manure in a long-term field experiment in Central Spain. Appl. Soil Ecol. 33, 278–285.
- Kemmit, J.J., Lanyon, C.V., Waite, I.S., Wen, Q., Addiscott, T.M., Bird, N.R.A., O'Donnell, A.G., Brookes, P.C., 2008. Mineralization of native soil organic matter is not regulated by the size, activity or composition of the soil microbial biomass—a new perspective. Soil Biol. Biochem. 40, 61–73.
- Ketterings, Q.M., Albrecht, G., Czymmek, K., Bossard, S., 2005. Nitrogen credits from manure. Agronomy Fact Sheet Series. Fact Sheet 4. Cornell University Cooperative Extension. http://nmsp.cals.cornell.edu/publications/factsheets/factsheet4.pdf.
- Keys, J.E., Van Soest, P.J., Young, E.P., 1969. Comparative study of the digestibility of forage cellulose and hemicellulose in ruminants and nonruminants. J. Anim. Sci. 29, 11–15.
- Kirchmann, H., Lundvall, A., 1993. Relationship between N immobilization and volatile fatty acids in soil after application of pig and cattle slurry. Biol. Fertil. Soils 15, 161–164.
- Kirchmann, H., Witter, E., 1992. Composition of fresh, aerobic and anaerobic farm animal dungs. Bioresour. Technol. 40, 137–142.
- Klapwyk, J.H., Ketterings, Q.M., 2006. Soil tests for predicting corn response to nitrogen fertilizer in New York. Agron. J. 98, 675–681.
- Klapwyk, J.H., Ketterings, Q.M., Godwin, G.S., Wang, D., 2006. Response of the Illinois soil nitrogen test to liquid and composted dairy manure applications in a corn agroecosystem. Can. J. Soil Sci. 86, 655–663.
- Knicker, H., 2011. Soil organic N—an under-rated player for C sequestration in soils? Soil Biol. Biochem. 43, 1118–1129.
- Koenig, K.M., McGinn, S.M., Beauchemin, K.A., 2013. Ammonia emissions and performance of backgrounding and finishing beef feedlot cattle fed barley-based diets varying in dietary crude protein concentration and rumen degradability. J. Anim. Sci. 91, 2278–2294.

- Koenig, R.T., Palmer, M.D., Miner Jr., F.D., Miller, B.E., Harrison, J.D., 2005. Chemical amendments and process controls to reduce ammonia volatilization during in-house composting. Compost Sci. Util. 13, 141–149.
- Kopke, U., 1995. Nutrient management in organic farming systems—the case of nitrogen. Biol. Agric. Hortic. 11, 15–29.
- Kuipers, A., Mandersloot, F., 1999. Reducing nutrient losses on dairy farms in the Netherlands. Livest. Prod. Sci. 61, 139–144.
- Külling, D.R., Menzi, H., Krober, T.F., Neftel, A., Sutter, F., Lischer, P., Kreuzer, M., 2001. Emissions of ammonia, nitrous oxide and methane from different types of dairy manure during storage as affected by dietary protein content. J. Agric. Sci. 137, 235–250.
- Kuzyakov, Y., 2002. Review: factors affecting rhizosphere priming effects. J. Plant Nutr. Soil Sci. 165, 382–396.
- Kwon, H.-Y., Hudson, R.J.M., Mulvaney, R.L., 2009. Characterization of the organic nitrogen fraction determined by the Illinois soil nitrogen test. Soil Sci. Soc. Am. J. 73, 1033–1043.
- Ladha, J.K., Pathak, H., Krupnik, T.J., Six, J., van Kessel, C., 2005. Efficiency of fertilizer nitrogen in cereal production: retrospects and prospects. Adv. Agron. 87, 85–156.
- Lalonde, R., Gagnon, B., Simard, R.R., Cote, D., 2000. Soil microbial biomass and enzyme activity following liquid hog manure application in a long-term field trial. Can. J. Soil Sci. 80, 263–269.
- Larney, F.J., Buckley, K.E., Hao, X.Y., McCaughey, W.P., 2006. Fresh, stockpiled, and composted beef cattle feedlot manure: nutrient levels and mass balance estimates in Alberta and Manitoba. J. Environ. Qual. 35, 1844–1854.
- Larney, F.J., Hao, X.Y., 2007. A review of composting as a management alternative for beef cattle feedlot manure in southern Alberta, Canada. Bioresour. Technol. 98, 3221–3227.
- Larney, F.J., Olson, A.F., Carcarno, A.A., Chang, C., 2000. Physical changes during active and passive composting of beef feedlot manure in winter and summer. Bioresour. Technol. 75, 139–148.
- Lauer, D.A., Bouldin, D.R., Klausner, S.D., 1976. Ammonia volatilization from dairy manure spread on the soil surface. J. Environ. Qual. 5, 134–141.
- Lehrsch, G.A., Brown, B., Lentz, R.D., Johnson-Maynard, J.L., Leytem, A.B., 2016. Winter and growing season nitrogen mineralization from fall-applied composted or stockpiled solid dairy manure. Nutr. Cycl. Agroecosyst. 104, 125–142.
- Leinweber, P., Schulten, H.-R., Körschens, M., 1995. Hot water extracted organic matter: chemical composition and temporal variations in a long-term field experiment. Biol. Fertil. Soils 20, 17–23.
- León Castro, L.X., Whalen, J.K., 2016. Ion exchange membranes as an indicator of soil mineral nitrogen availability and nitrogen uptake by arugula (*Eruca sativa* L.) in soils amended with green manure. Biol. Agric. Hortic. 32, 206–220.
- Levičnik-Höfferle, S., Nicol, G.W., Ausec, L., Mandić-Mulec, I., Prosser, J.I., 2012. Stimulation of thaumarchaeal ammonia oxidation by ammonia derived from organic nitrogen but not added inorganic nitrogen. FEMS Microbiol. Ecol. 80, 114–123.
- Levy, P.E., Famulari, D., Anderson, M., Reay, D.S., 2017. Nitrous oxide emission sources from a mixed livestock farm. Agric. Ecosyst. Environ. 243, 92–102.
- Lim, T.T., Heber, A.J., Ni, J.Q., Sutton, J.L., Shao, P., 2003. Odor and gas release from anaerobic treatment lagoons for pig manure. J. Environ. Qual. 32, 406–416.
- Linn, D.M., Doran, J.W., 1984. Aerobic and anaerobic microbial populations in no-till and plowed soils. Soil Sci. Soc. Am. J. 48, 794–799.
- Loecke, T.D., Liebman, M., Cambardella, C.A., Richard, T.L., 2004. Corn growth responses to composted and fresh solid pig manures. Crop. Sci. 44, 177–184.

- Lynch, D.H., Voroney, R.P., Warman, P.R., 2004. Nitrogen availability from composts for humid region perennial grass and legume-grass forage production. J. Environ. Qual. 33, 1509–1520.
- Ma, W.C., Brussaard, L., DeRidder, J.A., 1990. Long-term effects of nitrogenous fertilizers on grassland earthworms (Oligochaeta, Lumbricidae)—their relation to soil acifidication. Agric. Ecosyst. Environ. 30, 71–80.
- Mallarino, A.P., Stewart, B.M., Baker, J.L., Downing, J.D., Sawyer, J.E., 2002. Phosphorus indexing for cropland: overview and basic concepts of the Iowa phosphorus index. J. Soil Water Conserv. 57, 440–447.
- Mallory, E.B., Griffin, T.S., 2007. Impacts of soil amendment history on nitrogen availability from manure and fertilizer. Soil Sci. Soc. Am. J. 71, 964–973.
- Mallory, E.B., Griffin, T.S., Porter, G.A., 2010. Seasonal nitrogen availability from current and past applications of manure. Nutr. Cycl. Agroecosyst. 88, 351–360.
- Marriott, E.E., Wander, M.M., 2006. Total and labile soil organic matter in organic and conventional farming systems. Soil Sci. Soc. Am. J. 70, 950–959.
- Marschner, B., Kalbitz, K., 2003. Controls on bioavailability and biodegradability of dissolved organic matter in soils. Geoderma 113, 211–235.
- McGill, W.B., Cannon, K.R., Robertson, J.A., Cook, F.D., 1986. Dynamics of soil microbial biomass and water-soluble organic C in Breton L after 50 years of cropping two rotations. Can. J. Soil Sci. 66, 1–19.
- Meisinger, J.J., Jokela, W.E., 2000. Ammonia Volatilization from Dairy and Poultry Manure. Managing Nutrients and Pathogens from Animal Agriculture. NRAES-130. Natural Resource, Agriculture, and Engineering Service, Ithaca, NY, p. 21.
- Meluzzi, A., Sirri, F., Tallarico, N., Farachini, A., 2010. Nitrogen retention and performance of brown laying hens on diets with different protein content and constant concentration of amino acids and energy. Br. Poultry Sci. 42, 213–217.
- Miller, J.J., Bremer, E., Beasley, B.W., Drury, C.F., Zebarth, B.J., Larney, F.J., 2012. Longterm effect of fresh and composted cattle manure on the size and nutrient composition of dry-sieved soil aggregates. Can. J. Soil Sci. 92, 673–683.
- Mohanty, M., Reddy, K.S., Probert, M.E., Dalal, R.C., Rao, A.S., Menzies, N.W., 2011. Modelling N mineralization from green manure and farmyard manure from a laboratory incubation study. Ecol. Model. 222, 719–726.
- Morvan, T., Nicolardot, B., 2009. Role of organic fractions on C decomposition and N mineralization of animal wastes in soil. Biol. Fertil. Soils 45, 477–486.
- Morvan, T., Nicolardot, B., Péan, L., 2006. Biochemical composition and kinetics of C and N mineralization of animal wastes: a typological approach. Biol. Fertil. Soils 42, 513–522.
- Mowrer, J., Cabrera, M., Rasmussen, T., Cassity-Duffey, K., 2014. Nitrogen in stored poultry litter: uric acid and xanthine. J. Environ. Qual. 43, 2137–2145.
- Muck, R.E., 1982. Urease activity in bovine feces. Dairy Sci. 65, 2157–2163.
- Mulvaney, R.L., Khan, S.A., Hoeft, R.G., Brown, H.M., 2001. A soil organic nitrogen fraction that reduces the need for nitrogen fertilization. Soil Sci. Soc. Am. J. 65, 1164–1172.
- Murphy, D.V., Macdonald, A.J., Stockdale, E.A., Goulding, K.W.T., Fortune, S., Gaunt, J.L., Poulton, P.R., Wakefield, J.A., Webster, C.P., Wilmer, W.S., 2000. Soluble organic nitrogen in agricultural soils. Biol. Fertil. Soils 30, 374–387.
- Natural Resources Conservation Service (NRCS), 2008. Agricultural Waste Management Field Handbook. Part 651. United States Department of Agriculture, Washington, DC. [Online] Available: https://www.nrcs.usda.gov/wps/portal/nrcs/detailfull/national/ technical/ecoscience/mnm/?cid=stelprdb1045935 (12 December 2017).
- Nelson, L.A., Voss, R.D., Pesek, J., 1985. Agronomic and statistical evaluation of fertilizer response. In: Engelstad, O.P. (Ed.), Fertilizer Technology and Use, third ed. Soil Science Society of America, Madison, WI, pp. 53–90.

- Nieder, R., Benbi, D.K., Scherer, H.W., 2011. Fixation and defixation of ammonium in soils: a review. Biol. Fertil. Soils 47, 1–14.
- Ninh, H.T., Grandy, A.S., Wickings, K., Snapp, S.S., Kirk, W., Hao, J., 2015. Organic amendment effects on potato productivity and quality are related to soil microbial activity. Plant and Soil 386, 223–236.
- Nyiraneza, J., Chantigny, M.H., N'Dayegamiye, A., Laverdière, M.R., 2010. Long-term manure application and forages reduce nitrogen fertilizer requirements of silage corncereal cropping systems. Agron. J. 102, 1244–1251.
- Nyiraneza, J., Nolin, M.C., Ziadi, N., Cambouris, A.N., 2011. Short-range variability of nitrate and phosphate desorbed from anionic exchange membranes. Soil Sci. Soc. Am. J. 75, 2242–2250.
- Nyiraneza, J., Zebarth, B.J., Ziadi, N., Sharifi, M., Burton, D.L., Drury, C.F., Bittman, S., Grant, C.A., 2012. Prediction of soil nitrogen supply in corn production using soil chemical and biological indices. Soil Sci. Soc. Am. J. 76, 925–935.
- Oh, I., Burns, R.T., Moody, L.B., Lee, J., 2005. Optimization of phosphorus partitioning in dairy manure using chemical additives with a mechanical solids separator. Trans. ASAE 48, 1235–1240.
- Ontario Ministry of Agriculture Food and Rural Affairs (OMAFRA), 2009. Agronomy Guide for Field Crops. OMAFRA Publication 811, Toronto, Ontario. [Online] Available: http://-www.omafra.gov.on.ca/english/crops/pub811/9manure.htm. (Accessed 10 October 2017).
- Pan, J., Fadel, J.G., Zhang, R., El-Mashad, H.M., Ying, Y., Rumsey, T., 2009. Evaluation of sample preservation methods for poultry manure. Poult. Sci. 88, 1528–1535.
- Panetta, D.M., Powers, W.J., Lorimor, J.C., 2005. Management strategy impacts on ammonia volatilization from pig manure. J. Environ. Qual. 34, 1119–1130.
- Pansu, M., Thuries, L., Larre-Larrouy, M.C., Bottner, P., 2003. Predicting N transformations from organic inputs in soil in relation to incubation time and biochemical composition. Soil Biol. Biochem. 35, 353–363.
- Pattey, E., Trzcinski, M.K., Dejardins, R.L., 2005. Quantifying the reduction of greenhouse gas emissions as a result of composting dairy and beef cattle manure. Nutr. Cycl. Agroecosyst. 72, 173–187.
- Paul, J.W., Beauchamp, E.G., 1994. Short-term nitrogen dynamics in soil amended with fresh and composted cattle manures. Can. J. Soil Sci. 74, 147–155.
- Paul, J.W., Beauchamp, E.G., 1996. Soil microbial biomass C, N mineralization, and N uptake by corn in dairy cattle slurry-and urea-amended soils. Can. J. Soil Sci. 76, 469–472.
- Pelster, D.E., Chantigny, M.H., Rochette, P., Angers, D.A., Laganière, J., Zebarth, B., Goyer, C., 2013. Crop residue incorporation alters soil nitrous oxide emissions during freeze thaw cycles. Can. J. Soil Sci. 93, 415–425.
- Poincelot, R.P., 1975. The biochemistry and methodology of composting. Connecticut Agric. Exp. St. Bull. 754.
- Powell, J.M., Broderick, G.A., 2011. Transdisciplinary soil science research: impacts of dairy nutrition on manure chemistry and the environment. Soil Sci. Soc. Am. J. 75, 2071–2078.
- Pratt, P.F., Boadbent, F.E., Martin, J.P., 1973. Using organic wastes as nitrogen fertilizers. Calif. Agric. 27, 10–13.
- Prosser, J.I., Nicol, G.W., 2012. Archaeal and bacterial ammonia-oxidisers in soil: the quest for niche specialisation and differentiation. Trends Microbiol. 20, 523–531.
- Qafoku, O.S., Cabrera, M.L., Windham, W.R., Hill, N.S., 2001. Rapid methods to determine potentially mineralizable nitrogen in broiler litter. J. Environ. Qual. 30, 217–221.
- Qian, P., Schoenau, J.J., 1995. Assessing nitrogen mineralization from organic matter using anion exchange membranes. Fertil. Res. 40, 143–148.

- Qian, P., Schoenau, J.J., 2000. Use of ion exchange membrane to assess soil N supply to canola as affected by addition of liquid swine manure and urea. Can. J. Soil Sci. 80, 213–218.
- Qian, P., Schoenau, J.J., 2002. Availability of nitrogen in solid manure amendments with different C:N ratios. Can. J. Soil Sci. 82, 219–225.
- Rao, J.R., Watabe, M., Stewart, T.A., Millar, B.C., Moore, J.E., 2007. Pelleted organomineral fertilisers from composted pig slurry solids, animal wastes and spent mushroom compost for amenity grasslands. Waste Manag. 27, 1117–1128.
- Rashid, M.I., de Goede, R.G.M., Brussaard, L., Bloem, J., Lantinga, E.A., 2014. Production-ecological modelling explains the difference between potential soil N mineralisation and actual herbage N uptake. Appl. Soil Ecol. 84, 83–92.
- Rasouli, S., Whalen, J.K., Madramootoo, C.A., 2014. Reducing soluble and particulate nitrogen losses from agroecosystems in Quebec and Ontario: best management practices, policies and perspectives. Can. J. Soil Sci. 94, 109–127.
- Raun, W.R., Solie, J.B., Stone, M.L., Martin, K.L., Freeman, K.W., Mullen, R.W., Zhang, H., Schepers, J.S., Johnson, G.V., 2005. Optical sensor-based algorithm for crop nitrogen fertilization. Commun. Soil Sci. Plant Anal. 36, 2759–2781.
- Rees, H.W., Chow, T.L., Zebarth, B., Xing, Z., Toner, P., Lavoie, J., Daigle, J.-L., 2014. Impact of supplemental poultry manure application on potato yield and soil properties on a loam soil in north-western New Brunswick. Can. J. Soil Sci. 94, 49–65.
- Regueiro, I., Coutinho, J., Fangueiro, D., 2016. Alternatives to sulfuric acid for slurry acidification: impact on slurry composition and ammonia emissions during storage. J. Clean. Prod. 131, 296–307.
- Rochette, P., Gregorich, E.G., 1998. Dynamics of soil microbial biomass C, soluble organic C and CO₂ evolution after three years of manure application. Can. J. Soil Sci. 78, 283–290.
- Ros, G.H., Hanegraaf, M.C., Hoffland, E., van Riemsdijk, W.H., 2011. Predicting soil N mineralization: relevance of organic matter fractions and soil properties. Soil Biol. Biochem. 43, 1714–1722.
- Schefferle, H.E., 1965. The decomposition of uric acid in built up poultry manure. J. Appl. Microbiol. 28, 412–420.
- Schimel, J.P., Bennet, J., 2004. Nitrogen mineralization: challenges of a changing paradigm. Ecology 85, 591–602.
- Schimel, J.P., Weintraub, M.N., 2003. The implications of exoenzyme activity on microbial carbon and nitrogen limitation in soil: a theoretical model. Soil Biol. Biochem. 35, 549–563.
- Schmidt, J.P., Dellinger, A.E., Beegle, D.B., 2009. Nitrogen recommendations for corn: an on-the-go sensor compared with current recommendation methods. Agron. J. 101, 916–924.
- Sela, S., van Es, H.M., Moebius-Clune, B.N., Marjerison, R., Moebius-Clune, D., Schindelbeck, R., Severson, K., Young, E., 2017. Dynamic model improves agronomic and environmental outcomes for maize nitrogen management over static approach. J. Environ. Qual. 46, 311–319.
- Serna, M.D., Pomares, F., 1991. Comparison of biological and chemical methods to predict nitrogen mineralization in animal wastes. Biol. Fertil. Soils 12, 89–94.
- Sharifi, M., Lynch, D.H., Zebarth, B.J., Zheng, Z., Martin, R.C., 2009. Evaluation of nitrogen supply rate measured by *in situ* placement of plant root simulator[™] probes as a predictor of nitrogen supply from soil and organic amendments in potato crop. Am. J. Potato Res. 86, 356–366.
- Sharifi, M., Zebarth, B.J., Miller, J.J., Burton, D.L., Grant, C.A., 2014. Soil nitrogen mineralization in a soil with long-term history of fresh and composted manure containing straw or wood-chip bedding. Nutr. Cycl. Agroecosyst. 99, 63–78.

- Sharifi, M., Zebarth, B.J., Burton, D.L., Grant, C.A., Cooper, J.M., 2007. Evaluation of some indices of potentially mineralizable nitrogen in soil. Soil Sci. Soc. Am. J. 71, 1233–1239.
- Sharifi, M., Zebarth, B.J., Burton, D.L., Grant, C.A., Porter, G.A., 2008. Organic amendment history and crop rotation effects on soil nitrogen mineralization potential and soil nitrogen supply in a potato cropping system. Agron. J. 100, 1562–1572.
- Sharifi, M., Zebarth, B.J., Burton, D.L., Rodd, V.L., Grant, C.A., 2011. Long-term effects of semisolid beef manure application for forage grass on soil mineralizable nitrogen. Soil Sci. Am. J. 75, 649–658.
- Sharpley, A., 2016. Managing agricultural phosphorus to minimize water quality impacts. Sci. Agric. 73, 1–8.
- Sharpley, A.N., Kleinman, P.J.A., Flaten, D.N., Buda, A.R., 2011. Critical source area management of agricultural phosphorus: experiences, challenges and opportunities. Water Sci. Technol. 64, 945–952.
- Sheppard, S., Bittman, S., 2016. Ammonia. In: Clearwater, R.L., Martin, T., Hoppe, T. (Eds.), Environmental Sustainability of Canadian Agriculture. Agriculture and Agri-Food Canada, Ottawa, Canada, pp. 180–194. Agri-Environmental Indicators Report Series, Report #4.
- Sheppard, S.C., Bittman, S., Tait, J., 2009. Monthly NH₃ emissions from poultry in 12 ecoregions of Canada. Can. J. Anim. Sci. 89, 21–35.
- Sieling, K., Herrmann, A., Wienforth, B., Taube, F., Ohl, S., Hartung, E., Kage, H., 2013. Biogas cropping systems: short term response of yield performance and N use efficiency to biogas residue application. Eur. J. Agron. 47, 44–54.
- Silva, R.N., da Silva, S.P., Brandão, R.L., Ulhoa, C.J., 2004. Regulation of N-acetyl-beta-D-glucosaminidase produced by *Trichoderma harzianum*: evidence that cAMP controls its expression. Res. Microbiol. 155, 667–671.
- Sims, J.T., 1986. Nitrogen transformations in a poultry manure amended soil: temperature and moisture effects. J. Environ. Qual. 15, 59–63.
- Singurindy, O., Molodovskaya, M., Richards, B.K., Steenhuis, T.S., 2009. Nitrous oxide emission at low temperatures from manure-amended soils under corn (*Zea mays L.*). Agric. Ecosyst. Environ. 132, 74–81.
- Smith, J.L., Paul, E.A., 1990. The significance of soil microbial biomass estimations. In: Bollag, J.M., Stotzky, G. (Eds.), Soil Biochemistry. In: Vol. 6. Marcel Dekker, New York, pp. 357–396.
- Soderstrom, M., Piikki, K., Stenberg, M., Stadig, H., Martinsson, J., 2017. Producing nitrogen (N) uptake maps in winter wheat by combining proximal crop measurements with Sentinel-2 and DMC satellite images in a decision support system for farmers. Acta Agric. Scand. B. 67, 637–650.
- Sommer, S.G., Hutchings, N., 1995. Techniques and strategies for the reduction of ammonia emission from agriculture. Water Air Soil Pollut. 85, 237–248.
- Sommer, S.G., Hutchings, N.J., 2001. Ammonia emission from field applied manure and its reduction. Eur. J. Agron. 15, 1–15.
- Sommerfeldt, T.G., Chang, C., 1985. Changes in soil properties under annual applications of feedlot manure and different tillage practices. Soil Sci. Soc. Am. J. 49, 983–987.
- Son, M., Yu, J., Kim, K.-H., 2015. Five questions about mycoviruses. PLoS Pathog. 11 (11), e1005172. https://doi.org/10.1371/journal.ppat.1005172.
- Sørensen, P., 1998. Carbon mineralization, nitrogen immobilization and pH change in soil after adding volatile fatty acids. Eur. J. Soil Sci. 49, 457–462.
- Sørensen, P., Amato, M., 2002. Remineralisation and residual effects of N after application of pig slurry to soil. Eur. J. Agron. 16, 81–95.
- Sørensen, P., Thomsen, I.K., Schröder, J.J., 2017. Empirical model for mineralisation of manure nitrogen in soil. Soil Res. 55, 500–505.

- Spargo, J.T., Alley, M.M., Thomason, W.E., Nagle, S.M., 2009. Illinois soil nitrogen test for prediction of fertilizer nitrogen needs of corn in Virginia. Soil Sci. Soc. Am. J. 73, 434–442.
- Spargo, J.T., Cavigelli, M.A., Mirsky, S.B., Maul, J.E., Meisinger, J.J., 2011. Mineralizable soil nitrogen and labile soil organic matter in diverse long-term cropping systems. Nutr. Cycl. Agroecosyst. 90, 253–266.
- St. Luce, M., Whalen, J.K., Ziadi, N., Zebarth, B.J., 2011. Nitrogen dynamics and indices to predict soil nitrogen supply in humid temperate soils. Adv. Agron. 112, 55–102.
- St. Luce, M., Whalen, J.K., Ziadi, N., Zebarth, B.J., Chantigny, M.H., 2014. Labile organic nitrogen transformations in clay and sandy-loam soils amended with ¹⁵N-labelled faba bean and wheat residues. Soil Biol. Biochem. 68, 208–218.
- Stanford, G., Smith, S.J., 1972. Nitrogen mineralization potential of soils. Soil Sci. Soc. Am. Proc. 36, 465–472.
- Sterngren, A.E., Hallin, S., Bengtson, P., 2015. Archaeal ammonia oxidizers dominate in numbers, but bacteria drive gross nitrification in N-amended grassland soil. Front. Microbiol. 6, 1350. https://doi.org/10.3389/fmicb.2015.01350.
- Stevens, R.J., Laughlin, R.J., Frost, J.P., 1992. Effects of separation, dilution, washing and acidification on ammonia volatilization from surface-applied cattle slurry. J. Agric. Sci. 119, 383–389.
- Strokal, M., Ma, L., Bai, Z.H., Luan, S.J., Kroeze, C., Oenema, O., Velthof, G., Zhang, F.S., 2016. Alarming nutrient pollution of Chinese rivers as a result of agricultural transitions. Environ. Res. Lett. 11, 024014. https://doi.org/10.1088/1748-9326/11/2/024014.
- Szogi, A.A., Vanotti, M.B., Stansbery, A.E., 2006. Reduction of ammonia emissions from treated anaerobic pig lagoons. Trans. ASABE 49, 217–225.
- Tabatabai, M.A., Ekenler, M., Senwo, Z.N., 2010. Significance of enzyme activities in soil nitrogen mineralization. Commun. Soil Sci. Plant Anal. 41, 595–605.
- Tenuta, M., Barry, D.A.J., Fairchild, G., Beauchamp, E.G., 2001. Nitrous oxide production by manure samples collected from six manure-handling systems. Can. J. Soil Sci. 81, 33–38.
- Thomas, B.W., Larney, F.J., Chantigny, M.H., Goyer, C., Hao, X., 2017b. Fall rye reduced residual soil nitrate and dryland spring wheat grain yield. Agron. J. 109, 718–728.
- Thomas, B.W., Li, X., Nelson, V., Hao, X., 2017a. Anaerobically digested cattle manure supplied more nitrogen with less phosphorus accumulation than undigested manure. Agron. J. 109, 836–844.
- Thomas, B.W., Sharifi, M., Whalen, J.K., Chantigny, M.H., 2015. Mineralizable nitrogen responds differently to manure type in contrasting soil textures. Soil Sci. Soc. Am. J. 79, 1396–1405.
- Thomas, B.W., Whalen, J.K., Sharifi, M., 2016. Short-term nitrogen dynamics in soil amended with poultry litter containing woodchip bedding. Can. J. Soil Sci. 96, 427–434.
- Thompson, R.B., Ryden, J.C., Lockyer, D.R., 1987. Fate of nitrogen in cattle slurry following surface application or injection to grassland. J. Soil Sci. 38, 689–700.
- Thomsen, I.K., 2004. Nitrogen use efficiency of N-15-labeled poultry manure. Soil Sci. Soc. Am. J. 68, 538–544.
- Tian, L., Dell, E., Shi, W., 2010. Chemical composition of dissolved organic matter in agroecosystems: correlations with soil enzyme activity and carbon and nitrogen mineralization. Appl. Soil Ecol. 46, 426–435.
- Van Kessel, J.S., Reeves, J.B., 2002. Nitrogen mineralization potential of dairy manures and its relationship to composition. Biol. Fertil. Soils 36, 118–123.
- Vanotti, M.B., Hunt, P.G., 1999. Solids and nutrient removal from flushed pig manure using polyacrylamides. Trans. ASAE 42, 1833–1840.
- Verhoef, H.A., Brussaard, L., 1990. Decomposition and nitrogen mineralization in natural and agro-ecosystems: the contribution of soil animals. Biogeochemistry 11, 175–211.

- Viguria, M., Lopez, D.M., Arriaga, H., Merino, P., 2015. Ammonia and greenhouse gases emission from on-farm stored pig slurry. Water Air Soil Pollut. 226, 285. https://doi. org/10.1007/s11270-015-2548-6.
- Wall, D.P., Weisz, R., Crozier, C.R., Heiniger, R.W., White, J.G., 2010. Variability of the Illinois soil nitrogen test across time and sampling depth. Soil Sci. Soc. Am. J. 74, 2089–2100.
- Walters, D.T., 1995. Comparing the performance of preplant and presidedress soil nitrate tests for the North-Central region. In: Proc. 25th North Central Extension Industry Soil Fertility conference. St. Louis, MO.
- Wang, W.J., Smith, C.J., Chen, C., 2004. Predicting soil nitrogen mineralization dynamics with a modified double exponential model. Soil Sci. Soc. Am. J. 68, 1256–1265.
- Webb, J., Paine, B., Bittman, S., Morgan, J., 2010. The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response—a review. Agric. Ecosyst. Environ. 137, 39–46.
- Webb, J., Sommer, S.G., Kupper, T., Groenestein, K., Hutchings, N.J., Eurich-Menden, B., Rodhe, L., Misselbrook, T.H., Amon, B., 2011. Emissions of ammonia, nitrous oxide and methane during the management of solid manures. In: Lichtfouse, E. (Ed.), Agroecology and Strategies for Climate Change. Sustainable Agriculture Reviews 8. Springer Science and Business Media B.V, pp. 67–107. https://doi.org/10.1007/978-94-007-1905-7_4.
- Webb, J., Sørensen, P., Velthof, G., Amon, B., Pinto, M., Rodhe, L., Salomon, E., Hutchings, N., Burczyk, P., Reid, J., 2013. An assessment of the variation of manure nitrogen efficiency throughout Europe and an appraisal of means to increase manure-N efficiency. Adv. Agron. 119, 371–442.
- Webb, J., Thorman, R.E., Fernanda-Aller, M., Jackson, D.R., 2014. Emission factors for ammonia and nitrous oxide emissions following immediate manure incorporation on two contrasting soil types. Atmos. Environ. 82, 280–287.
- Weinbauer, M.G., 2004. Ecology of prokaryotic viruses. FEMS Microbiol. Rev. 28, 127–181.
- Whalen, J.K., 2014. Managing soil biota-mediated decomposition and nutrient mineralization in sustainable agroecosystems. Adv. Agric, 384604. https://doi.org/10.1155/2014/ 384604.
- Whalen, J.K., Bottomley, P.J., Myrold, D.D., 2000b. Carbon and nitrogen mineralization from light-and heavy-fraction additions to soil. Soil Biol. Biochem. 32, 1345–1352.
- Whalen, J.K., Chang, C., 2001. Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. J. Environ. Qual. 30, 229–237.
- Whalen, J.K., Chang, C., 2002. Macroaggregate characteristics in cultivated soils after 25 annual manure applications. Soil Sci. Soc. Am. J. 66, 1637–1647.
- Whalen, J.K., Chang, C., Clayton, G.W., Carefoot, J.P., 2000a. Cattle manure amendments can increase the pH of acid soils. Soil Sci. Soc. Am. J. 64, 962–966.
- Whalen, J.K., Chang, C., Olson, B.M., 2001. Nitrogen and phosphorous mineralization potentials of soils receiving repeated annual cattle manure applications. Biol. Fertil. Soils 34, 334–341.
- Whalen, J.K., Kernecker, M.L., Thomas, B.W., Sachdeva, V., Ngosong, C., 2013. Soil food web controls on nitrogen mineralization are influenced by agricultural practices in humid temperate climates. CAB Rev. 8, 1–18.
- Whalen, J.K., Parmelee, R.W., 2000. Earthworm secondary production and N flux in agroecosystems: a comparison of two approaches. Oecologia 124, 561–573.
- Whalen, J.K., Parmelee, R.W., Edwards, C.A., 1998. Population dynamics of earthworm communities in corn agroecosystems receiving inorganic and organic fertilizer amendments. Biol. Fertil. Soils 27, 400–407.

- Wilkinson, S.R., 1997. Response of Tifway 2 bermudagrass to fresh or composted broiler litter containing boric acid-treated paper bedding. Commun. Soil Sci. Plant Anal. 28, 259–279.
- Williamson, K.E., Radosevich, M., Smith, D.W., Wommack, K.E., 2007. Incidence of lysogeny within temperate and extreme soil environments. Environ. Microbiol. 9, 2563–2574.
- Wilson, T.C., Paul, E.A., Hardwood, R.R., 2001. Biologically active soil organic matter fractions in sustainable cropping systems. Appl. Soil Ecol. 16, 63–76.
- Wu, T.Y., Schoenau, J.J., Li, F.M., Qian, P.Y., Malhi, S.S., Shi, Y.C., 2005. Influence of fertilization and organic amendments on organic carbon fractions in Heilu soil on the loess plateau of China. J. Plant Nutr. Soil Sci. 168, 100–107.
- Xu, T., 2005. Ion exchange membranes: state of their development and perspective. J. Membr. Sci. 63, 1–29.
- Yan, Y., Tian, J., Fan, M., Zhang, F., Li, X., Christie, P., Chen, H., Lee, J., Kuzyakov, Y., Six, J., 2012. Soil organic carbon and total nitrogen in intensively managed arable soils. Agric. Ecosyst. Environ. 150, 102–110.
- Yang, J.Y., Huffman, E.C., Drury, C.F., Yang, X.M., De Jong, R., 2011. Estimating the impact of manure nitrogen losses on total nitrogen application on agricultural land in Canada. Can. J. Soil Sci. 91, 107–122.
- Yordpratum, U., Tattawasart, U., Wongratanacheewin, S., Sermswan, R.W., 2010. Novel lytic bacteriophages from soil that lyse *Burkholderia pseudomallei*. FEMS Microbiol. Lett. 314, 81–88.
- Yoshida, N., Hoashi, J., Morita, T., McNiven, S.J., Yano, K., Yoshida, A., Nakamura, H., Karube, I., 2001. Monitoring of the composting process using a mediator-type biochemical oxygen demand sensor. Analyst 126, 1751–1755.
- Zebarth, B.J., Drury, C.F., Tremblay, N., Cambouris, A.N., 2009. Opportunities for improved fertilizer nitrogen management in production of arable crops in eastern Canada: a review. Can. J. Soil Sci. 89, 113–132.
- Zebarth, B.J., Leclerc, Y., Moreau, G., Sanderson, J.B., Arsenault, W.J., Botha, E., Wang-Pruski, G., 2005. Estimation of soil nitrogen supply in potato fields using a plant bioassay approach. Can. J. Soil Sci. 85, 377–386.
- Zebarth, B.J., Paul, J.W., Schmidt, O., McDougall, R., 1996. Influence of the time and rate of liquid-manure application on yield and nitrogen utilization of silage corn in south coastal British Columbia. Can. J. Soil Sci. 76, 153–164.
- Ziadi, N., Simard, R., Allard, G., Lafond, J., 1999. Field evaluation of anion exchange membranes as a N soil testing method for grasslands. Can. J. Soil Sci. 79, 281–294.
- Zsolnay, A., 2003. Dissolved organic matter: artefacts, definitions, and functions. Geoderma 113, 187–209.

FURTHER READING

- Beversdorf, L.J., Miller, T.R., McMahon, K.D., 2015. Long-term monitoring reveals carbon-nitrogen metabolism key to microcystin production in eutrophic lakes. Front. Microbiol. 6, 456. https://doi.org/10.3389/fmicb.2015.00456.
- Chantigny, M.H., Angers, D.A., Kaiser, K., Kalbitz, K., 2008. Extraction and characterization of dissolved organic matter. In: Carter, M.R., Gregorich, E.G. (Eds.), Soil Sampling and Methods of Analysis. CRC Press, Boca Raton, FL, pp. 617–632.
- Drury, C.F., Voroney, R.F., Beauchamp, E.A., 1991. Availability of NH⁺₄-N to microorganisms and the soil internal N cycle. Soil Biol. Biochem. 23, 165–199.