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Complete List of Authors:	Johannesson, Gudmundur; University of Guelph, School of Environmental Science Lauzon, John; University of Guelph, School of Environmental Sciences Crolla, Anna; University of Guelph Gilroyed, Brandon; University of Guelph, School of Environmental Science Vanderzaag, Andrew; AAFC, Gordon, Robert; Wilfrid Laurier University, Geography and Environmental Studies
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Impact of manure storage conditions and time on decomposition and losses from liquid dairy manure stored in a temperate climate

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*Johannesson, Gudmundur H.; School of Environmental Sciences, University of Guelph, 50 Stone Road East, Guelph, ON, N1G 2W1

Lauzon, John; University of Guelph, School of Environmental Sciences, 50 Stone Road East, Guelph, ON, N1G 2W1

Crolla, Anna; Ontario Ministry of Agriculture, Food and Rural Affairs, Environmental Management Branch, 59 Ministry Road, Kemptville, ON, K0G 1J0

Gilroyed, Brandon; School of Environmental Sciences, University of Guelph Ridgetown Campus, 120 Main Street East, ON, N0P 2C0

Vanderzaag, Andrew; Agriculture and AgriFood Canada (AAFC), 960 Carling Ave, K.W. Neatby Building, Ottawa, ON, K1A 0C6

Gordon, Robert; Geography and Environmental Studies, Wilfrid Laurier University, 75 University Avenue West, Waterloo, ON, N2L 3C5

*Corresponding author: gjohanne@uoguelph.ca

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ABSTRACT

Large volumes of generated animal manures necessitate knowledge of how its production and storage affects composition, losses, and utilization potential. Stratification of liquid dairy manure was the main source of observed variability within outdoor uncovered manure storage, during a yearlong monitoring of 24 physicochemical manure parameters. Coefficient of variation (CV) ranged from 4-24% for plant nutrients and 33-89% for biogas feedstock parameters. Nitrogen (N) volatilization losses during storage between manure additions were $\sim 10\% \text{ mo}^{-1}$ of total Kjeldahl nitrogen (TKN). Acetic acid was up to 100% of total volatile fatty acid (tvFA) concentration. Bioavailability and solubility of manure parameters, reflected in ratios of volatile solids to total solids (VS:TS), total ammoniacal nitrogen to total Kjeldahl nitrogen (TAN:TKN), and dissolved phosphorus to total phosphorus (O-PO₄:TP) ratios was high. There was substantial pathogen survival during the study with an increased count with added manure. Manure temperature changes and precipitation levels likely played a major role in mineralization and volatilization rates of nutrients and reduction of solids, especially in surface levels of manure in storage. Study results underline the importance of sampling method, timing, and location within stored manure to obtain representative samples unless thorough mixing is previously applied. Further work related to manure properties might benefit from a higher number of farms sampled, provided that consistency in sampling method and analysis is maintained to minimize errors and provide reliable results.

INTRODUCTION

Animal manures are unavoidable products of livestock systems, and can have considerable value if properly utilized. Cattle farming in Canada generates up to 85% of an estimated 180 million tonnes of annual manure production (e.g. Hofman and Beaulieu 2006), which can create problems from excessive nutrient loads on a regional basis. Ontario, in particular, has watersheds where manure production reaches maximum levels of 6,000-9,000 kg ha⁻¹ annually (Statistics Canada 2008), resulting in potential environmental concerns. Manure storage can allow for optimal manure application timing to minimize environmental impacts and maximize crop nutrient use; however, prolonged storage of manure may alter its composition. Analysis of manure is often limited to nutrient analysis, while broadened application and environmental concerns related to its use merit more thorough characterization. Depending on animal type and production system, farm manure can be collected as solids or liquid and stored stockpiled or in liquid storages which often are in excess of 2.5 m deep with storage times of several months (AAFC 2016).

Historically, manure has been valued based on the macronutrients nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), and organic matter (OM) content. There is considerable nutrient variability in excreted manure, arising from feed ration composition, feed intake, and animal type and production levels (Koelsch 2006; Safley et al. 1984). After excretion, manure nutrient concentrations are affected by type of housing, manure management system, bedding and timing of manure removal, storage conditions, and storage duration (Higgins et al. 2004; Mathot et al. 2012; Umetsu et al. 2005; Wightman and Woodbury 2016). For liquid dairy manure systems, additions of milk waste and cleaning water affect manure properties (Wu et al. 2011). Consequently, large farm to farm variations in manure properties may arise (Jokela et al. 2010) and the use of estimates of manure volume and nutrient content (e.g. ASABE 2005) may result in large errors in nutrient application on farms. Thus, it is important to gain a better understanding of the impact of handling and storage on manure properties so as to address its agronomic value (Schroder 2005) and nutrient availability (Pagliari and Laboski 2012).

Stored manure may contain a range of undesirable components from indigenous animal gut flora to zoonotic agents, bacteria and weeds that require management (Martens and Bohm 2009). More than 250

types of microbial pathogens have been identified in animal manures, and these can survive for months in storages and after land application (Gerba and Smith 2005; Nicholson et al. 2005). From soil, pathogens may be transferred into waterways to become a human health hazard (Goss and Richards 2008; Jacobsen and Bech 2012). However, results of pathogen survival in laboratory condition are known to differ from those under field condition (Manyi-Loh et al. 2016), thus, knowledge of the type and amounts of pathogens and their survival rates in farm storages is needed to improve estimates of risks from land application of manure.

More recently, dairy manure has been assessed as a suitable feedstock for agricultural anaerobic digester (AD) biogas systems; however, variability in biogas yields, and thus AD efficacy, suggests a need for further characterization of this substrate (Godbout et al. 2010; Labatut et al. 2011). Total and volatile solid (TS, VS) concentrations, and carbon (C) and N content, are commonly used to estimate biogas generation potential but are also used in waste management research (e.g. El-Fadel et al. 1997). Chemical oxygen demand (COD) has traditionally been used to indicate wastewater energy content (Heidrich et al. 2011) and may be used to estimate methane (CH_4) generation potential. However, biogas generation can be inhibited by various feedstock properties, including volatile fatty acid (VFA), ammonia (NH_3), K and S concentrations (Chen et al. 2008). For these reasons, broad characterization of dairy manure properties could increase manure value for multiple uses, while minimizing environmental impacts of storage and use.

Manure sampling can be a source of variation in manure analysis results, coefficient of variation (CV) values may range from 6-8% to as high as 20-30%, even within farms, depending on sampling location and number of subsamples taken (Davis et al. 2002; Dou et al. 2001). Manure sampling for nutrient content is frequently done following homogenizing mechanical mixing of manure, while sampling for feedstock properties and research purposes is often based on grab samples from undisturbed barn or outdoor manure storages. Therefore, effects of sampling location and subsampling on manure composition are of greater importance for grab samples to explain sources of variability in results than for homogenized stored manure. There is also a lack of studies that systematically evaluate manure feedstock parameter variability, such as VFA or COD.

Although some studies have measured the effect of storage condition and time on manure properties (e.g. Patni and Jui 1987), few have considered on-farm open liquid storage conditions, which is the focus of this study. Study objectives were to: (i) quantify and characterize spatial and temporal variability of liquid dairy manure composition stored under typical temperate climate condition, (ii) assess biological activity and nutrient value, and (iii) discuss the implications for manure storage and utilization.

MATERIALS AND METHODS

Manure Management and Sampling

The experimental site was on a commercial dairy farm near Drayton, Ontario (43° 45' N, 80° 40' W). Livestock consisted of 170 Holstein cows and 45 heifers kept in 3 barns. The feeding regime consisted of a total mixed ration as described in Ngwabie et al. (2014). Manure was mechanically scraped from the dairy and dry cow barn several times a day into an under barn collection tank, which had up to 6 week storage capacity. Wash water and milk waste was added to manure, as was the liquid part of heifer manure. Wheat straw was used as bedding in all barns. The dairy barn collection tank content was periodically land applied or emptied into an uncovered outdoor concrete storage tank that was 30.5 m in diameter and 3.7 m in depth with about 1.5 m above grade. Levels of manure in the storage tank varied, with depths from 1.2 m to 3.2 m, resulting in 900 m³ to 2,550 m³ volumes throughout the study.

Manure was sampled from the storage tank every 1 to 3 months from August 2010 to August 2011 using a sampler consisting of a PVC pipe (3.7 m long, 5.1 cm ID) and a steel rod (0.64 cm OD) running the length of the PVC pipe, attached to a rubber stopper at the sampler bottom end and to a wingnut at the top end, used to open and close the sampler. By-depth sampling was conducted at 0.5 m increments from the manure surface to the tank bottom, starting with 0.25 m as the target depth. Hence, eight by-depth sampling dates yielded 38 samples. A separate composite sample of the continuous depth profile from surface to bottom was taken nine times during the study. Each sample consisted of 5 subsamples from different locations around the perimeter of the tank with an aliquot stored in a 0.5 or 1.0 L wide mouth plastic bottles (Nalgene®). Sample bottles were placed in a cooler in the field and stored at 4°C until shipped for analysis, up to 7 days after sampling.

Sampling method consistency was assessed by sampling (3 replicates) at same location and depth (1.25 m) in the tank (22 Oct. 2010). Subsequently, tank variability was investigated by repeated sampling (5 replicates) at the same depth (1.25 m) but different locations around the perimeter of the tank on 29 October 2010. Each of the 3 and 5 replicates consisted of 5 subsamples as described for regular sampling.

Manure depth was measured manually biweekly until 15 November 2010 and then by a sonic distance sensor (model SR50A, Sonic Ranging Sensor, Campbell Scientific Canada Corp, Edmonton AB).

Temperature was measured by copper-constantan thermocouples at three depths (0.05 and 1.0 m from surface, 0.5 m from bottom) and three locations; in tank center and two opposite locations by tank perimeter. Air temperature was measured by a shielded copper constantan thermocouple sensor at about 2.0 m height and rainfall with a rain gauge (model 7499, RIMCO Syphon Tipping Bucket Rain Gauge, McVan Instruments Pty Ltd, Victoria Australia). Measurements from all sensors were collected at 30 min average intervals.

Manure Analysis and Data Processing

In total 24 parameters were quantified, including nutrient content and forms, digester feedstock and waste properties and pathogen content. Not all parameters were quantified for all sampling dates or sample type (composite and by-depth) due to resource restraints.

An electrometric method (4500-H⁺ B, APHA et al. 2005) was used to assess pH of samples with a glass electrode (AccumetTM). Alkalinity was estimated by titration method (2320 B, APHA et al. 2005). Total solids (TS) were determined by drying at 105°C for 12 h. and volatile solids (VS) through ignition at 550°C for 12 h. (2540 B, 2540 E, APHA et al. 2005). Total nitrogen (TKN) analysis was based on a Macro-Kjeldahl method (4500-N_{org} B, APHA et al. 2005). Total ammoniacal nitrogen (NH₄ + NH₃, TAN) was measured with NH₃ selective electrode (OrionTM) (4500-NH₃ D, APHA et al. 2005), and nitrate nitrogen (NO₃⁻) by nitrate-selective electrode (OrionTM) (4500-NO₃⁻ D, APHA et al. 2005). Use of electrode method was due to inherent colour and solids content of manure samples. A colorimetric method could not be used due to the high solids and colour of the samples.

Total phosphorus (TP) was assessed using persulfate digestion (4500-P B) and ascorbic acid method (4500-P E), also used to quantify dissolved phosphorus (O-PO_4) after pre-filtering of samples with 0.45 μm filter (APHA et al. 2005). Analysis of total potassium (K), magnesium (Mg), and sulfur (S) was by acid digestion based on Anderson (1996) and inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Total carbon content (TC) was determined by dry combustion and oxidation (LECO SC444TM) and inorganic carbon (IC) by the same method following ashing procedure at 475°C for 3 hrs. Organic carbon (OC) was determined by difference (Nelson and Sommers 1982). Analyses of total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD) were based on the closed reflux standard method (5220 D, APHA et al. 2005). Samples for sCOD analysis were pretreated by centrifugation at 1500 rpm and filtering with 0.45 μm filter. Butyric (BTA), propionic (PPA), and acetic acid (AcOH) values were assessed through a standard volatile fatty acid determination procedure (EIT 2007), summation gives total volatile fatty acid concentration (tvFA). Membrane filter technique for members of the coliform group was used for all pathogenic agents (9222 B, APHA et al. 2005) accompanied with appropriate culture media for each species.

Processing of data from manure analysis included descriptive statistics, variance analysis, and regressions, generated by MS ExcelTM 2010 (Microsoft Corp. 2010). This analysis utilized built-in Excel statistical functions (e.g. STDEV, MEDIAN, MIN, MAX) and Analysis ToolPak add-in program (e.g. Regression using least squares method and the LINEST function). Graphs were generated using Grapher 10 Graphing System (Golden Software Inc.).

RESULTS AND DISCUSSION

Environmental Conditions During Study

Manure levels fell slightly during warmer periods of both years, especially in 2011 when manure levels fell by 2.1% May to August despite 410 mm of accumulated rainfall, likely due to evaporation. Contrarily, during colder seasons accumulated water from rain and snow was an estimated 0.5-0.6 m in increased depth from late November 2010 to end of May 2011 (Fig. 1). This accumulated water amounted to an

estimated 16-19% of total manure volume at the time or 365-438 m³. Manure was added to the storage tank on 19-20 July 2010 and partly emptied on 1 November 2010. Further manure additions took place on 14-15 January and 24-25 February 2011.

The temperature difference between the surface and bottom of the tank was about 1°C in July to October 2010 and as high as 12° C in July 2011. However, surface temperatures (~0.05 m below surface) closely followed air temperatures except for 4.5 months when the storage tank surface was frozen solid and snow covered, decoupling manure surface temperatures from air temperatures. In January 2011 average air temperature fell to -9°C, while manure temperatures averaged 2 to 7°C and remained 4 to 5°C until spring (Fig. 1).

Solids Concentration

TS and VS concentration in composite samples averaged 48.6 g L⁻¹ (4.9%) and 36.0 g L⁻¹(3.6%), respectively (Table 1). This is less TS than 71 and 104 g L⁻¹ reported by Massé et al. (2008), but within the reported range of 1 to 14% in dairy manures from Ontario farms (Brown 2013). Lower TS concentration may cause higher CH₄ emissions from manure per unit of solids. For example, Massé et al. (2003) incubated dairy manure with 4 and 9% TS concentration and found that the lower TS resulted in significantly greater biogas generation. VS concentration, which is more bioavailable, was 74 to 77% of TS (n=8), indicating that 23 to 26% of solids were more recalcitrant in nature. Kafle and Chen (2016) found that 9.3% of TS in fresh dairy manure to be lignin which negatively affected manure bioavailability for biochemical methane potential. In this study, feed was substantially sourced from forages; 76% and 89% for high producing and low producing cows, respectively (Ngwabie et al. 2014), addition of straw used for bedding could have resulted in relatively higher levels of lignin in the stored manure.

From September 2010 to August 2011, VS concentration decreased steadily above 2.0 m depth, by 76% at 0-0.5 m depth (from 41.8 to 10.1 g L⁻¹) and by 51% (44.4 to 21.8 g L⁻¹) at the 1.0-1.5 m layer (Fig. 2). At the same time VS concentration at the 1.5-2.0 m depth level fell over winter, probably from dilution due to added water but increased during summer, possibly affected by evaporation, resulting in 8.2% change over a year period (43.3 to 39.7 g L⁻¹). Below 2.0 m depth VS concentration remained stable at about 50 g L⁻¹ throughout the study. This bottom sludge layer became thicker with increasing depth and storage time;

on average the layer was about 0.5 m thick in 2010 and over 1.0 m thick in 2011, while average manure depth was 1.35 m and 3.15 m, respectively. By August 2011, there was a strong gradient of VS concentration with depth (line graph, Fig. 2). These results suggest a combination of initial settling to depth, and OM degradation from aerobic and anaerobic processes at shallower depths (<1.5 m), possibly temperature driven in the warmer months. It is also likely that dilution by precipitation (rain and snow) decreased solids concentration in surface layers. Patni and Jui (1987) also found large changes in TS and VS concentration in the top 1 m layer of a 2.85 m manure depth, but their system was closed and manure depth did not change. They suggested that this was probably due to more active aerobic processes and volatilization at shallower depths. Similarly as in this study they observed small change in solids below 1.8 m, suggesting that loss of solids primarily took place in the upper levels of manure storage.

Chemical Oxygen Demand Content and Variability

The average tCOD and sCOD concentrations in composite samples were 25.1 g L⁻¹ (CV=32.5%) and 9.0 g L⁻¹ (CV=43.5%), respectively (Table 1). The tCOD values from this study are comparable to those others have found for dairy manure, i.e. 23.6 g L⁻¹ (Li et al. 2010) and 39.8 g L⁻¹ by Neves et al. (2009) but lower than those obtained from raw manure (87.6-104.6 g L⁻¹) by Massé et al. (2008). The relatively high CV is likely due to the gradual change in COD over time and with depth, as the CV for sampling for horizontal tank variability was only ~6% (Table 1). The sCOD:tCOD ratio in composite samples was 59% in August 2010, fell to a low of 24% in December 2010, before rising again to 52% in August 2011. This reflects seasonal temperature changes that limit OM decomposition overwinter leading to lower partially decomposed and soluble OM levels that sCOD indicates.

Average tCOD in by-depth samples increased by 82% from the surface to the bottom of the tank (19.2 to 34.9 g L⁻¹, R²=0.97, p<0.001), while sCOD increased by 40% (7.1 to 9.9 g L⁻¹, R²=0.96, p<0.001), suggesting more organic compounds by depth. Levels of sCOD in composite samples dropped by 65% from August to October 2010 (16.9 to 5.9 g L⁻¹) but only by 23% from April to August 2011 (8.5 to 6.5 g L⁻¹), both periods without manure additions or removals. The sCOD values are an indirect indicator of bioavailable OM, therefore these changes could reflect temperature-dependent biological activity in the

manure during the warmer seasons and less readily available OM in 2011. In 2010 manure temperatures, were similar throughout the manure profile and monthly averages reached a high of over 20°C while in 2011 manure temperatures below 1 m never rose above 16°C possibly due to greater manure volumes (Fig. 1). The increased tCOD with depth correlates well with VS concentration ($R^2=0.99$, $p<0.001$) and more significantly than sCOD ($R^2=0.88$, $p<0.01$). Perhaps this reflects lower decomposition rate at greater depth where the tCOD reflects total oxidizable OM while sCOD reflects the bioavailable or partially decomposed OM.

Volatile Fatty Acid Contents and Manure Decomposition Dynamics

There was substantial spatial and temporal variation in VFA concentration in this study. The tVFA in composite samples averaged 4.4 g L⁻¹, with a CV of 83% (Table 1). Similarly, high variability was observed in by-depth samples with time. Between 15 April, around surface thaw, and 8 August 2011 the average tVFA concentration above 1.0 m depth fell by 82%, from 3.5 to 0.63 g L⁻¹, while during the same time period average tVFA content below 2.0 m depth fell by 2% (3.4 vs 3.3 g L⁻¹). A review by Page et al. (2014) reported high spatial and temporal variability in manure VFAs for a range of studies, suggesting that this was likely due to both real variation in manure properties and differences in study methods.

In September and October 2010, tVFA was comprised of nearly 50% each of acetic and propionic acid at all 5 sampling depths, with butyric acid making up between 1-3% of the share. However, for the remainder of the study period, tVFA was comprised mostly of acetic acid (92-100% from December 2010 to August 2011). The predominance of acetic acid in tVFA is similar to what other studies (Patni and Jui (1985) and Page et al. (2014) found. Since acetic acid originates both from acidification and from degradations of propionate and butyrate (Nozhevnikova et al. 2000), the increasing dominance of acetic acid may indicate kinetic instability between acid producing and consuming microbes (Ahring et al. 1995). It is also possible that hydrogenotrophic production of CH₄ became preferential over acetoclastic methanogenesis as suggested by Barret et al. (2013) and Nozhevnikova et al. (2000). In this study temperature differences from surface to bottom were less than 1 °C in summer of 2010, but up to 10 °C in 2011 due to greater manure volumes (Fig. 1), which slowed down warming at depth. It is therefore probable that shifting manure temperatures affected environmental conditions that limited or disrupted the

anaerobic degradation process by depth in the manure storage and thereby VFA production and consumption.

The consistently high variability for VFA in this study, 83% CV for composite samples, 60% CV for tank variability, and 112% CV for sampling variability (Table 1) likely had multiple sources including spatial variability, sampling error and analytical errors. The 112% CV for sampling variability suggests either sampling or analytical error as the repeated sampling was done at the same depth and location.

Generally the analytical equipment used for VFA quantification are reported to give good precision and accuracy (Fernández et al. 2015), even for manure (Peu et al. 2004). However, Raposo et al. (2013) claimed human error in sample preparation and equipment calibration as primary reason for 75% of 25 participating laboratories in 15 countries to miss quality standard limits for VFA analysis. The errors they found were particularly high for short chain VFAs that include Acetic acid, the main source of tvFA in this study. It would be difficult to quantify sources of the observed errors in this study but the high variability suggests a need to scrutinize results of VFA analysis from manure storages or AD facilities using manure as feedstock.

Ammoniacal N and pH Dynamics, Carbon Contents and C:N Ratios

Relatively stable concentrations of TAN in composite samples averaged 1.1 g L^{-1} (Table 1), with levels in April to August 2011 (0.85 g L^{-1}) 35% lower than those in August to October 2010 (1.3 g L^{-1}).

Correspondingly, average concentration in three by-depth (5 depths) samples taken September to October 2010 remained similar with depth and averaged 1.3 g L^{-1} ($R^2=-0.33$, ns), while three samples from six depth layers April to August 2011 averaged 0.91 g L^{-1} and increased from 0.56 to 1.2 g L^{-1} ($R^2=0.92$, $p<0.001$) at 0.25 m to 2.75 m depth, respectively. There was 30% lower TKN levels in composite samples and up to 50% less TAN at shallower depths (0-1.5 m) in summer 2011 compared to summer 2010. These findings agree with Kirchmann and Witter (1989) who found nitrogen losses during 201 day storage were <1% from anaerobically stored manure while up to 44% of total N was lost during aerobic storage. Post-storage levels of total N were >95% organically bound in aerobic manure compared to ~40% in anaerobic manure. These results can be applied to this study; the liquid manure at deeper levels was under anaerobic condition while closer to surface aerobic condition dominated. These different

environments resulted in contrasting N decomposition and volatilization dynamics between shallower (approx. 0 to 1.5 m) and deeper levels (i.e. 2 to 3 m), particularly in 2011 when manure levels were higher and storage times longer compared to 2010.

Generally, immobilization of N begins to take place with C:N ratio >20 but in this study C:N was below 20 in 38 by-depth samples and average C:N ratio increased by depth between 6.5 and 12.3 from 0.25 m to 2.75 m, respectively ($R^2=0.98$, $p<0.001$). Correspondingly average C contents increased somewhat by depth (Fig. 3), 35.9% to 41.4% from 0.25 m to 2.75 m, respectively ($R^2=0.92$, $p<0.01$), while N content (as % DM) fell from 5.7% to 3.7% ($R^2=0.97$, $p<0.001$). Consequently the increasing C:N ratio by depth can be explained by the relatively modest increase of C by depth and comparatively higher drop in N with depth.

No clear trends were observed in pH, either temporally nor spatially; over the year pH averaged 7.3 and ranged from 6.9 to 7.5 in composite samples (Table 1), while 38 by-depth samples had an identical mean and range as composite samples ($R^2=0.08$, ns). Generally pH in manure are partly regulated by NH_3 concentration, along with CO_2 , VFAs and other parameters (Hafner et al. 2013), while pH will influence the ratio of NH_4 and NH_3 in the manure. Considering the relatively low and stable pH, likely drivers of volatilized NH_3 are initial urea concentration (Webb and Misselbrook 2004), particularly near surface, as pointed out by Kirchmann and Witter (1989). Further longer term NH_3 losses are probably through mineralization of organically bound N that subsequently may be volatilized and depleted under the oxygenated zone at shallower depth while accumulating as TAN at depth (Aguerre et al. 2012). Presence of a naturally forming crust, not noteworthy in this study, was found to reduce NH_3 losses (Smith et al. 2007; Sommer 1997) but crust may also lead to increased N_2O emissions (Aguerre et al. 2012), offsetting the NH_3 loss reduction. More effective NH_3 volatilization mitigation strategy for open manure storages, albeit more expensive, are synthetic surface covers (Hou et al. 2015; VanderZaag et al. 2008).

Agronomic Aspects: Nutrient Contents and Transformations

The average TKN concentration in the composite samples was 2.1 g L^{-1} over 9 sampling dates (Table 1), which are similar to published values in Ontario of 2.5 g L^{-1} (0.25%) (Brown 2013). Average TKN concentration increased by 28% from 0.25 m to 2.75 m depth (1.8 to 2.3 g L^{-1} , $R^2=0.53$, ns). From October 2010 to January 2011, TKN decreased by 31.2% (2.7 to 1.9 g L^{-1}), for an average loss of 0.32%

per day. From April to August 2011, another period in which no manure was added to the tank, TKN dropped by 40% from 2.1 g L^{-1} to 1.2 g L^{-1} , or 0.35% loss per day. For the same period, a TKN reduction of 33% was found in by-depth samples using a mass balance calculation ($n=3$ for each depth, total 18 samples), or 1,478 kg N in 115 days resulting in 12.9 kg N d^{-1} losses from 15 April 2011 to 8 August 2011. These storage losses are similar to the range reviewed by Welty et al. (1986) for liquid manure storages, averaging 30% but as high as 65% depending on manure handling and storage design. Similarly Oenema et al. (2007) estimated average manure N losses during storage in the EU to be 30% of total excreted N. These N losses represent an opportunity for nutrient recovery (e.g. Hou et al. 2017) and a monetary replacement value in a farm nutrient cycle as well as impacting on air quality from NH_3 emissions.

Readily available plant mineral N (TAN) averaged 54% of composite sample TKN, with a minimum of 34% in April 2011 but ranging from 48% to 72% in summers of 2010 and 2011. The TAN content in this manure is comparable with 66% that Kessel and Reeves (2002) reported, while NO_3^- concentrations were low in this study (Table 1, Fig. 4). Mineral N content variability is consistent with NH_3 volatilization processes described for ammoniacal N (section 3.5) and subsequent losses of TKN reviewed above. At first sight the relationships between TKN and TAN seemed weak; no relationship for composite samples ($R^2=0.32$, ns) but stronger with depth ($R^2=0.73$, $p<0.05$). During the periods previously discussed for TKN losses, September to October 2010 and April to August 2011, seemingly two contrasting processes were active in by-depth samples; during the fall of 2010 (September-October) no relationship is detected between TKN and TAN ($R^2=-0.22$, ns) while in 2011 (April-August) a strong association is observed in the data ($R^2=0.99$, $p<0.001$). Potentially in 2010, with relatively fresh manure in the storage tank, the main source of TAN was from urinary N, which is known to be easily converted to NH_3 (Hou et al. 2015; Lee et al. 2012; Nahm 2003), which explains the lack of relationship with TKN. Conversely in 2011 the stored manure had been in the storage up to a year more likely making organically bound N the main source of TAN in the manure as the more easily available forms of N had been depleted. This could also explain the lower amounts of TAN in 2011 compared to 2010 previously discussed.

The mean TP concentration was 0.34 g L^{-1} for composite samples (Table 1) and 0.32 g L^{-1} in 38 “by-depth” samples, with increased average concentration of 44% from surface to bottom (0.26 to 0.37 g L^{-1} ,

$R^2=0.84$, $p<0.01$). These means are lower but comparable to the 0.4 g L^{-1} (0.04%) reported for Ontario dairy manure of similar solids concentration (Brown 2013). Orthophosphate-P (O-PO_4) concentration, representing soluble P in the manure averaged 88% (77%-99%) of TP in the composite samples. This implies high plant availability of this manure P and perhaps higher than current liquid dairy manure P source coefficient (PSC) of 0.45 currently used in Ontario (Reid 2011). Other research has suggested that the PSC used in Ontario should be 0.65 (Wang et al. 2016), and that manure P can be up to 100% bioavailable (Eghball et al. 2005; Pagliari and Laboski 2012), indicating the potential for elevated risk of P losses to the environment after land application. Conversely, high manure P bioavailability would also create opportunity for reduced P application from manufactured fertilizer and thereby reduce total P application to soil (Ribey et al. 2016).

The K amounts in composite samples were similar for both August 2010 and August 2011 (36 and $34 \text{ mg} \cdot \text{g DM}^{-1}$, respectively). Average “by-depth” K quantities fell 54% from surface to bottom (62 to 29 mg g^{-1} , $R^2=0.91$, $p<0.01$) with overall average of 44.1 mg g^{-1} ($n = 38$). K in manure is reported to be up to 80% suspended in the liquid phase (Lorimor et al. 2000) and the remainder mostly associated with particles $<0.125 \text{ mm}$ size (Meyer et al. 2007). However, due to increasing TS with depth in this study the percent K content in the as is manure was similar throughout the depth profile, averaging 0.20% with a range of 0.18-0.21% for the six depth layers sampled.

Manure S content in this study was $4.4 \text{ mg} \cdot \text{g DM}^{-1}$ in 2 composite samples (October 2010). In 38, by-depth samples from September 2010 to August 2011, S content averaged 5.0 mg g^{-1} . These values are lower but comparable to Petersen et al. (2012). From April to August 2011, S concentration increased by 17% in the top layer (6.6 to 7.7 mg g^{-1}) but decreased by 10% in the deepest layer (4.2 to 3.8 mg g^{-1}), probably indicating higher levels of decomposition and lower solids concentration at shallower depth. This is further suggested by 79% increase in S content in surface layer (0-50 cm) from September 2010 to August 2011 (7.7 vs. 4.3 mg g^{-1}). Similar to Eriksen et al. (1995) levels of S were significantly related to both average TS and VS at each depth ($R^2=0.98$, $p<0.001$) while relating less significantly to TKN concentration ($R^2=0.73$, $p<0.05$). Overall mass balance S content changes indicated negligible losses during storage (i.e. September to October 2010 and April to August 2011), and increase with added

manure. Likewise Beard and Guenzi (1983) found only 1.7% of total S being volatilized from incubated slurry and Banwart and Bremner (1976) found no volatilized S from range of soils incubated under both aerobic and anaerobic condition. Consequently, risk for volatilization of S may be higher during mixing and spreading of manure (Moeller and Mueller 2012), and only small losses might occur during undisturbed storage of liquid manure.

Bacterial Pathogen Counts and Survival, Implications for Land Application of Manure

During 11 months of monitoring pathogen contents in stored manure (September 2010 to August 2011), *E.coli* and *Salmonella* numbers fell 1-2 log counts, while Enterococci and *C. perfringens* counts were similar at the beginning and the end of study (Fig. 5). Effects of manure additions in January and February 2011 were still evident in April 2011 samples, 2-3 months after manure addition, when *E. Coli* and Enterococci counts increased 2.2 and 1.6 log counts respectively compared to January 2011 sampling. Numbers of *Salmonella* or *C. perfringens* were unchanged for the same period. Calculated rate of decline for *E. coli* and *Salmonella* between sampling dates was within 12.5-21.6 days for one log reduction reported by Goss et al. (2013), for September 2010 sampling when manure was relatively warm. Decline rates were higher during the remainder of the study and overall survival rates during storage exceeded those reviewed by Manyi-Loh et al. (2016). Nicholson et al. (2005) found *E. coli* O157, *Salmonella* and *Campylobacter* survived up to three months in slurry storage compared to 11 mo storage in this study. A range of factors may affect pathogen inactivation rates in manure including temperature, pH, water content, nutrient availability, organic content, biological interactions, time, and organism density in manures (Manyi-Loh et al. 2016). In this study low overwinter temperatures and slow warming of manure in 2011 may have been important factors for high observed survival of pathogens as suggested by Plachá et al. (2001).

Additional to observed survival rates during storage, manure pathogens can survive up to 1 year in soil and on plants (Gerba and Smith 2005). Incidentally, animal manures have been identified as a leading cause of pathogen contamination of streams and rivers in United States (Soupir et al. 2006). For example, Samarajeewa et al. (2012) found *E. coli* and *C. perfringens* in shallow groundwater and tile drainage water samples within 3-10 days of applying swine manure to loamy soil in southern Ontario. The

practice of injecting manure into the soil as a mean to reduce greenhouse gas emissions and nutrient losses may increase survival times of pathogens after manure application (Hodgson et al. 2016).

Consequently, the survival of pathogens during prolonged storage in this study may indicate a heightened risk of contamination after land application and before pathogen counts diminish sufficiently, especially if pathogens are transported from fields by drainage water.

CONCLUSIONS

This is one of the few studies reporting in situ transformations in manure composition during storage in temperate climate. It reflects that exposure of stored manure to seasonal changes in temperature and precipitation had extensive impacts on solids concentration and decomposition rates.

High storage losses of N from the 730 m² uncovered manure surface, estimated to be 10% mo⁻¹, are known, and there seems an opportunity to improve on-farm storage design to reduce the N losses. These losses of N coupled with 51-76% drop in VS concentration at shallower depth with time, and 23-65% COD seasonal fluctuations in this study reflect the importance of sampling time and location, as well as opportunity to better preserve the value of the manure resource during current liquid manure storage practices.

High spatial and temporal variability of VFAs, sCOD and NO₃⁻ concentrations in this study, with CV up to almost 90% in regular sampling and over 120% in consistency sampling, indicates that grab sampling often used for research, such as emission measurements, and feedstock analysis may give skewed information of the actual concentration of the manure sampled. Conversely, nutrient and solids content showed lower variability with CV normally <25% and down to only a few percent, using the sampling methods applied in this study. It is likely that grab sampling would lead to higher variability in results for the nutrient and solids analysis while for liquid manure best results will come from sampling following manure agitation. These findings have implications for improving storage condition and manure utilization as well as interpretation of research related to manure, such as greenhouse gas inventories.

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Figure captions

Fig. 1. Monthly average manure depth (top), accumulated rainfall (center) and ambient average temperatures (bottom) in and around concrete liquid manure storage during the study and the month before and after study duration (August 2010 to August 2011). Manure storage tank activities are indicated relative to time of month: manure additions (A), manure removal (R), manure surface freeze (F), manure surface thaw (T), manure sampling events ($\downarrow$). Temperature measurements: Air temperature (x), manure temperatures at 0.05 m depth ($\bullet$), 1 m depth ($\blacksquare$) and 0.5 m from storage bottom ($\diamond$).

Fig. 2. Volatile solids (VS) concentration (g VS L^{-1}) trends by depth in uncovered concrete liquid dairy manure storage over 11-month period (September 2010 to August 2011), selected sampling dates, sampled in 0.5 m increments. Each sample is based on 5 sub-samples from each manure depth layer sampled taken from different locations around manure storage perimeter. Sampling category for 2.5-3.0 m depth is missing for September and October 2010 due to lower manure depth levels at time of sampling. Line graph indicates VS concentration at August 2011 sampling for each depth.

Fig. 3. Average total carbon (TC), inorganic carbon (OC) and inorganic carbon (IC) content (% DM) in a liquid dairy manure sampled by depth in 50 cm increments from an outdoor uncovered storage over a year period (September 2010 to August 2011), $n=6-8$ for depths 0-50 cm to 201-250 cm, $n=3$ for 251-300 cm depth due to fluctuating depth in storage. Error bars are the standard error of the sample mean (SEM).

Fig. 4. Development in composite samples concentrations (g L^{-1}) of total Kjeldahl nitrogen (TKN), ammoniacal nitrogen (TAN), total phosphorus (TP) and dissolved phosphorus (O-PO_4) over a 13-month period (August 2010 to August 2011) in an uncovered liquid dairy manure storage. In all 9 sampling dates are presented except TP value for 8 August 2010 is missing.

Fig. 5. Changes in manure pathogen content over an 11-month period (September 2010 to August 2011) based on composite samples from uncovered liquid dairy manure storage, 8 sampling dates for each pathogen type except for *Clostridium perfringens* which is missing value for 6 December 2010.

Table 1. Liquid dairy manure concentrations in an uncovered manure storage sampled regularly from August 2010 to August 2011. Each sample consisted of 5 sub-samples taken from different locations around manure storage perimeter. Composite samples represent depth profile of manure taken while not all parameters were quantified for every sampling date. Special one-time sampling to assess tank variability (n=5) and sampling consistency (n=3) took place in October 2010.

----- Composite samples -----								Tank variability	Sampling consistency
Parameter ^{a)}	Units	Mean(±CI)	SEM	CV (%)	Min	Max	n	CV (%)	CV (%)
pH		7.3(±0.2)	0.1	3.1	6.9	7.5	8	0.1	0.4
TS		48.6(±6.9)	3.5	20.5	37.3	65.8	8	1.4	4.4
VS		36.0(±5.9)	3.0	23.4	25.2	49.7	8	11.2	4.8
tCOD		25.1(±5.3)	2.7	32.5	12.5	34.5	9	6.1	11.1
sCOD		9.0(±2.6)	1.3	43.5	5.2	16.9	9	6.2	20.3
tVFA		4.4(±4.1)	2.1	83.0	0.3	7.3	3	59.8	111.8
BTA	g L ⁻¹	0.3(±0.3)	0.2	88.9	0.1	0.5	3	n/a	n/a
PPA		1.3(±0.6)	0.3	38.7	1.0	1.7	3	n/a	n/a
AcOH		3.4(±3.0)	0.2	79.7	0.3	5.1	3	54.7	123.5
TKN		2.1(±0.3)	0.2	24.2	1.2	2.7	9	4.6	3.8
TAN		1.1(±0.2)	0.9	24.4	0.6	1.4	9	15.0	5.2
NO ₃ ⁻		0.04(±0.02)	0.08	63.4	0.01	0.08	9	53.6	25.5
TP		0.34(±0.04)	0.02	17.5	0.28	0.46	8	8.3	9.1
O-PO ₄		0.28(±0.04)	0.02	20.8	0.17	0.40	9	8.4	5.3
Mg		9.2(±0.6)	0.3	4.6	8.9	9.5	2	5.8	4.9
K	mg·g DM ⁻¹	35.0(±2.0)	1.0	4.0	34.0	36.0	2	5.1	6.5
S		4.4(±0.3)	0.15	4.9	4.2	4.5	2	4.8	3.6
TC		41.2(±0.5)	0.3	0.9	40.9	41.4	2	1.8	0.5
IC	% DM	0.59(±0.39)	0.2	47.5	0.4	0.8	2	22.3	15.8
OC		40.6(±0.1)	0.1	0.2	40.5	40.6	2	2.2	0.9
<i>Escherichia coli</i>		3.3E+05(±3.6E+05)	1.9E+05	158.0	8.0E+03	1.2E+06	8	28.4	16.9
<i>Salmonella spp.</i>	CFU	2.1E+05(±2.6E+05)	1.3E+05	178.1	1.0E+04	1.1E+06	8	160.3	117.5
Enterococci	100 ml ⁻¹	9.2E+05(±8.8E+05)	4.5E+05	138.0	1.8E+04	3.7E+06	8	42.6	14.4
<i>Clostridium perfringens</i>		5.6E+06(±2.1E+06)	1.1E+06	51.9	1.9E+06	9.1E+06	7	29.4	29.3

NOTE: CI = 95% confidence interval, SEM = standard error of sample mean, CV = coefficient of variation.

^{a)} TS = total solids, VS = volatile solids, tCOD = total chemical oxygen demand, sCOD = soluble chemical oxygen demand, tVFA = total volatile fatty acids, BTA = butyric acid, PPA = propionic acid, AcOH = acetic acid, TKN = total Kjeldahl nitrogen, TAN = total ammoniacal nitrogen, NO₃⁻ = nitrate, TP = total phosphorus, O-PO₄ = dissolved P, Mg = magnesium, K = potassium, S = sulfur, TC = total carbon content, IC = inorganic carbon, OC = organic carbon

Fig. 1

187x153mm (300 x 300 DPI)

Fig. 2

168x123mm (300 x 300 DPI)

Fig. 3

176x127mm (300 x 300 DPI)

Fig. 4

170x118mm (300 x 300 DPI)

Fig. 5

170x118mm (300 x 300 DPI)