Agricultural and Forest Meteorology 258 (2018) 80–88

Contents lists available at ScienceDirect

Agricultural and Forest Meteorology

journal homepage: www.elsevier.com/locate/agrformet

Ammonia emissions from liquid manure storages are affected by anaerobic digestion and solid-liquid separation

Hambaliou Baldé[a], Andrew C. VanderZaag[a,*], Stephen D. Burtt[a], Claudia Wagner-Riddle[b], Leigh Evans[c], Robert Gordon[d], Raymond L. Desjardins[a], J. Douglas MacDonald[e]

[a] Agriculture and Agri-Food Canada, Ottawa, Ontario, Canada
[b] School of Environmental Sciences, University of Guelph, Ontario, Canada
[c] Golder and Associates, Ottawa, Ontario, Canada
[d] Department of Geography & Environmental Studies, Wilfrid Laurier University, Waterloo, Ontario, Canada
[e] Environment and Climate Change Canada, Gatineau, Quebec, Canada

ARTICLE INFO

Keywords:
Ammonia emissions
Manure storage
Anaerobic digestion
Solid-liquid separation

ABSTRACT

The effects of manure management practices on ammonia (NH_3) emissions were evaluated using a micrometeorological technique at four contrasting dairy storage facilities: untreated raw manure slurry (RM), solid-liquid separation with storage of separated liquids (SL), anaerobic digestion of manure and off-farm materials (AD), and anaerobic digestion with solid-liquid separation and storage of the liquid fraction (ADL). Annual average NH_3 emissions per surface area were lowest for RM (2.7 $g\,m^{-2}\,d^{-1}$), followed by SL (4.5 $g\,m^{-2}\,d^{-1}$), AD (10.0 $g\,m^{-2}\,d^{-1}$), and ADL (15.5 $g\,m^{-2}\,d^{-1}$). Lower NH_3 emissions from the RM storage were partly due to the 30 cm thick surface crust which formed on the storage surface in summer (wood shavings was used as bedding). Greater surface crusting at the AD storage compared to the ADL storage was also likely the reason for higher emissions at the ADL storage. Relationships between NH_3 emissions, temperature, and wind-speed were observed at all sites but were strongest at sites with minimal crusting (SL, ADL) and weak at the RM storage with a crust cover. Total NH_3 emissions from each storage facility ($kg\,y^{-1}$) did not simply track the differences in fluxes; rather, facilities with greater storage (RM, AD, ADL) had higher emissions than the facility with less storage (SL) due to removal of solids and more frequent field application. Overall, bedding material, manure processing, and storage management all have important effects on NH_3 emissions from manure storage.

1. Introduction

Agriculture is the largest source of anthropogenic ammonia (NH_3) emissions in Canada and livestock and fertilizer account for over 90% (Carew, 2010). Ammonia is a toxic gas that contributes to poor air quality and environmental degradation. Atmospheric ammonia leads to the formation of fine particulates that contribute to respiratory and cardiovascular diseases (Bittman and Mikkelsen, 2009). In the United States, health costs associated with NH_3 emissions were estimated to be 36 billion in 2006 (Paulot and Jacob, 2013). In Canada, NH_3 is the only gaseous pollutant which has increased in recent years. NH_3 emissions in 2014 were 21% higher than in 1990 mainly due to increased agricultural fertilizer use and larger livestock populations (Environment and Climate Change Canada, 2016). Ammonia emissions from manure storage and land application reduce the fertilizer value of manure, which is detrimental for farm efficiency (Sommer et al., 2006).

Strategies of NH_3 emission reduction are needed to meet international agreements including the Gothenburg Protocol (UNECE, 1999). Furthermore, management practices that mitigate greenhouse gas emissions must take into account the impact on NH_3 emissions to avoid pollution-swapping. Studies suggest that manure management practices including anaerobic digestion (AD), solid-liquid separation (SLS) and AD combined with SLS could be effective to mitigate greenhouse gas emissions and provide extra economic benefits to farmers, but these technologies could increase NH_3 emissions from storage (Aguerre et al., 2012; VanderZaag et al., 2015; Holly et al., 2017).

Anaerobic digestion of manure produces renewable energy from biogas and reduces methane emissions during digestate storage. Digestion also improves the nutrient availability in digestate (Karim et al., 2005). However, anaerobic digestion alone is not a viable mitigation strategy for NH_3 emissions. Digestate has high levels of ammoniacal nitrogen ($TAN = NH_3 + NH_4^+$) and a higher pH than raw

Abbreviations: NH_3, ammonia; AD, anaerobic digestion; ADL, anaerobically digested liquid fraction; RM, manure slurry; SL, separated liquid

* Corresponding author at: Agriculture and Agri-Food Canada, K.W. Neatby Bldg., C.E.F., 960 Carling Ave., Ottawa, Ontario, K1A 0C6, Canada.
E-mail address: Andrew.VanderZaag@agr.gc.ca (A.C. VanderZaag).

https://doi.org/10.1016/j.agrformet.2018.01.036
Received 16 July 2017; Received in revised form 18 November 2017; Accepted 26 January 2018
Available online 06 February 2018

Table 1
Summary characteristics of each farm, manure processing system, and storage. Where applicable, values are mean ± SD.

Parameters	RM	SL	AD	ADL
Housing type	Free stall	Free stall	Tie Stall	Free stall
Bedding	wood shavings	separated solids	Straw	separated solids
Number of lactating cows	408 ± 8	146 ± 6	117 ± 3	143 ± 7
Number of other animals	≈316	≈100	≈135	≈114
Milking system and frequency	Parlour, 3× per day.	Robots, 2.5× per day	Pipeline, 2× per day	Robots, 2.5× per day
Milk production, $L\ head^{-1}\ d^{-1}$	35 ± 1	34 ± 2	35 ± 2	28 ± 1
Fat-Protein Corrected Milk, $kg\ head^{-1}\ d^{-1}$	34 ± 1	34 ± 2	34 ± 2	28 ± 1
Days in Milk	182 ± 4	177 ± 9	171 ± 5	200 ± 14
MUN $mg\ dL^{-1}$	14.3 ± 1.8	13.5 ± 2.1	11.3 ± 1.2	13.3 ± 3.2
Storage type	Earthen	Tank	Earthen	Tank (measured) Earthen (estimated)
Slurry type	Slurry	Liquid fraction	Digested	Digested liquid fraction
Source surface area (SA), m^2	6,665	1,571	4,140	Tank: 707 Earthen: 2,257
Crust present	Thick	Little/None	Little	Little/None
Storage volume, m^3	24,230	3,910	10,090	Tank: 2,600 Earthen: 4,020
SA:Volume	0.27	0.40	0.41	Tank: 0.27 Earthen: 0.56
Storage completely emptied	Spring and fall	Spring and fall	Fall	Spring and fall
Digester(s) volume, m^3	N/A[a]	N/A	1,000	2,204
Generator capacity, kW	N/A	N/A	370	250
Biogas produced, $m^3\ d^{-1}$	N/A	N/A	3,260	3,840
Measuring periods (mm/yy)	08/15–10/16	06/13–12/14	05/13–11/14	06/14–04/15

[a] Not applicable.

manure (Fillingham et al., 2017a) resulting in higher NH_3 emissions compared to untreated manure (VanderZaag et al., 2015). Holly et al. (2017) found NH_3 emissions increased by 81% from digested storage compared to untreated manure storage in a pilot-scale study.

Solid-liquid separation is an effective method of manure treatment to remove particulate organic matter from the liquid portion of the manure. This technology reduces GHG emissions, provides additional space for liquid fraction storage and produces bedding for animals from the solids fraction. Combining anaerobic digestion and solid separation is expected to increase TAN and pH, and limit the formation of surface crusts, thereby increasing NH_3 emissions during storage (Aguerre et al., 2012; VanderZaag et al., 2015). A number of studies showed that the floating natural crusts on liquid manure reduce NH_3 emissions. On the other hand, crusts increase N_2O emissions (VanderZaag et al., 2008; VanderZaag et al., 2009; Nielsen et al., 2010), but the overall contribution is small (Le Riche et al., 2016). Averaged over 6 types of dairy manure, the CO_2-equivalent contribution of N_2O emissions was the same as indirect NH_3 emissions, each being 2.0% of the GHG budget (whereas CH_4 was 96%; Le Riche et al. 2016).

Despite the growing use of these technologies for manure treatment at farm-scale, only few studies at pilot or lab-scale have focused on NH_3 losses, especially from AD and ADL storage. It is extremely difficult to create realistic conditions in the laboratory that represent on-farm storages including continuous manure loading, surface crusting, solar radiation, and wind speed. Results from these studies vary from no impact of AD (Amon et al., 2006) to significant higher NH_3 emissions from AD storage than those from the storage of untreated manure slurry (RM) (Clemens et al., 2006; Neerackal et al., 2015; Holly et al., 2017). Furthermore, Holly et al. (2017) found NH_3 emissions from separated AD storage was reduced by 28% compared to NH_3 emissions from unseparated AD storage. In addition, Neerackal et al. (2015) reported a 64% decrease in NH_3 emissions from the separated liquid fraction of AD compared to unseparated AD storage, and found no significant difference in NH_3 emissions between storage of RM and storage of the separated liquid fraction of RM.

The variability in results and lack of farm-scale studies highlights the importance of conducting on farm measurements to explore the effects of manure management on NH_3 emissions from storage. To date there has been no on-farm study of the impacts of AD, solid-liquid separation, and AD combined with separation on NH_3 emissions from manure storage at dairy farms. Therefore, the objective of this study was to quantify the effects of manure management practices on NH_3 emissions during storage at farm-scale.

2. Materials and methods

From June 2013 to November 2016, four storages facilities were monitored for NH_3 emissions. All storages were located at commercial dairy farms in Ontario, Canada. Each facility used a different manure management, resulting in storage of: raw manure slurry (RM), separated liquid manure (SL), anaerobically digested manure (AD), and the separated liquid fraction from anaerobically digested manure (ADL).

2.1. Farm descriptions

Three farms were located near Ottawa, Ontario (RM, SL, and AD) and the fourth farm (ADL) was located about 500 km away, near Drayton, Ontario. Two farms used earthen basins (RM, AD) and two used circular concrete tanks (SL, ADL). All of the farms used a dairy herd management service (Canwest DHI, Guelph, ON) that visited the farms approximately monthly. At each visit, data was gathered on each lactating cow and the whole herd including: the number of lactating cows, milk production, milk components, and days-in-milk. In addition, we contracted Canwest DHI to measure milk urea nitrogen (MUN) from each cow's milk, which has previously been suggested as an indicator of N use efficiency and NH_3 emissions (Powell et al., 2011).

Farm RM was composed of three free-stall naturally ventilated barns including a main barn for the milking and dry cows, and separate barns for the heifers and calves. The herd consisted of 419 ± 8 milking cows, about 114 dry and transitional cows, 240 heifers, and 200 calves. Bedding material in all barns was wood shavings. Liquid manure from cows and heifers was removed from the floor using scrapers and stored in an underfloor tank in each barn before being pumped (every 2–3 days) through an underground pipe to the center of the earthen storage. Semi-solid manure from the calf barn was dumped into the earthen storage using a tractor. Herd-average milk production was among the highest of all farms (Table 1). MUN was the highest of all farms, and in-line with the industry average of 14 $mg\ dL^{-1}$ reported by

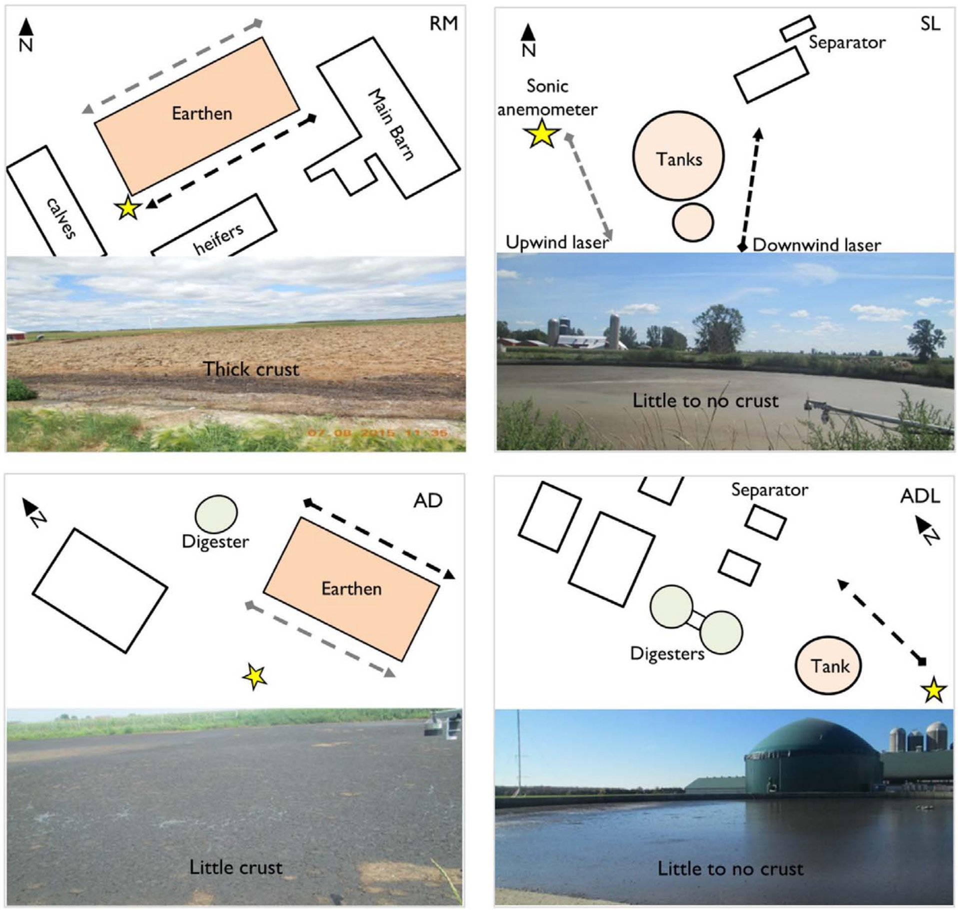

Fig. 1. Approximate farm configurations with approximate positions of laser sensors and sonic anemometers (star). Diagrams are not to scale. The main barn at SL is north-east of the separator and is not visible. The upwind laser at ADL was west of the tank and is not shown. Photos indicate typical surface condition in summer at each farm.

Powell et al. (2011).

Farms SL, AD and ADL are described in Ngwabie et al. (2014; ADL); Maldaner et al. (2017; ADL); Baldé et al. (2016a, c; SL,b; AD) and summarized below and in Table 1.

The SL facility consisted of two naturally ventilated barns (a 3,270-m^2 free-stall barn and a 1,710-m^2 barn for heifers), a naturally ventilated building containing a screw-press solid-liquid separator (DariTech, Lynden, Washington) and composted solids, and two outdoor concrete manure storage tanks (Fig. 1, SL). The Holstein-Friesian herd included about 146 milking cows, ~30 dry cows, ~60 heifers, and calves. Composted solids was the primary bedding for dry cows, milking cows, and heifers. Milk production, DIM, and MUN were similar to the RM farm.

The AD farm had a 1510-m^2 naturally ventilated barn containing milking cows (tie-stall) and heifers and dry cows (free-stall), an anaerobic digester, a building containing a pre-heating tank and a biogas engine, and an outdoor earthen storage. The Holstein-Friesian herd typically included 117 lactating cows, 15 dry cows, and 136 heifers and calves. Straw was the main bedding. Herd-average milk production was similar to the RM farm, while DIM was the lowest of all farms. This farm was more efficient than the others in dietary N management since MUN was at least 2 mg dL^{-1} lower than all other farms (Powell et al., 2011).

The ADL farm had two naturally ventilated barns, two anaerobic digesters, a solid-liquid separator building, and a small building containing a biogas engine. The farm had two digestate storages: an outdoor digestate storage tank (where measurements took place), and an off-site earthen digestate storage basin that was not monitored but was included in calculations of overall farm storage NH_3 emissions. The main barn housed milking cows and heifers, and the second barn housed dry cows and calves. The Holstein-Friesian herd typically had 143 milking cows, 100 heifers, 14 dry cows and 22 calves. A rubber mat base covered with straw and separated solids provided bedding in the main barn. Milk production was lower than the other farms despite similar feed intake, which is consistent with this farm having the highest DIM indicating more cows in late stages of lactation than the other farms.

The manure-handling systems and crust present on the storage surface varied between farms as described below (Table 1, Fig. 1) and with more details in Ngwabie et al. (2014); Baldé et al. (2016a,b), Maldaner et al. (2017):

- RM farm: untreated manure slurry was stored in an outdoor earthen storage of 6,665 m^2 surface area and 24,230 m^3 capacity which was emptied in spring and fall. A thick surface crust (~30 cm) formed during summer and remained until manure was agitated for land application in fall.
- SL farm: raw manure within the new barn was removed by scrapers and stored in a 37-m^3 underground tank in the corner of the barn. Manure was pumped periodically throughout the day to the solid-liquid separator. After separation the liquid fraction was stored in two concrete tanks with surface areas of 1,570 m^2 and 314 m^2, and total volume of 3,910 m^3. Tanks were emptied in spring and fall, and some manure was removed in summer. A thin (< 2 cm) surface crust occasionally formed and dispersed during the summer.
- AD farm: raw manure within the barn was removed from the floor using scrapers for the free-stall section, and gutter cleaners in the tie-stall area. Manure was stored in an underfloor tank (~30 m^3) and pumped to the digester twice per day where it was combined

with off-farm materials. Throughout the day, digestate (including all solids, since there was no solids-liquid separation) was transferred by gravity through an underground pipe to the earthen storage with 4,140 m^2 surface area and 10,090 m^3 volume. A small quantity of digestate was removed in spring and summer, and then completely emptied in fall. A moderate crust (< 5 cm) formed during summer.

- At the ADL farm, raw manure in the main barn was scraped from the floor into an underfloor pit system. From there, raw manure was pumped into a 20-m^3 mixing tank where raw manure and off-farm material were mixed then pumped into the digesters. After digestion, approximately 75% of the digestate passed through a screw-press solid-liquid separator. A portion of digested liquid from the separator was pumped to the 707-m^2 tank of ~2,600 m^3 volume through an underground pipe. The tank was emptied in spring and fall. Occasionally a thin (< 2 cm) crust formed and dispersed on the surface during summer. The remaining portion of digestate was stored at the earthen storage ~900 m away.

2.2. Ammonia concentrations and wind measurements

The concentration of NH_3 was measured using open-path lasers (GasFinder2 OP, Coldfire Processor V1.10.h, Boreal Laser Inc., Edmonton, Canada). At the farms with earthen storage (RM and AD), lasers and the retro-reflector arrays were placed along the berms. At the farms with storage tanks (SL and ADL), laser paths were situated 15–20 m away from the tank edges. Concentration measurements were conducted over at least one year at each site, covering May 2013–October 2016 (Table 1). At any given time up to two sites were monitored simultaneously using two identical sensor systems. Background concentrations were measured by upwind lasers at each site and found to be zero most of the time. This was consistent with Rumburg et al. (2007) who found background NH_3 concentrations were at the detection limit of the instrument. Concentrations were measured approximately every second and stored in onboard memory. Concentration data were removed when the light level was < 2,000 or > 15,000 (unitless) or the status code of the laser was abnormal (i.e., ≠ 1, 101, 4,001, or 4,101). Since the NH_3 concentration measured can be zero, no filtering on R^2 between sample signal and reference signals was used; but the graph of R^2 vs ppmm was inspected to identify possible outliers for manual removal, as per manufacturer instructions.

Monin-Obukhov similarity theory was used to characterize turbulence near the surface including the friction velocity (u_*), Monin-Obukhov stability length (L), surface roughness length (z_0), and wind direction (WD). These parameters were calculated from measurements of wind components (horizontal, lateral, and vertical) and air temperature at 2.5 m height using a high-frequency 3-dimensional CSAT3 sonic anemometer (Campbell Scientific Inc., Edmonton, Alberta) connected to a CR1000 or CR3000 datalogger (Campbell Scientific Inc., Edmonton, Alberta). In addition, air temperature was measured at 2 m height using a Type T (copper-constantan) shielded thermocouple.

The datalogger calculated and recorded 15-min wind statistics including variances and covariances of the wind components and temperature, averages and standard deviations of wind components and temperature. The 3-D sonic anemometers were located on flat fields or on the downwind berm of the earthen storage (at RM) as suggested by Ro et al. (2014).

The total number of 15-min periods of data (i.e. after synchronization of anemometer and laser data) were about 13,880 at RM farm, 15,980 at SL, 6,230 at AD, and 12,820 at the ADL farm. Data at each farm was filtered based on wind direction, so that data was processed only when wind was coming from the upwind open area towards the source (storage) before reaching the downwind laser (Fig. 1). Specifically, the WD intervals were: between 270° and 45° at RM; between 220° and 330° at SL; between 210° and 330° at AD; and between 210° and 340° at ADL.

2.3. Emission calculations

To determine NH_3 emission rate (kg h^{-1} and kg h^{-1} m^{-2}), the backward Lagrangian Stochastic (bLS) inverse-dispersion technique was used as described by Flesch et al. (1995, 2004, 2005) and implemented in WindTrax (version 2.0.8.8, Thunder Beach Scientific). The accuracy of this technique has been evaluated in several on-farm controlled-release experiments (Ro et al., 2014; Baldé et al., 2016a,b). Results of these studies have shown that estimated emissions were within 15% of actual emissions.

After NH_3 emissions rates were calculated in WindTrax, data were removed when $u_* < 0.15$ m s^{-1}, $|L| < 5$ m, $z_0 > 0.25$ m, the fraction covered by touchdowns < 0.65, or the coefficient of variation for the model > 20%. After filtering, the number of 15-min emission rates for each farm were: RM = 2,870, SL = 3,870, AD = 2,470, ADL = 1,650. Filtered NH_3 emission rates data were then binned into hourly averages and calculated for each hour of day in each month, and then the monthly average was calculated from binned hourly means (Gao et al., 2009). Monthly averages of emissions were grouped per season: spring (March, April, May), summer (June, July, August), fall (September, October, November) and winter (December, January, February). Seasonal averages were then scaled by source surface area, as well by volume stored.

Relationships between air temperature, surface temperature, windspeed, and NH_3 emissions were assessed with linear and non-linear regression. Comparisons of emissions between seasons at the same sites were compared using a paired *t*-test on binned hourly means. Analyses were performed in Matlab (Mathworks Inc., Natick, MA) with a level of statistical significance of $p < .05$.

2.4. Sampling storages for chemical characteristics of manure and digestate

Samples were taken from storages at least once per month from spring to fall during all study periods. The samples were taken either using a sampling pipe to collect a column of manure or digestate from the surface to the bottom (at RM, SL and AD) (Baldé et al., 2016a,b), or a telescopic sampling pole to sample the liquid portion near the surface (at ADL) (Maldaner et al., 2017). At RM, samples were also obtained from the in-barn manure holding pits prior to transfer to the manure storage (main barn and heifer barn). Manure samples were placed in a cooler for transport and then frozen until they were analyzed for pH, DM, Total N, and TAN, based on recommended methods (Peters et al., 2003).

2.5. Volume and temperature in storage

At RM, SL and AD, depth changes in storages were measured using a Sonic Ranging sensor (SR50AT, Campbell Scientific Canada Inc., Edmonton, Alberta) positioned above the manure or digestate on a metal pole and connected to a CR800 datalogger (Campbell Scientific). Volume stored was calculated based on depth measurements as described in Baldé et al. (2016a,b). At ADL, stored depth variations were measured manually at least weekly using a tape measure from the tank edge to the digestate surface. The mass of TAN and N in storage were calculated monthly based on the measured volume and the concentration of TAN or TKN. Temperatures in the bulk manure were measured using submerged thermistors at a fixed location above the bottom (approximately 40 cm at SL and 150 cm at RM, AD), and using submerged thermocouples at several depths at ADL.

Crust characteristics of the storages surface were determined by observing time-lapse photographs from each site to estimate crust coverage and crust thickness. Surface temperature of the storages was measured by a precision infrared radiometer that measured surface temperature without physical contact (SI-111, Campbell Scientific, Edmonton, Alberta). This radiometer was mounted on the same pole as the sonic ranging sensor (for example see photos for SL or AD in Fig. 1).

Table 2
Chemical characteristics of dairy manure samples at each storage (RM = Raw Manure, SL = Separated Liquid, AD = Anaerobically Digested, ADL = Anaerobically Digested Liquid fraction). Dry matter (DM) at farm RM is also reported for in-barn samples.

Parameter	RM	SL	AD	ADL
pH	7.3 ± 0.2	7.1 ± 0.3	7.4 ± 0.1	7.9 ± 0.1
TAN (mg kg^{-1})	1082 ± 198	944 ± 143	1542 ± 364	3120 ± 446
Total N (g kg^{-1})	2.5 ± 0.04	1.9 ± 0.1	3.4 ± 1	3.2 ± 0.4
DM (g kg^{-1})	39 ± 7 (storage) 128 (main barn) 92 (heifer barn)	40 ± 12	47 ± 7	39 ± 2

3. Results and discussion

3.1. Characteristics of manure slurry, separated liquid, and digestate

The farms with digesters generally had higher pH (7.9 ± 0.1 for ADL and 7.4 ± 0.1 for AD) than non-digested manures (7.1 ± 0.3 for SL, 7.3 ± 0.2 for RM) (Table 2). Similarly, the highest concentrations of TAN were observed at the farms with digesters, and ADL was about twice as high as AD (Table 2; perhaps due to the longer digestion time and different off-farm materials used at ADL). Total N concentration was similar between ADL and AD, both of which were higher than RM and SL (Table 2). This is consistent with studies suggesting digestate has higher TAN and pH, compared to undigested manure (Clemens et al., 2006).

Despite the different manure treatments, there was little difference in dry matter (DM) content in the samples collected from the storages. It was expected that RM should have higher DM than the others, and indeed in-barn samples at RM were much higher (Table 2). Moreover, extensive surface crusting at the RM farm was evidence of solids. The lack of measured DM difference in the RM storage is likely an artifact of the different manure sampling techniques used at each farm and the difficulty sampling with the thick crust. Due to the extensive crust, manure samples were also taken during agitation prior to land application, which was not the case at other farms. Other contributing factors are that the RM farm used water to cool the milk through a heat exchanger, and substantial volumes of excess water were discharged into the manure storage. Crusts likely also reduce evaporation and increase dilution from precipitation as seen with permeable covers (VanderZaag et al., 2010).

Differences in surface crust formation between the storages were important for ammonia emissions. Crust formation occurred from early summer to fall at some farms. Farms with solid-liquid separators and separated solids bedding (SL and ADL) formed a very thin crust (< 2 cm) from time to time, which was easily dissipated by wind and rain. Digestion without separation (AD) with use of straw bedding was associated with a modest crust (< 5 cm) that was usually present but had many cracks and moist areas, and was partially dissipated by rain. Without any manure treatment, and using wood shavings for bedding, farm RM had a solid, thick, crust (> 30 cm) that was usually completely dry on the surface and could easily support birds that landed upon it (Fig. 1).

The mean monthly air temperature measured on-site during measurement campaigns ranged from −11 °C to 25 °C. The mean monthly temperature measured inside storages was above 15 °C from July to September. The highest monthly average manure or digestate temperatures were observed in August at RM (~19 °C), July at SL (~22 °C), August at AD and ADL (~22 °C and ~21 °C, respectively). Peak surface temperatures were higher than the bulk manure temperatures at all sites.

3.2. Temporal variations in NH_3 flux

Ammonia emissions varied over time and had distinct annual and hourly cycles at each farm (Figs. 2 and 3). Throughout the year, 15-min fluxes varied from: 0 to 0.55 g m^{-2} h^{-1} with an average of 0.11 ± 0.11 g m^{-2} h^{-1} at RM; 0 to 1.64 g m^{-2} h^{-1} with an average of 0.23 ± 0.24 g m^{-2} h^{-1} at SL; 0 to 2.38 g m^{-2} h^{-1} with an average of 0.44 ± 0.41 g m^{-2} h^{-1} at AD; and 0 to 4.91 g m^{-2} h^{-1} with an average of 0.77 ± 0.64 g m^{-2} h^{-1} at ADL. The maximum emissions

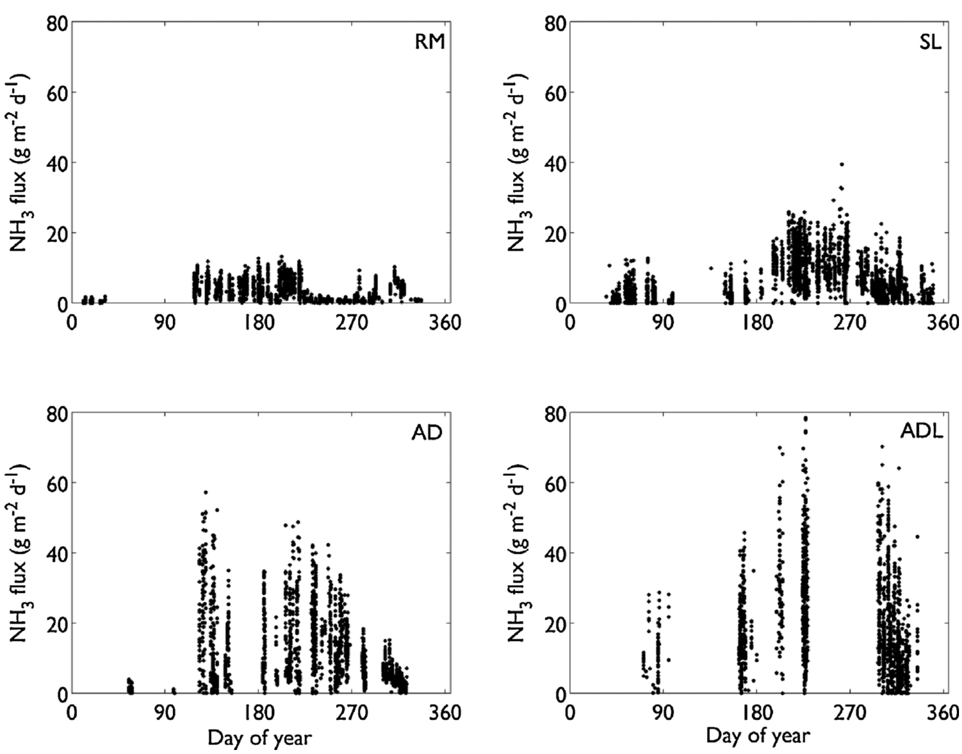

Fig. 2. Annual variation of NH_3 emissions from each storage. The number of 15-min periods was: 2,870 at RM, 3870 at SL, 2,470 at AD, and 1,650 at ADL. NH_3 emissions were above 80 g m^{-2} d^{-1} during some periods (around DOY of 225) at ADL.

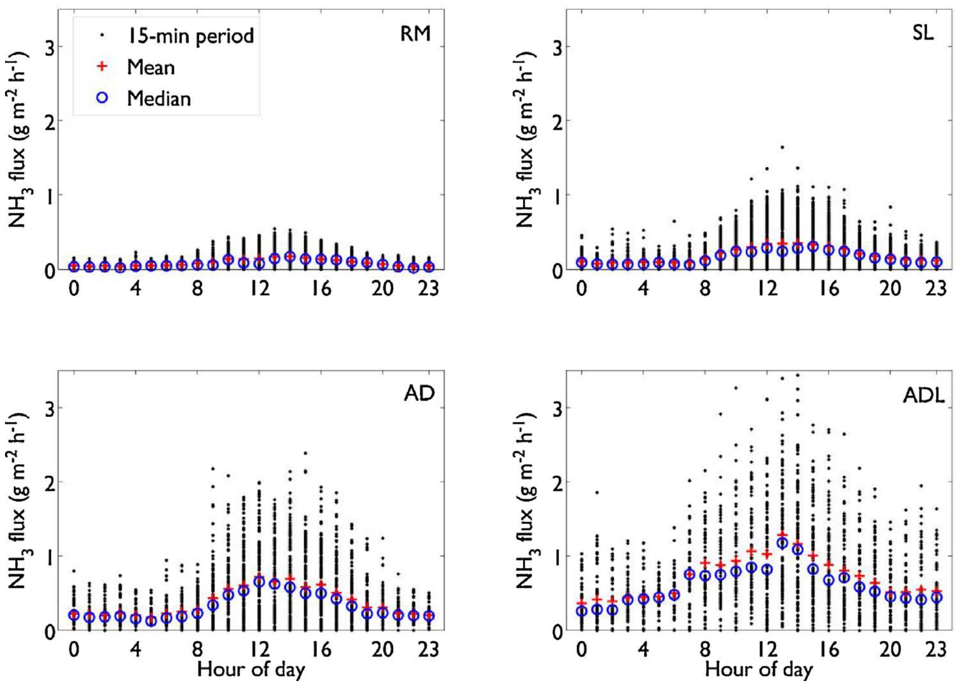

Fig. 3. Binned hourly average NH_3 fluxes during all measurement period from each farm. Note that 4 data points are above the scale (3.5–5 g m^{-2} h^{-1}) for ADL at 11:00 h–14:00 h.

occurred between 12:00 and 14:00 h at all farms (Fig. 3) which is consistent with the release of ammonia being driven the temperature and wind speed at the storage surface, both of which tend to be highest in the early afternoon.

3.3. Relationships between NH_3 flux, temperature, and wind-speed

On a daily average basis, relationships were observed between NH_3 emissions and air temperature at all sites (Fig. 4). The strongest correlations were observed at sites which had received treatment (SL: $R^2 = 0.66$, $p < .0001$; AD: $R^2 = 0.65$, $p < .0001$; ADL: $R^2 = 0.52$, $p < .0001$), but the RM site had a much weaker relationship ($R^2 = 0.23$, $p = .02$). This confirms that storage with a thick surface crust had greater decoupling from the atmosphere, leading to lower NH_3 flux. At the other sites with minimal crusting, the non-linear influence of air temperature is consistent with the observations of Grant et al. (2013) during NH_3 emissions measurements from earthen swine manure storages which also do not form appreciable crusts.

On an hourly basis, the relationships between NH_3 flux, surface temperature, and wind-speed was evident at all sites (Fig. 5). Multiple

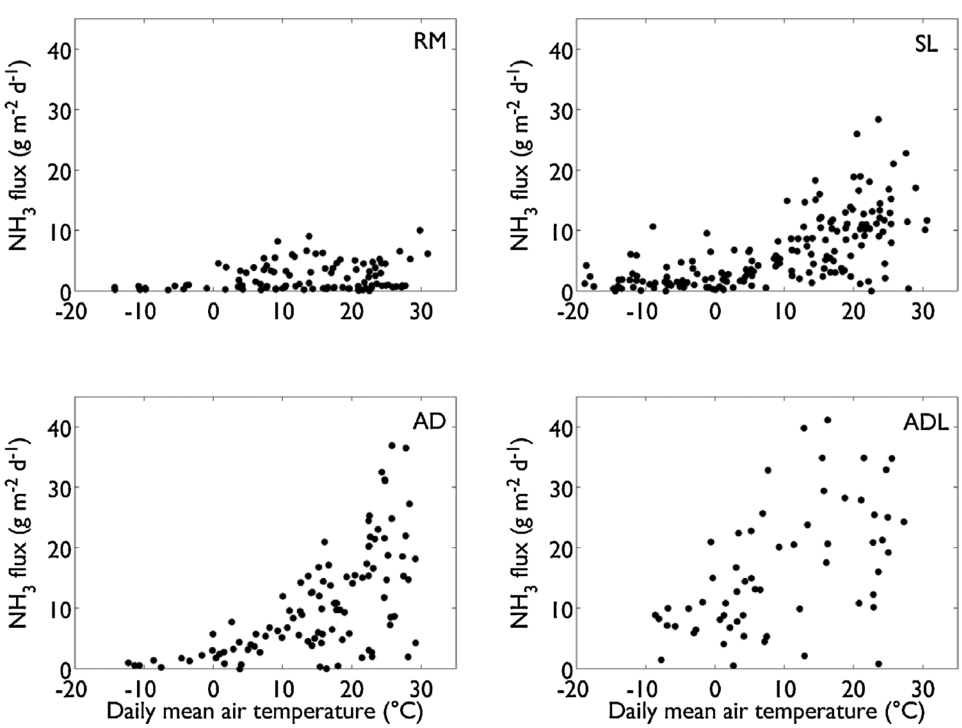

Fig. 4. Relationship of air temperature and daily NH_3 emissions from four storages of different manure treatments. The number of days at each site are: 103 for RM, 172 for SL, 102 for AD, and 60 for ADL.

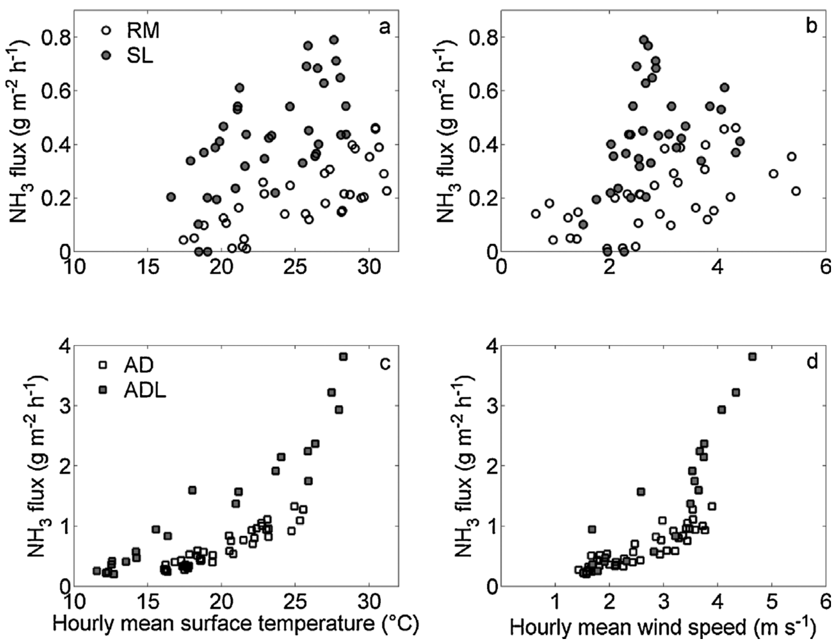

Fig. 5. Relationship of surface temperature and NH_3 emissions from (a) non-digested storages, and (c) digested storages. Relationship of wind-speed and NH_3 emissions from (b) non-digested storages, and (d) digested storages. Data for non-digested storages are raw manure (RM) on 2016-06-28 and 2016-08-06, and separated liquid (SL) on 2014-08-08, 2014-08-27 and 2014-08-28. Data for digested storages are anaerobic digestate (AD) on 2014-08-21 and 2014-08-22, and separated liquid digestate (ADL) on 2014-06-28.

regressions of these data produced the following relationships between NH_3 flux (F_{NH3}, $g\,m^{-2}\,h^{-1}$), surface temperature (T, °C; over a range from 15 to 24 °C), and wind-speed (WS, $m\,s^{-1}$; over a range from 1 to 6 $m\,s^{-1}$):

RM: $F_{NH3} = -0.34 + 0.019\,T + 0.02\,WS \quad R^2 = 0.61,\ p < .001$

SL: $F_{NH3} = -1.02 + 0.045\,T + 0.16\,WS \quad R^2 = 0.72,\ p < .001$

AD: $F_{NH3} = -1.15 + 0.070\,T + 0.15\,WS \quad R^2 = 0.94,\ p < .001$

ADL: $F_{NH3} = -0.99 + 0.057\,T + 0.18\,WS \quad R^2 = 0.94,\ p < .001$

While these relationships are based on short windows of time during the summer, they are informative in quantifying the relationships between NH_3 flux and environmental variables, and the difference between treatments. The weakest relationship was observed at the RM storage, which also had the lowest coefficient for both T and WS, supporting the decoupling between NH_3 emitting surface and the atmosphere caused by the surface crust. By comparison, the WS coefficient was 7.5× larger at the AD farm with a slight crust, and 8× to 9× larger at SL and ADL farms which did not have crusts. The coefficient for T was largest at the farms with digestion (AD, ADL), which had the greatest emission potential due to higher pH and TAN concentration.

The windows of time were selected because the storages were not disturbed by farm activities. Furthermore, in the selected periods all storages had significant depth of manure which avoids the tank walls acting as windbreaks. Finally, the periods were chosen when surface crusts had developed and were stable. If the period were extended we would need to add model parameters for crust dynamics, ice, snow, emptying/mixing, and so on, which would require a more in-depth modeling study. Nevertheless, when all data was used at each site the multiple regressions noted above were still statistically significant ($p < .001$) but the fit statistics worsened.

The positive correlation with wind-speed has implications for calculating emission factors. This is because micrometeorological techniques such as the one used in the present study require a minimum wind-speed (in this case, low wind-speeds are removed, c.f. Fig. 5). As a result, the measurement periods are biased towards windier conditions, and the NH_3 flux would likely be an over-estimate of the true annual average. That said, due to the paucity of farm-scale measurements of NH_3 flux, we consider these data to be highly valuable in informing science and policy, improving understanding of emission processes related to management practices, and reducing uncertainty of emission factors.

3.4. Seasonal average flux scaled by surface area

When scaled by surface area, NH_3 emission rates were substantially higher from AD and ADL storages compared to RM and SL storages (Table 3). In spring, emissions were 16.7 $g\,m^{-2}\,d^{-1}$ at ADL, and 15.9 $g\,m^{-2}\,d^{-1}$ at AD, compared to 4.1 $g\,m^{-2}\,d^{-1}$ and 2.0 $g\,m^{-2}\,d^{-1}$

Table 3
NH_3 emission rates from four differently managed farm–scale storages containing raw manure (RM), separated liquid manure (SL), anaerobically digested manure (AD), and separated liquid anaerobic digestate (ADL). Values are based on mass of NH_3 (not NH_3-N).

Season	NH_3 emissions by manure treatment			
	RM	SL	AD	ADL
	a) $kg\,NH_3\,d^{-1}$			
Winter	5	2	4	nd[a]
Spring	30	3	66	38
Summer	26	13	63	55
Fall	16	10	32	45
	b) $g\,NH_3\,m^{-2}\,d^{-1}$			
Winter	0.68	1.26	0.87	nd
Spring	4.13	1.97	15.89	16.75
Summer	3.61	8.20	15.28	24.31
Fall	2.26	6.46	7.77	19.72
	c) $g\,NH_3\,m^{-3}\,d^{-1}$			
Winter	0.29	0.93	0.65	nd
Spring	1.74	2.05	6.62	7.12
Summer	1.59	5.42	6.68	12.47
Fall	1.33	5.24	4.23	6.06
	d) $g\,NH_3\,kg^{-1}$ N stored d^{-1}			
Winter	0.11	0.44	0.19	nd
Spring	0.66	0.98	1.91	1.63
Summer	0.60	2.58	1.93	2.85
Fall	0.51	2.50	1.22	1.38
	e) $g\,NH_3\,kg^{-1}$ TAN stored d^{-1}			
Winter	0.26	0.94	0.40	nd
Spring	1.53	2.07	4.09	2.17
Summer	1.40	5.47	4.12	3.81
Fall	1.17	5.29	2.61	1.85

[a] No data.

at RM and SL, respectively. In summer, emissions were 24.3 $g\,m^{-2}\,d^{-1}$ at ADL and 15.3 $g\,m^{-2}\,d^{-1}$ at AD, compared to 3.6 $g\,m^{-2}\,d^{-1}$ and 8.2 $g\,m^{-2}\,d^{-1}$ at RM and SL, respectively. In fall, emissions were 19.7 $g\,m^{-2}\,d^{-1}$ at ADL and 7.8 $g\,m^{-2}\,d^{-1}$ at AD, compared to 2.3 $g\,m^{-2}\,d^{-1}$ at RM and 6.5 $g\,m^{-2}\,d^{-1}$ at SL. Averaged over all 15-min periods, compared to ADL, NH_3 fluxes were about 86% lower at RM, 70% lower at SL, and 43% lower at AD. These findings are consistent with the increase of NH_3 emissions during digestate storage compared to untreated dairy manure slurry (Holly et al., 2017) owing to greater concentration of TAN and higher pH (Table 2; Sommer and Husted, 1995; Sommer et al., 2006; Blanes-Vidal et al., 2009; Frear et al., 2011).

The findings also confirm that thick surface crusts reduce NH_3 emissions (VanderZaag et al., 2008; Aguerre et al., 2012). Storages with crust formation in summer (RM and AD) had no significant difference ($p = .61$) between spring and summer emissions because the crust reduced emissions to offset warmer temperatures (Table 3b). In contrast, storages with little or no surface crust in summer had a significant increase ($p < .0001$) from spring to summer (Table 3b), reflecting a closer coupling between the emitting surface and atmospheric conditions when no crust was present.

This study is unique in performing farm-scale measurements of NH_3 emissions from four storages of different dairy manure management practices. There are few on farm studies to compare our results with and the few available have been done from untreated storages. McGinn et al. (2008) studied NH_3 emissions from an untreated dairy manure earthen storage over summer in Alberta, finding on average 5.1 $g\,m^{-2}\,d^{-1}$ compared with 3.6 $g\,m^{-2}\,d^{-1}$ in this study over summer at RM. This difference can be explained by the minimal crust (about 1-cm) on the manure surface in McGinn et al. (2008) compared to the thick crust present during the summer at the RM farm. This is likely due to differences in bedding material, although McGinn et al. (2008) did not specify the bedding used. Our spring NH_3 emissions at RM (4.13 $g\,m^{-2}\,d^{-1}$) when crust formation was limited (~1-cm) are closer to the emissions found by McGinn et al. (2008), but are understandably less due to cooler temperatures in spring compared to summer. Harper et al. (2009) measured NH_3 emissions from three untreated dairy manure earthen storages in Wisconsin and found NH_3 emissions ranged from 4.68 to 6.00 $g\,m^{-2}\,d^{-1}$ in summer and from 2.23 to 3.24 $g\,m^{-2}\,d^{-1}$ in fall. Their emissions are higher than our findings likely due to the lack of crust formation in summer in their study (using sand bedding) compared to our study where wood shavings were used. This suggests that using wood shavings as bedding helps to reduce NH_3 losses and retain N in the storage by producing a thicker crust.

3.5. Seasonal average facility-scale emissions from each storage

Ammonia emissions ($kg\,d^{-1}$) represent the entire loss of NH_3 from the liquid storage facility, unlike the NH_3 flux densities discussed previously scaled per m^2 of surface area. Seasonally averaged NH_3 emissions reflect both the emission potential (per m^2 or per m^3) combined with the management practices related to storage volume, surface area, and spreading time. Consequently, facility-scale emissions followed quite a different pattern between the farms (Table 3). Farms with large storage surface areas had the highest total daily NH_3 emissions, on an annual average basis (41.2 $kg\,d^{-1}$ and 35.3 $kg\,d^{-1}$, 19.4 $kg\,d^{-1}$, respectively at AD, ADL, RM) compared to the farm with the smallest surface area (SL) which had 7.1 $kg\,d^{-1}$, on an annual average basis (Table 3a). The SL facility had the smallest storage volume and surface area, mainly due to three factors: 1) having fewer replacement animals on-site (this was also done at ADL), 2) solid separation reduced the liquid storage requirements, and 3) spreading of manure during the growing season (on hay crops) in addition to removal in spring and fall. By contrast, the two farms with digesters (AD and ADL) bring off-farm materials onto the farm, thereby increasing the total volume and total N processed and stored at the facility and requiring more overall storage capacity.

Ultimately, however, emissions from liquid storage only represent a portion of the overall NH_3 emissions from a manure management system. For example, the lower total NH_3 emissions at the SL farm liquid storage is offset to some extent by higher NH_3 emissions from the solid-liquid separator and composter (Fillingham et al., 2017b). Additional modeling would be required to fully assess the effect of management on overall whole-farm ammonia emissions (Chai et al., 2016).

3.6. Ammonia emissions scaled by volume and N in storage

Scaled by the volume stored (Table 3c), NH_3 emission rates had similar trends as emissions scaled by surface area (Table 3b). The NH_3 emissions ranged from (Table 3c): 0.29 (in winter) to 1.74 (in spring) $g\,m^{-3}\,d^{-1}$ from RM storage; 0.93 (in winter) to 5.42 (in summer) $g\,m^{-3}\,d^{-1}$ from SL; 0.65 (in winter) to 6.68 (in summer) $g\,m^{-3}\,d^{-1}$ at AD; and 6.06 (in fall) to 12.47 (in summer) $g\,m^{-3}\,d^{-1}$ at ADL. To our knowledge there is no farm-scale data for comparison. However, these results are comparable with some pilot-scale studies including Amon et al. (2006) who studied pilot-scale NH_3 emissions during dairy manure storage under warm conditions and found about 2.83 $g\,m^{-3}\,d^{-1}$ from untreated manure and 5.04 $g\,m^{-3}\,d^{-1}$ from SL. Misselbrook et al. (2016) found about 3.67 $g\,m^{-3}\,d^{-1}$ from pilot-scale cattle slurry storage.

When scaled by the quantity of N stored, NH_3 emission rates showed different trends than the previous ones (e.g. scaled by surface area or volume stored). The highest emission rates in summer occurred from storages with separation (SL, ADL) likely due to the lack of crust and removal of organic N through separation leaving these sites with the highest TAN/TN ratio (Table 2). Scaled by the quantity of TAN stored, emissions in spring were highest from AD, followed by ADL and SL (Table 3e). In summer and fall, scaled emissions were highest from SL, followed by AD and ADL. The RM site had the lowest emission in every season, per unit of TAN stored.

3.7. Annual emission estimates

Annual emission estimates were calculated based on seasonal average fluxes. Data from ADL in winter was not available so 1 $g\,m^{-2}\,d^{-1}$ and 1 $g\,kg^{-1}$ TAN d^{-1} was assumed. The resulting annual values were inversely related to the extent of manure processing: ADL (5.6 $kg\,m^{-2}\,y^{-1}$), followed by AD (3.6 $kg\,m^{-2}\,y^{-1}$), SL (1.6 $kg\,m^{-2}\,y^{-1}$), and RM (1.0 $kg\,m^{-2}\,y^{-1}$). It is worth noting that the number of farm products also differs with the level of processing. All farms produce milk, but farms ADL and SL also produce bedding from manure processing, and farms AD and ADL produce electricity and heat from processing manure and co-feedstocks. Additional assessment and modeling would be required to fully assess NH_3 emissions in the context of productivity.

Annual emissions per unit of TAN stored were calculated with the assumption that 1 kg of TAN was stored for ~6 months (182.5 d). In this case the highest emission factor was 2× to 3× greater for processed manures compared to RM. The % of TAN emitted as NH_3-N was highest for SL (52%), followed by AD (42%), ADL (33%), and RM (16%). If we consider that manure was stored for less time, on average, at the SL farm than the others, and use 160 d as the storage time for that farm, then the SL emission factor becomes 45% which is more similar to the other sites with processing.

4. Conclusion

Ammonia-N concentration, nitrogen content and pH were higher in both AD and ADL storages compared to the separated liquid alone (SL) and raw manure storage (RM). Annual NH_3 emissions scaled by surface area from ADL (5.6 $kg\,m^{-2}\,y^{-1}$) were 55% higher than digestion without separation (AD), 3.5× higher than SL, and 5.6× higher than untreated RM storage. Total NH_3 emissions at a facility-scale, however, were higher from storages with greater manure storage capacity (and greater surface area), resulting in the SL storage having the lowest emissions. Storages with either moderate or thick surface crusts (AD, RM) in summer had similar emissions in spring and summer, while farms without crusts (i.e. with separation: SL, ADL) had increased emissions in summer compared to spring. Besides a lack of crust, separation (SL, ADL) led to greater proportions of TAN/TN, resulting in higher NH_3 emissions scaled per kg N stored. Correlations between fluxes, temperature, and wind-speed, were observed at all storages, but were strongest at sites without crusts. Additional assessment and modeling would be required to fully assess integrated whole-farm NH_3 emissions and to put emissions in the context of the co-products produced by manure processing (electricity, heat, bedding).

Acknowledgements

Funding was provided by Agriculture and Agri-Food Canada through Abase project #1254, Natural Resources Canada's Program of Energy Research and Development (project #022), and a scholarship from Ontario Ministry of Agriculture, Food, and Rural Affairs to LE. The warm reception from the cooperating farms is greatly appreciated. Technical assistance was provided by Dirk Anderson, Jordan Forsyth, Lia Maldaner, Darcy Snyder, Marc Lefebvre, and Melanie Fillingham. Chris Duke, Amadou Thiam, and Terrence Sauvé of Ontario Ministry of Agriculture, Food, and Rural Affairs are appreciated for providing guidance and assistance in coordinating the research sites.

References

Aguerre, M.J., Wattiaux, M.A., Powell, J.M., 2012. Emissions of ammonia, nitrous oxide, methane, and carbon dioxide during storage of dairy cow manure as affected by dietary forage-to-concentrate ratio and crust formation. J. Dairy Sci. 95, 7409–7416. http://dx.doi.org/10.3168/jds.2012-5340.

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. http://dx.doi.org/10.1016/j.agee.2005.08.030.

Baldé, H., VanderZaag, A.C., Burtt, S., Evans, L., Wagner-Riddle, C., Desjardins, R.L., MacDonald, D.J., 2016a. Measured versus modeled methane emissions from separated liquid dairy manure show large model underestimates. Agric. Ecosyst. Environ. 230, 261–270. http://dx.doi.org/10.1016/j.agee.2016.06.016.

Baldé, H., VanderZaag, A.C., Burtt, S.D., Wagner-Riddle, C., Crolla, A., Desjardins, R.L., Macdonald, D.J., 2016b. Methane emissions from digestate at an agricultural biogas plant. Bioresour. Technol. 216, 914–922. http://dx.doi.org/10.1016/j.biortech.2016.06.031.

Baldé, H., VanderZaag, A.C., Burtt, S.D., Gordon, R.J., Desjardins, R.L., 2016c. Does fall removal of the dairy manure sludge in a storage tank reduce subsequent methane emissions? J. Environ. Qual. 45, 2038–2043. http://dx.doi.org/10.2134/jeq2016.03.0083.

Bittman, S., Mikkelsen, R., 2009. Ammonia emissions from agricultural operations: livestock. Better Crops Plant Food 93, 28–31.

Blanes-Vidal, V., Sommer, S.G., Nadimi, E.S., 2009. Modelling surface pH and emissions of hydrogen sulphide, ammonia, acetic acid and carbon dioxide from a pig waste lagoon. Biosyst. Eng. 104, 510–521. http://dx.doi.org/10.1016/j.biosystemseng.2009.09.008.

Carew, R., 2010. Ammonia emissions from livestock industries in Canada: feasibility of abatement strategies. Environ. Pollut. 158, 2618–2626. http://dx.doi.org/10.1016/j.envpol.2010.05.004.

Chai, L., Kröbel, R., MacDonald, D., Bittman, S., Beauchemin, K., Janzen, H., McGinn, S., 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.

Clemens, J., Trimborn, M., Weiland, P., Amon, B., 2006. Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. Agric. Ecosyst. Environ. 112, 171–177. http://dx.doi.org/10.1016/j.agee.2005.08.016.

Environment and Climate Change Canada, 2016. Canadian Environmental Sustainability Indicators: Air Pollutant Emissions. (Accessed 09 July 2017). http://www.ec.gc.ca/indicateurs-indicators/default.asp?lang=en&n=E79F4C12-1.

Fillingham, M.A., VanderZaag, A.C., Singh, J., Burtt, S., Crolla, A., Kinsley, C., MacDonald, J.D., 2017a. Characterizing the performance of gas-permeable membranes as an ammonia recovery strategy from anaerobically digested dairy manure. Membranes 7 (59), 13. http://dx.doi.org/10.3390/membranes7040059.

Fillingham, M.A., VanderZaag, A.C., Burtt, S., Baldé, H., Ngwabie, N.M., Smith, W., Hakami, A., Wagner-Riddle, C., Bittman, S., MacDonald, D., 2017b. Greenhouse gas and ammonia emissions from production of compost bedding on a dairy farm. Waste Manage. http://dx.doi.org/10.1016/j.wasman.2017.09.013.

Flesch, T.K., Wilson, J.D., Yee, E., 1995. Backward-time Lagrangian stochastic dispersion models and their application to estimate gaseous emissions. J. Appl. Meteorol. 34, 1320–1332.

Flesch, T.K., Wilson, J.D., Harper, L.A., Crenna, B.P., Sharpe, R.R., 2004. Deducing ground-to-air emissions from observed trace gas concentrations: a field trial. J. Appl. Meteorol. 43, 487–502.

Flesch, T.K., Wilson, J.D., Harper, L.A., Crenna, B.P., 2005. Estimating gas emissions from a farm with an inverse-dispersion technique. Atmos. Environ. 39, 4863–4874.

Frear, C., Liao, W., Ewing, T., Chen, S., 2011. Evaluation of co-digestion at a commercial dairy anaerobic digester. Clean—Soil Air Water 39, 697–704.

Gao, Z., Mauder, M., Desjardins, R.L., Flesch, T.K., van Haarlem, R.P., 2009. Assessment of the backward Lagrangian stochastic dispersion technique for continuous measurements of CH4 emissions. Agric. For. Meteorol. 149, 1516–1523. http://dx.doi.org/10.1016/j.agrformet.2009.04.004.

Grant, R.H., Boehm, M.T., Lawrence, A.F., Heber, A.J., 2013. Ammonia emissions from anaerobic treatment lagoons at sow and finishing farms in Oklahoma. Agric. For. Meteorol. 180, 203–210. http://dx.doi.org/10.1016/j.agrformet.2013.06.006.

Harper, L.A., Flesch, T.K., Powell, J.M., Coblentz, W.K., Jokela, W.E., Martin, N.P., 2009. Ammonia emissions from dairy production in Wisconsin. J. Dairy Sci. 92, 2326–2337. http://dx.doi.org/10.3168/jds.2008-1753.

Holly, M.A., Larson, R.A., Powell, J.M., Ruark, M.D., Aguirre-Villegas, H., 2017. Greenhouse gas and ammonia emissions from digested and separated dairy manure during storage and after land application. Agric. Ecosyst. Environ. 239, 410–419. http://dx.doi.org/10.1016/j.agee.2017.02.007.

Karim, K., Hoffmann, R., Klasson, T., Al-Dahhan, M.H., 2005. Anaerobic digestion of animal waste: waste strength versus impact of mixing. Bioresour. Technol. 96, 1771–1781. http://dx.doi.org/10.1016/j.biortech.2005.01.020.

Le Riche, E.L., VanderZaag, A.C., Wood, J.D., Wagner-Riddle, C., Dunfield, K., Ngwaie, N.M., McCabe, J., Gordon, R., 2016. Greenhouse gas emissions from stored dairy slurry from multiple farms. J. Environ. Qual. 45, 1822–1828.

Maldaner, L., Wagner-Riddle, C., VanderZaag, A.C., Gordon, R., Duke, C., 2017. Methane Emissions from Field Storage of Digestate Derived from Dairy Manure Biogas Production. (In Revision, AFM).

McGinn, S.M., Coates, T., Flesch, T.K., Crenna, B., 2008. Ammonia emission from dairy cow manure stored in a lagoon over summer. Can. J. Soil. Sci. 88, 611–615. http://dx.doi.org/10.4141/CJSS08002.

Misselbrook, T., Hunt, J., Perazzolo, F., Provolo, G., 2016. Greenhouse gas and ammonia emissions from slurry storage: impacts of temperature and potential mitigation through covering (pig slurry) or acidification (cattle slurry). J. Environ. Qual. 45, 1520–1530. http://dx.doi.org/10.2134/jeq2015.12.0618.

Neerackal, G.M., Ndegwa, P.M., Joo, H.S., Wang, X., Harrison, J.H., Heber, A.J., Ni, J.-Q., Frear, C., 2015. Effects of anaerobic digestion and solids separation on ammonia emissions from stored and land applied dairy manure. Water Air Soil Pollut. 226, 1–12.

Ngwabie, N.M., VanderZaag, A.C., Jayasundara, S., Wagner-Riddle, C., 2014. Measurements of emission factors from a naturally ventilated commercial barn for dairy cows in a cold climate. Biosyst. Eng. 127, 103–114.

Nielsen, D., Schramm, A., Revsbech, N., 2010. Oxygen distribution and potential ammonia oxidation in floating liquid manure crusts. J. Environ. Qual. 39, 1813–1820.

Paulot, F., Jacob, D.J., 2013. Hidden cost of U.S. agricultural exports: particulate matter from ammonia emissions. Environ. Sci. Technol. 48, 903–908.

Peters, J., Combs, S., Hoskins, B., Jarman, J., Kovar, J., Watson, M., Wolf, A., Wolf, N., 2003. Recommended Methods of Manure Analysis. University of Wisconsin, pp. A3769. (Accessed 09 July 2017). http://learningstore.uwex.edu/assets/pdfs/A3769.PDF.

Powell, J.M., Wattiaux, M.A., Broderick, G.A., 2011. Short communication: evaluation of milk urea nitrogen as a management tool to reduce ammonia emissions from dairy farms. J. Dairy Sci. 94, 4690–4694.

Ro, K.S., Stone, K.C., Johnson, M.H., Hunt, P.G., Flesch, T.K., Todd, R.W., 2014. Optimal sensor locations for the backward Lagrangian stochastic technique in measuring lagoon gas emission. J. Environ. Qual. 43, 1111–1118. http://dx.doi.org/10.2134/jeq2013.05.0163.

Rumburg, B., Mount, G.H., Yonge, D., Lamb, B., Westberg, H., Neger, M., Jenny Filipy, J., Kincaid, R., Johnson, K., 2007. Measurements and modeling of atmospheric flux of ammonia from an anaerobic dairy waste lagoon. Atmos. Environ. 42, 3380–3393. http://dx.doi.org/10.1016/j.atmosenv.2007.02.046.

Sommer, S.G., Husted, S., 1995. The chemical buffer system in raw and digested animal slurry. J. Agric. Sci. 124, 45–53. http://dx.doi.org/10.1017/S0021859600071239.

Sommer, S.G., Zhang, G.Q., Bannink, A., Chadwick, D., Misselbrook, T., Harrison, R., 2006. Algorithms determining ammonia emission from buildings housing cattle and pigs and from manure stores. Adv. Agron. 89, 261–335.

United Nations Economic Commission for Europe, 1999. Protocol to the 1979 CLRTAP to Abate Acidification, Eutrophication and Ground-Level Ozone. (Accessed 09 July 2017). http://www.unece.org/fileadmin/DAM/env/lrtap/full%20text/1999%20Multi.E.Amended.2005.pdf.

VanderZaag, A.C., Gordon, R.J., Glass, V., Jamieson, R.C., 2008. Floating covers to reduce gas emissions from liquid manure storages: a review. Appl. Eng. Agric. 24, 657–671. http://dx.doi.org/10.13031/2013.25273.

VanderZaag, A., Gordon, R., Jamieson, R., Burton, D., Stratton, G., 2009. Gas emissions from straw covered liquid dairy manure during summer storage and autumn agitation. Trans. ASABE 52 (2), 599–608.

VanderZaag, A.C., Gordon, R., Burton, D., Jamieson, R., Stratton, G., 2010. Permeable synthetic covers for controlling emissions from liquid dairy manure. Appl. Eng. Agric. 26, 287–297.

VanderZaag, A., Amon, B., Bittman, S., Kuczyński, T., 2015. Ammonia abatement with manure storage and processing techniques. In: Reis, S., Howard, C., Sutton, M. (Eds.), Costs of Ammonia Abatement and the Climate Co-Benefits. Springer, Dordrecht, pp. 75–112. http://dx.doi.org/10.1007/978-94-017-9722-1_5.