

Compilation file of literature relating to storage covers

This file is a compilation of the following reports.

Liquid Manure Storage Covers

Prepared by:

Sandy English and Ron Fleming
University of Guelph Ridgetown Campus
Ridgetown, Ontario, Canada

Prepared for:

Ontario Pork

Economic Evaluation of Manure Storage Covers

Larry D. Jacobson and David R. Schmidt,
Dept. of Biosystems and Agricultural Engineering
Bill Lazarus,
Dept. of Applied Economics
University of Minnesota, St. Paul, MN 55108

Factsheet: Covers for Manure Storage Units

Richard Nicolai and Steve Pohl, South Dakota State University, and
David Schmidt, University of Minnesota

Livestock Development in South Dakota: *Environment and Health FS 925-D*

FLOATING COVERS TO REDUCE GAS EMISSIONS FROM

LIQUID MANURE STORAGE: A REVIEW

A. C. VanderZaag, R. J. Gordon, V. M. Glass, R. C. Jamieson

PERMEABLE SYNTHETIC COVERS FOR CONTROLLING

EMISSIONS FROM LIQUID DAIRY MANURE

A. C. VanderZaag, R. J. Gordon, R. C. Jamieson, D. L. Burton, G. W. Stratton

GAS EMISSIONS FROM STRAW COVERED

LIQUID DAIRY MANURE DURING SUMMER

STORAGE AND AUTUMN AGITATION

A. C. VanderZaag, R. J. Gordon, R. C. Jamieson, D. L. Burton, G. W. Stratton

Liquid Manure Storage Covers

Final Report

Prepared by:
Sandy English and Ron Fleming
University of Guelph Ridgetown Campus
Ridgetown, Ontario, Canada

Prepared for:
Ontario Pork

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UNIVERSITY
of GUELPH
RIDGETOWN CAMPUS

Introduction

Every livestock operation requires some kind of manure storage. Manure is typically stored so that it may be used as a nutrient source for crops - allowing for spreading at the appropriate time. Most livestock manure is handled as either a liquid or as a solid. Liquid manure may be defined as having a moisture content greater than 82% (OMAFRA, 2005). It is commonly stored in either concrete tanks or earthen basins. During storage, biological activity occurs in the manure. Methane, ammonia, hydrogen sulfide, and carbon dioxide are four important gases produced from decomposing manure (FSA, 2002). The release of these and other gases has environmental consequences, mainly associated with odour, loss of nutrients and release of gases responsible for global warming. Livestock manure may account for six to 10% of the annual global emissions of methane, a greenhouse gas (Sommer et al., 2000). Ammonia can contribute to acid precipitation. Hydrogen sulfide poses a health and safety risk to humans and livestock. About 25% of the total odour emission from an animal facility comes from the manure storage (Zhang and Gaakeer, 1998). Therefore, reducing emissions from a manure storage can have environmental benefits.

Covers for liquid manure storages significantly reduce odour and gas emissions by creating a physical barrier between the liquid and the air. Zhang and Gaakeer (1998) include covers in their list of methods to effectively reduce odour emissions from storages.

Covers are classified as either impermeable or permeable. Impermeable covers do not allow any gases coming from the manure to be emitted to the atmosphere. On the other hand, permeable covers permit transmission of some gases. Various types of covers have been tried and each has its own advantages and disadvantages. The following covers will be discussed in this report:

- Permeable:
- a) Straw
 - b) Geotextile
 - c) Clay Balls
 - d) Perlite
 - e) Rigid Foam
 - f) Oil
 - g) Natural Crust
 - h) Corn Stalks, Sawdust, Wood Shavings, Rice Hulls, Ground Corncobs, Grass Clippings
- Impermeable:
- a) Inflatable Plastic (positively pressurized)
 - b) Floating Plastic (negatively pressurized)
 - c) Floating Plastic
 - d) Suspended Plastic
 - d) Concrete
 - e) Wood/Steel

Permeable Covers

Permeable covers are less expensive than impermeable covers but they do not last as long and are not as effective at reducing the emissions of odours and gases.

a) Straw - Straw covers are popular because they are cheap and fairly effective at reducing emissions. The straw forms an organic floating mat on the manure surface. There is no significant difference between the performance of barley or wheat straw covers (Nicolai et al., 2002).

Odour reduction with straw covers will vary from 90% for a thick, newly applied cover to 40% or less depending on straw thickness and uniformity (Nicolai et al., 2002). University of Minnesota researchers (Clanton et al., 2001) have shown that a 10 cm thick layer of straw reduces odours by 47%, a 20 cm layer by 69% and a 30 cm layer by 76%. Another study showed that a straw cover varying in depth between five and 15 cm reduced odour emissions by about 84% (Hornig et al., 1999). Straw covers reduce hydrogen sulfide emissions by 80 to 95% (Bicudo et al., 2003). Xue et al. (1999) found that a five to 10 cm thick layer of straw, along with a naturally forming crust on dairy manure, suppressed hydrogen sulfide emissions by 95%. The effectiveness of straw at reducing ammonia emissions varies widely - between 25 and 85% (Nicolai et al., 2002). With a straw depth of 5 to 15 cm, ammonia emission was shown to reduce by 80% (Hornig et al., 1999). A different study using the same thickness, along with a natural crust, showed a 95% reduction (Xue et al., 1999). Sommer et al. (2000) found that a straw cover was more effective than a natural crust or Leca® pebbles at reducing the emissions of methane.

The effectiveness of straw covers reduces with time, due to the saturation and sinking of the straw. Straw covers usually last between two and six months, depending on the amount applied (depth), evenness of application, basin size, and climatic conditions of the area (Bicudo et al., 2003). Most storage basins successfully using straw covers are located in the western United States and Canada where the amount of precipitation is less than in other livestock areas of North America (e.g. Ontario). Since the straw eventually sinks, a chopper pump is required so the pumping system does not get blocked when emptying the manure storage (Zhang and Gaakeer, 1998).



Figure 1 Blowing straw on to a manure storage basin (Bicudo et al., 2003)

The straw is applied to the manure storage using a straw blower, as seen in Figure

1. Using this method, it is difficult to judge the thickness of the straw and apply it evenly. The recommended thickness of straw is 30 cm (with a minimum thickness of 20 cm). Even though little additional odour, hydrogen sulfide, and ammonia reduction is gained by increasing the thickness to 30 cm, a thickness of 30 cm is needed to keep the straw afloat or keep the upper portion dry. This allows the straw to absorb gases and act as a biofilter (Clanton et al., 2001).

The amount of straw needed depends on the area of the manure storage and the desired depth of the straw layer. A single large round straw bale (1.8 m diameter) can cover about 47 m² with a 30 cm layer (Nicolai et al., 2002). A 25 to 30 m diameter storage tank with a 30 cm layer of straw would cost CDN\$110 to \$154 at CDN\$11 per bale. Sometimes oil is added to the straw at the time of application to increase the longevity of the cover (Clanton et al., 1999). In summary, straw has been proven to be an effective short term solution to odour and gas emissions.

b) Geotextile - Geotextile covers are alternatives to straw covers. These covers are non-woven fabric, composed of thermally bonded, continuous polypropylene filaments. Polypropylene is resistant to rot, moisture, and chemical attack (Clanton et al., 2001). The performance at reducing emissions is variable. Nicolai et al. (2002) have documented odour reductions of 40 to 65%, hydrogen sulfide reductions of 30 to 90%, and an ineffectiveness at removing ammonia. Bicudo, et al. (2004) showed that a geotextile cover reduced odours by 50%, hydrogen sulfide by 72%, and ammonia by 30 to 45%. In contrast, Clanton et al. (2001) demonstrated that geotextile fabric was not statistically effective in reducing odour and gases.

Any effectiveness in reducing odours and gases decreases over time compared to straw, because the fabric becomes plugged with biomass growth. This creates an impermeable barrier that allows gases to build up and move to open spaces along sidewalls, where they are vented (Bicudo, et al., 2004). Geotextile thickness has no impact on odour and gas emissions (Clanton et al., 2001).

Problems have been encountered in the spring, when the snow melts and the covers are saturated with water and manure. They may no longer float. Some covers may be completely submerged (Bicudo, et al., 2004). These researchers also found that



Figure 2 Opening for the access of agitation and pumping equipment in a geotextile-covered manure storage (Bicudo et al., 2003)

management and safety were challenging during agitation and pumping. Many types of agitation equipment pump manure over the surface to help with the stirring but this is not possible with geotextile covers. To agitate, the cover must be partially removed, typically from one corner of the basin. Alternatively, the cover is lifted by a cable and winch system and the agitation/pumping equipment is positioned under the cover (Nicolai et al., 2002). Neither of these options allows for vigorous agitation. Procedures and equipment to agitate under the cover through an access opening are being developed (Nicolai et al., 2002). Figure 2 shows an opening for agitation.

The disposal of geotextile material after its usable life (three to five years), can be costly (Nicolai et al., 2002). One producer paid US\$1000 for pick-up and hauling and US\$800 in landfill fees, although numbers will vary (Bicudo et al., 2003). Adding a layer of closed-cell foam between two types of geotextile materials has doubled the life of the covers and prevented sinking - see Figure 3 (Nicolai et al., 2002). Also some geotextile covers are protected against UV radiation, which reduces deterioration from the sunlight, thus increasing life expectancy (Bicudo et al., 2003). Geotextile covers cost between US\$1 to \$1.30/m² (Nicolai et al., 2002). Bicudo, et al. (2004) estimated the cost to be slightly higher, at US\$1.50 to \$2.40/m². Using these numbers, the cover for a 50 m by 50 m tank would cost in the range of US\$3750 to \$6000.



Figure 3 Geotextile floating permeable cover with closed-cell floatation (Nicolai et al., 2002)

c) Clay Balls - Air-filled clay balls

can also be used as a floating cover. These are low density spheres with minute independent closed air cells surrounded by a tough outer shell making them impermeable to water and other fluids (Clanton et al., 1999). Leca® (lightweight expandable clay aggregate) and Macrolite® are two brands of clay balls (Nicolai et al., 2002). Leca® pebbles reduced 90% of the odour and were 65 to 95% effective at reducing ammonia emissions, while Macrolite® pebbles reduced only 60% of the odour and were 64 to 84% effective at reducing hydrogen sulfide emissions (Nicolai et al., 2002). Leca® pebbles were also shown to significantly reduce methane emissions (Sommer et al., 2000). Berg et al. (2006) established that Leca® with saccharose reduced methane emissions by 10% and lactic acid was even more effective. In one experiment, the clay balls ranged in diameter from 1.9 to 2.5 cm and were placed to a depth of 20 cm (Clanton et al., 1999). Results showed that the clay balls reduced emissions but not as well as straw, oil,

geotextile, and PVC/rubber covers. Reducing the diameter to reduce void volume and increasing the thickness may help to significantly increase the effectiveness (Clanton et al., 1999).

Clay balls last for approximately 10 years, which is significantly longer than straw and even geotextiles, but when they eventually sink into the manure, they form clumps and can plug the pumping equipment (Funk et al., 2004). Both Leca® and Macrolite® cost about US\$13 /m² (Nicolai et al., 2002).

d) Perlite - Perlite is a white, buoyant naturally-occurring siliceous mineral (Hornig et al., 1999). One brand that has been tested as a manure storage cover is Pegulit® - see Figure 4. In a study by Hornig et al. (1999), Pegulit® granules were spread over the manure surface with a blower to a thickness of 10 cm. Results showed that this cover reduced odour emissions between 30 and 93%. Ammonia emissions were reduced by 63 to 91%, depending on the type of Pegulit® (Hornig et al., 1999).

Pegulit® usually lasts for 10 years before it needs replacing and costs about US\$1.30 to \$2/m²/year (Hornig et al., 1999). The ability of Pegulit® to float quickly back to the surface after mixing is one clear advantage over straw.



Figure 4 Pegulit® as a covering for a 16m diameter storage container (Hornig et al., 1999)

e) Rigid Foam - Miner et al. (2003) evaluated the effectiveness of a 5 cm thick composite cover made from recycled closed-cell polyethylene foam chips topped with a geotextile layer containing zeolite particles. Under field conditions, the cover survived severe storms and allowed intense rainfall to pass through without causing inundations. The cover also eliminated odour and reduced ammonia emissions. Miner et al. (2003) compared the effectiveness of four different covers at reducing ammonia emissions. The full foam cover reduced ammonia by 70%, half the cover reduced ammonia by 55%, the cover plus geotextile reduced ammonia by 77%, and the cover plus zeolite reduced ammonia by 82%. It was clear that the presence of zeolite improved the cover's effectiveness.

Microbial populations were found on the cover after four months of use and since an aerobic bacterial population is essential for ammonia oxidation, the cover tended to become more effective with time (Miner et al., 2003). The surface of the cover also became covered with algal populations within two weeks of installation but this vegetative

growth had no discernible impact on the performance of the cover. Thicker covers achieved a greater ammonia reduction than thinner ones. These foam covers have a 10 to 20 year life expectancy (Miner et al., 2003).

Ethafoam® 220 was tested by DeVries et al. (1980) by placing 3.2 and 5 cm thick layers in concrete storage tanks. Installation involved welding the planks together and then placing a layer of crushed stone on the cover to resist wind uplift. This process was complicated and labour intensive and there were a number of failures during the experiment itself. The results showed that the cover reduced odours effectively, except in strong winds. However, no gas emission reductions were measured.

Ethafoam® 220 can be ignited by contact with a flame. Under normal combustion, carbon monoxide and dense smoke are generated. Ethafoam® is also a good electrical insulator, therefore accumulation and discharge of static electricity is possible. However, methane quantities are low and no known explosions have occurred so static electricity is not considered a problem. Ethafoam® deteriorates when exposed to sunlight. Life estimates are placed at five years for white Ethafoam® and ten years for black (DeVries et al., 1980).

f) Oil - Rapeseed oil was applied at thicknesses of 3 and 6 mm to evaluate its effectiveness as a cover (Hornig et al., 1999). Ammonia emissions were reduced 85% with the 6 mm thick oil layer, while the 3 mm layer showed an insignificant effect (Hornig et al., 1999). Clanton et al. (1999) discovered that the use of a soybean oil mat of 10 mm thickness produced a distinctive offensive odour. This may be due to the high carbon concentration of oil mixing with the nitrogen of the manure. Clanton et al. (1999) concluded that oil should not be used alone as a cover.

g) Natural Crust - Natural floating covers are those formed by the fibrous material contained in the manure (Bicudo et al., 2003). Dairy manure usually contains high amounts of such material and therefore a natural crust is common on the surface of dairy manure. Stored swine manure can sometimes develop a natural crust but its consistency is much different from dairy manure (Bicudo et al., 2003). Sommer et al. (2000) found that a 7 to 10 cm thick cover developed naturally over the cattle manure in a concrete tank. This crust reduced methane emissions by 38%. Bicudo, et al. (2004) found that natural crust can be at least as effective as a geotextile cover in reducing emissions of hydrogen sulfide. There was no indication of the effectiveness of natural crusts at reducing odours. Bicudo et al. (2003) concluded that the effectiveness of natural crust at reducing odours and gases was difficult to quantify. So much depends on the thickness and other physical properties of the crust. The effectiveness varied in the range of 10 to 90%. A natural crust only has a life expectancy of two to four months (Bicudo et al., 2003).

h) Corn stalks, Sawdust, Wood Shavings, Rice Hulls, Ground Corncobs, Grass Clippings - Artificial floating organic covers, also called biocovers, include chopped corn stalks, sawdust, wood shaving, rice hulls, ground corncobs, and grass clippings (Bicudo et al., 2003). Covers made of rice hulls with oil resulted in the lowest ammonia and hydrogen

sulfide emissions at 31 and 4% respectively (Clanton et al., 2001). Grass clippings with oil produced the least odour emissions, followed by corncobs with oil, corn stalks with oil, and rice hulls with oil (Clanton et al., 2001).

Impermeable Covers

a) Inflatable Plastic (positively pressurized) - Impermeable covers (see Figure 5) are more expensive than permeable covers but they have a longer life expectancy and are more effective at reducing odours and gases. In order to construct an inflatable plastic cover, the tarp must be tightly sealed around the top perimeter of the concrete storage tank by first laying down a sheet of plastic fitting, then two rubber strips which grip the tarp - see Figure 6 (Zhang and Gaakeer, 1998).

Inflatable plastic domes are not common with earthen basins because installation is more difficult. The cover includes an air delivery system (a low pressure blower and variable speed fan controller) and pressure control system (a mechanical damper by which a bypass opening can be adjusted so the cover is inflated at a constant operating pressure) - see Figure 7 (Zhang and Gaakeer, 1998).

A grid of ropes is fastened across the top of the tank to prevent the cover from falling into the manure when the blower is deactivated for agitation and pumping, or when the power is off. The cover will remain inflated for an hour after the blower is turned off to allow for back-up power (Zhang and Gaakeer, 1998). These higher domes prevent snow



Figure 5 An Inflatable cover on the top of a 23 m diameter concrete manure storage tank (Zhang and Gaakeer, 1998)

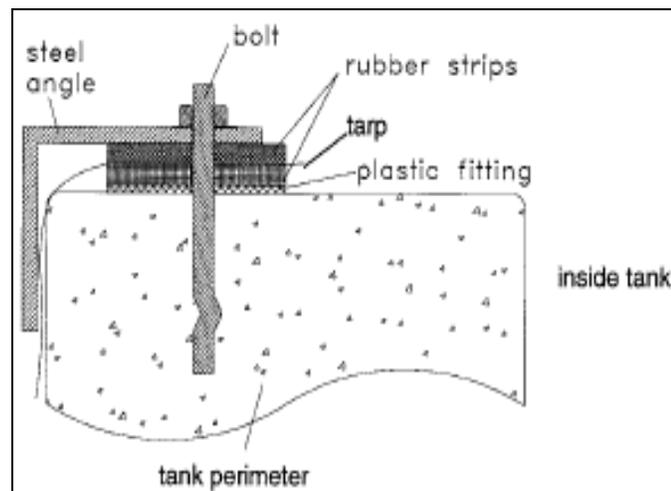


Figure 6 The attachment of the tarp to the perimeter of a concrete tank (Zhang and Gaakeer, 1998)

accumulation but wind resistance increases. Zhang and Gaakeer (1998) found that air leakage was minimal and equivalent to a typical bathroom exhaust fan. Provision to collect and treat biogas can be made through the installation of perforated pipes and an exhaust fan, to direct the gas to a biofilter or some other air treatment system before it is discharged to the atmosphere.

An inflatable plastic cover is 95% effective at reducing odours, hydrogen sulfide, and ammonia concentrations (Nicolai et al., 2002). The cover has a life expectancy of 10 years and costs US\$5.80 to 12.50 /m² (Nicolai et al., 2002). Zhang and Gaakeer (1998) estimated the cost to be US\$15 /m² plus US\$16/month for electricity to run the blower fan.

Inflatable covers appear to have gone out of favour on several Ontario livestock farms in the last few years due to problems with high winds, especially associated with power outages (Bradshaw, 2006; Hilborn, 2006).

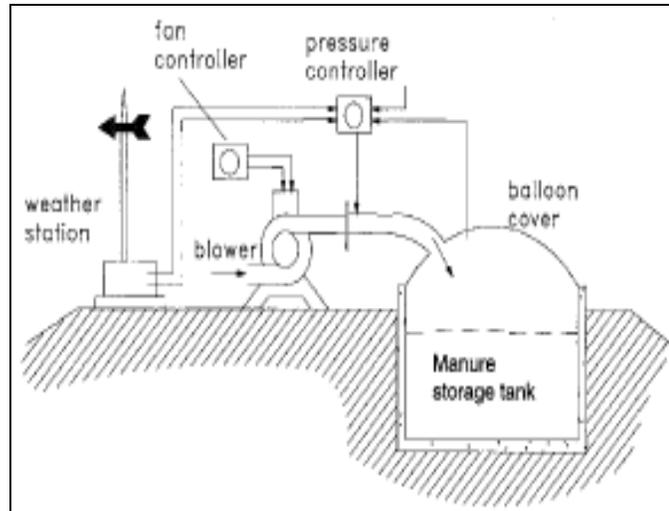


Figure 7 A sketch of the storage tank cover and the control systems (Zhang and Gaakeer, 1998)

b) Floating Plastic (negatively pressurized) - The opposite to the positively pressurized plastic cover is the negatively pressurized cover. This cover is a flexible, reinforced, high density polyethylene (HDPE) membrane. Unlike the inflatable cover, this floating cover can be installed in both concrete and earthen storages (Funk et al., 2004). For earthen basins, the cover is either fastened using anchor trenches or tethered with ropes to metal or wooden stakes located around the perimeter, as shown in Figure 8 (Bicudo et al., 2003). Blowers, connected to a ducting system, draw the air out from under the cover, creating a vacuum - see Figure 9 (Hodgkinson, 2003). This gas can also be directed to a biofilter before being discharged into the atmosphere, as shown in Figure 10. Precipitation

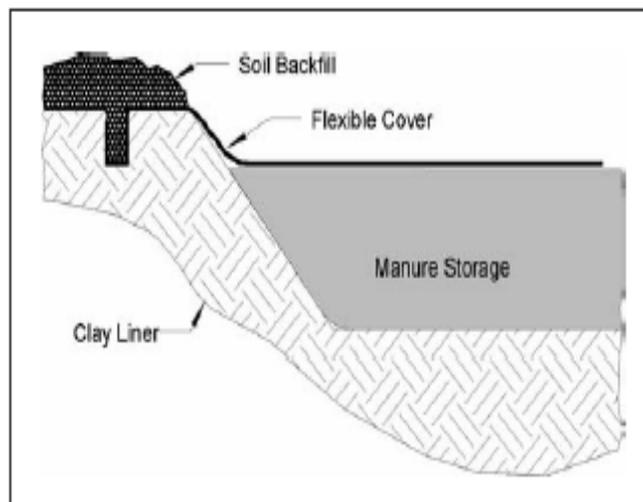


Figure 8 Fastening a cover to a berm using anchor trenches (Nicolai et al., 2002)

collected on the cover can be drained through a series of perforated collection pipes laid on the surface, which are connected to an activated pumping system (Bicudo et al., 2003).

Hodgkinson (2003) found that the cover reduced ammonia and greenhouse gas emissions. In one installation on a 30 by 40 m earthen basin, a 0.41 mm thick plastic cover cost US\$7,800 installed, and US\$36 per month for operating costs (Funk et al., 2004).

Barry (2006) studied a negatively pressurized floating cover on a concrete tank in Guelph, Ontario. Perforated pipe was laid around the perimeter of the storage under the cover and was connected to small exhaust fans. The fans drew out air to create a negative air pressure that held the airtight barrier in place. Gas bubbles emitted from the manure formed under the cover and eventually worked their way to the edge of the storage and were picked up by the fan and ducting system. An agitation system using compressed air was installed on the floor of the storage (Barry, 2006).

Precautions are recommended for the winter season to prevent the cover from tearing. During the late fall months in this study, sump pumps were used regularly to remove as much rainwater as possible on top of the cover, to minimize ice formation over winter - see Figure 11. During the winter, manure at the perimeter of the tank was agitated using a small electric air compressor, in the hopes of softening the ice so that fresh manure could be safely added to the storage. This technique proved to be ineffective. Barry (2006) suggested that, unless a better system can be developed, the precautions required to prevent tearing of the cover during the winter season seem too restrictive for widespread use of the cover design. The expected life of the cover is about 7 years (Barry, 2006).



Figure 9 This blower is connected to a ducting system so the cover remains tight on the manure surface (Hodgkinson, 2003)

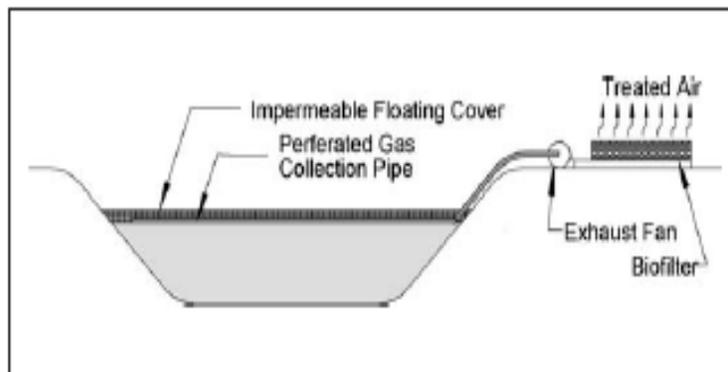


Figure 10 A system to remove and treat biogas from a manure storage using an impermeable cover and biofilter (Nicolai et al., 2002)

Wagner-Riddle (2004) compared the methane emissions from two liquid swine manure concrete storage tanks, one covered with a negatively pressurized membrane and the other, an uncovered tank. The methane flux from the covered and uncovered tanks were not significantly different, except during early winter when emissions were slightly higher for the uncovered tank (Wagner-Riddle, 2004).



Figure 11 The negative air pressure cover during manure agitation by forced air in early winter (Barry, 2006)

c) Floating Plastic - Another alternative to the negatively pressurized floating cover is a floating cover that simply lays on the manure surface. This cover is anchored in the same way as the negatively pressurized floating cover but no fan is required. The gases are vented out through the sides to prevent build-up of excess pressure (Nicolai et al., 2002). Precipitation collected in the cover can be drained through a series of perforated collection pipes laid on the surface, connected to an activated pumping system (Bicudo et al., 2003). Styrofoam floats can also be sewn into pockets around the edges (Clanton et al., 1999).

Floating plastic reduced odour by 60 to 78% and hydrogen sulfide by 90% (Nicolai et al., 2002). Hornig et al. (1999) glued two 2 mm thick polyethylene film layers together and found that the cover decreased ammonia emissions by 99%. These covers are expected to last about 10 years and cost US\$2.50 to \$4 /m² (Nicolai et al., 2002).

The problem with floating plastic covers is that they are difficult to use when the manure level fluctuates during the year. Enough material is needed so that when the tank is low, the cover can still float on the manure surface, but when the tank is full, the excess tarp along the edges will bunch up (Zhang and Gaakeer, 1998). This could create problems with agitation or pumping. Disposal of plastic material after it is no longer usable can also be costly (Nicolai et al., 2002).

d) Suspended Plastic - A type of cover that is popular in northern of Europe consists of a solid vertical support post in the centre of a circular concrete tank, strips of material from the support to the walls and a plastic cover laid on top and stretched tight to the walls, as shown in Figure 12. This cover excludes all precipitation, reduces ammonia losses and reduces odour emissions (Holm-Nielsen, 2006). An access panel can be removed to allow for pump installation during agitation and spreading. No costing information is available for this report.

e) Concrete - Concrete lids are very reliable and capture 95% of odours, but are capital intensive (Nicolai et al., 2002). For example, a 30 m diameter concrete lid, 20 cm thick, is estimated to cost as much as CDN\$76,000 (i.e. CDN\$108/m²) (Johnson, 2006). Concrete lids can have a life expectancy of 30 to 50 years if the lid is well designed (Johnson, 2006). Poorly



Figure 12 Plastic cover supported by central pillar and series of guy ropes

designed concrete lids can lead to too much deflection or sagging in the centre of the lid, causing cracks that allow ammonia to corrode the reinforcing steel quickly. Concrete lids have been commonly used over the years on concrete tanks in Ontario and many have been in place over 30 years.

e) Wood/Steel - Wood or steel lids are also reliable but capital-intensive. A steel or wooden lid is estimated to cost US\$20,000 for a 23 m diameter concrete manure tank (i.e. US\$48/m²) (Zhang and Gaakeer, 1998). Wooden lids are 95% effective at reducing odours and gases and have a life expectancy of 10 to 15 years (Nicolai et al., 2002). Steel lids are not commonly used because the high concentrations of ammonia cause the steel to corrode rapidly unless careful consideration is taken to ventilate the storage area or coat the steel (Johnson, 2006).

General Discussion

Tables 1, 2, and 3 summarize much of the information discussed in this report. Table 1 documents, for each type of cover, the effectiveness at reducing odour and gas emissions, typical life expectancy and capital cost. Table 2 summarizes the main advantages and disadvantages of each type of cover. Table 3 lists common manure storage covers considered by livestock producers in southern Ontario and compares them using the most important performance indicators considered by the farmers, including: ability to reduce odour and gas emissions, ability to exclude precipitation, amount of labour involved, ease of agitation, life expectancy and cost.

Table 1 -Types of covers, effectiveness, life expectancy, and capital costs.

Material	Reduction Effectiveness (%)			Life Expectancy	Capital Cost (US\$/m ²)
	Odour	H ₂ S	NH ₃		
Permeable Covers					
Straw	40 to 90 ^a	80 to 95 ^a	25 to 85 ^a	< 6 months ^a	0.2 to 0.8 ^a
Geotextile	40 to 65 ^a	30 to 90 ^a	0 to 45 ^{a, c}	3 to 5 years ^a	1 to 2.4 ^{a, c}
Geotextile/straw	50 to 80 ^a	60 to 98 ^a	8 to 85 ^a	N/A	1.3 to 2.2 ^a
Leca®	90 ^a	N/A	65 to 95 ^a	10 years ^a	13 ^a
Macrolite®	60 ^a	64 to 84 ^a	N/A	10 years ^a	13 ^a
Perlite	30 to 93 ^d	N/A	63 to 91 ^d	10 years ^d	1.3 to 2 ^d
Rigid Foam	70 to 82 ^e	N/A	N/A	10 to 20 years ^e	N/A
Oil	0 ^d	N/A	85 ^d	N/A	N/A
Natural crust	10 to 90 ^b	10 to 90 ^b	10 to 90 ^b	2 to 4 months ^b	0 ^b
Impermeable Covers					
Inflatable plastic	95 ^a	95 ^a	95 ^a	10 years ^a	5.8 to 15 ^{a, f}
Floating plastic (neg. pressure)	95 ^b	95 ^b	95 ^b	5 to 10 years ^b	N/A
Floating plastic	60 to 95 ^a	90 to 95 ^a	95 ^b	10 years ^a	2.5 to 4 ^a
Concrete lid	95 ^a	N/A	N/A	30 to 50 years ^g	(CDN) 108 ^g
Wood/Steel lid	95 ^a	N/A	95 ^a	10 to 15 years ^a	48 ^f

^a (Nicolai et al., 2002)

^b (Bicudo et al., 2003)

^c (Bicudo et al., 2004)

^d (Hornig et al., 1999)

^e (Miner et al., 2003)

^f (Zhang and Gaakeer, 1998)

^g (Johnson, 2006)

Table 2 - Summary of advantages and disadvantages of various manure storage covers

Type of Cover	Advantages	Disadvantages
Permeable Covers		
Straw	<ul style="list-style-type: none"> - very low cost - effective odour and gas reduction 	<ul style="list-style-type: none"> - very short lifetime - requires a manure pump that can chop straw - difficult to spread evenly and measure thickness - deteriorates with intense rainfall and wind
Straw and Oil	<ul style="list-style-type: none"> - low cost - stays afloat longer than straw alone - effective odour and gas reduction 	<ul style="list-style-type: none"> - short lifetime - requires a manure pump that can chop straw - difficult to spread evenly and measure thickness
Geotextile	<ul style="list-style-type: none"> - low cost - relatively effective odour and gas reduction - resistant to rot, moisture, and chemical attack 	<ul style="list-style-type: none"> - short lifetime - effectiveness at reducing odour and gases decreases over time - disposal is costly - can be submerged (e.g. intense rainfall, snow melt) - safety an issue during agitation and pumping
Clay Balls	<ul style="list-style-type: none"> - effective odour and gas reduction - relatively long lifetime 	<ul style="list-style-type: none"> - when they sink, they form clumps and can plug the pumping equipment - relatively expensive
Perlite	<ul style="list-style-type: none"> - low cost - relatively effective odour and gas reduction - floats quickly to surface after application, compared to straw - relatively long lifetime 	<ul style="list-style-type: none"> - relatively little performance information available - effectiveness varies significantly

Rigid Foam	<ul style="list-style-type: none"> - relatively low cost - relatively effective odour and gas reduction - survives intense storms - long lifetime 	<ul style="list-style-type: none"> - complicated installation - good electrical insulator - may cause sparks - can be ignited, producing poisonous gases
Oil	<ul style="list-style-type: none"> - low cost 	<ul style="list-style-type: none"> - short lifetime - produces a distinctive offensive odour
Natural Crust	<ul style="list-style-type: none"> - no cost 	<ul style="list-style-type: none"> - very short lifetime - does not always form (especially on swine manure) - poor odour and gas reduction
Cornstalks, Sawdust, Wood Shavings, Rice Hulls, Ground Corncobs, Grass Clippings	<ul style="list-style-type: none"> - low cost 	<ul style="list-style-type: none"> - very short lifetime - poor odour and gas reduction
Impermeable Covers		
Inflatable Plastic (positive pressure)	<ul style="list-style-type: none"> - long lifetime - tarp never touches manure - very effective odour and gas reduction with biofilter - prevents precipitation accumulation on top and in manure storage 	<ul style="list-style-type: none"> - high cost - more wind resistance - must be deactivated to pump or agitate - not appropriate for earthen basins
Floating Plastic (negative pressure)	<ul style="list-style-type: none"> - relatively long lifetime - very effective odour and gas reduction with biofilter - prevents precipitation accumulation in manure storage 	<ul style="list-style-type: none"> - relatively high cost - collects precipitation - bunches up when manure level fluctuates - potential for damage due to ice

Floating Plastic	<ul style="list-style-type: none"> - long lifetime - relatively effective odour and gas reduction with biofilter - prevents precipitation accumulation in manure storage 	<ul style="list-style-type: none"> - relatively high cost - gas bubbles in cover - potential for wind damage - collects precipitation - bunches up when manure level fluctuates
Suspended Plastic	<ul style="list-style-type: none"> - effective odour and gas reduction - prevents precipitation accumulation in manure storage 	<ul style="list-style-type: none"> - no cost information available - may not be available in North America
Concrete	<ul style="list-style-type: none"> - very long lifetime - very effective odour and gas reduction - very low maintenance - prevents precipitation accumulation in manure storage 	<ul style="list-style-type: none"> - very high cost
Wood/Steel	<ul style="list-style-type: none"> - long lifetime - very effective odour and gas reduction - low maintenance - prevents precipitation accumulation in manure storage 	<ul style="list-style-type: none"> - very high cost

Table 3 - Comparison of the common liquid manure storage covers considered by livestock producers in southern Ontario

	Straw	Geotextile	Inflatable Plastic	Floating Plastic (negative pressure)	Floating Plastic	Concrete
Odour Control	poor	very poor	good	good	good	very good
Reduced Gas Emissions	good	poor	very good	very good	good	very good
Excludes Precipitation	no	no	yes	yes	yes	yes
Labour/ Maintenance	very high	high	low	medium	medium	very low
Ease of Agitation	easy	hard	easy	hard	hard	very easy
Life Expectancy	< 6 months	< 5 years	< 10 years	<10 years	<10 years	>30 years
Cost	low	medium	medium	high	high	very high

Future Research Needed

The majority of research on liquid manure storage covers has involved earthen basins and the main manure type has been swine manure. Less information is available on concrete tanks and on cattle manure. More research is needed especially in the area of covers for concrete tanks (a very common storage option in many areas).

Impermeable covers offer the opportunity for collecting and using methane gas for firing water boilers for barn, shop, or home heating needs, an on-farm incinerator, or simply flaring the gas (MacLeod, 2006). A more advanced methane treatment option is the production of electricity using a methane-fired engine and matched power generation unit. Increased on-farm income through energy generation and the sale of greenhouse gas emission reduction credits are becoming a feasible option through the advancement of manure storage cover technology (MacLeod, 2006). No research results could be found where an attempt had been made to cash in on the trapped methane gas.

In summary, more research on covers for concrete tanks and energy generation from methane emitted from manure storage basins is needed.

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Economic Evaluation of Manure Storage Covers

**Larry D. Jacobson and David R. Schmidt,
Dept. of Biosystems and Agricultural Engineering
Bill Lazarus,
Dept. of Applied Economics
University of Minnesota, St. Paul, MN 55108**

FINAL REPORT

INTRODUCTION

Odor emissions from outdoor manure storage basins remain a major issue for animal producers whose manure-handling systems include them. Although limited data exists to verify outdoor air quality problems, the ambient odor and gas levels at or near animal production systems that have been indicated as a concern, are often presumed to originate from manure storage sources. This is especially true for outside, uncovered manure storage units (i.e. earthen storage basins, and below and above ground concrete or steel pits or tanks).

One method of reducing the odor released from outdoor manure storage basins that has had some success is the use of a floating cover. Based on research conducted in small tanks, various covers on outdoor manure storage units do reduce odor concentrations from this important odor source (Clanton, 1997). With the information collected to date, covers offer the best practical option for reducing odors from a manure storage source. Various research projects have shown the benefits of covering manure storage units to reduce the odor concentrations and emissions. Experiments in the laboratory and/or with small tanks at Iowa State University (Bundy et al., 1997), the University of Minnesota (Clanton, 1997), and Purdue University (Heber, 1997) have shown that a floating cover of straw or other materials do reduce odors. In addition to these control studies, several investigations (Mannebeck, 1985 and Miner, J.R., 1995) have shown odor reductions resulting from covers on farm manure storage systems.

OBJECTIVE

The objective of the project was to evaluate the use of primarily straw floating covers on commercial manure storage units to control odor and gas emissions and to identify the management requirements and cost of the covers.

MATERIAL AND METHODS

To evaluate the performance of the straw covers on existing manure storage units, five different pork producers with outdoor storage systems in Minnesota were selected. Producers were selected from a group of participants with manure storage units in two different odor-monitoring projects that were carried out in 1996-97. This provided past information of the particular manure storage unit so some retrospective analysis could be accomplished before and after a cover was installed.

During June and July of 1998, the five Minnesota pork producers participating in this project had straw blown on their manure storage unit to reduce odor and gas emissions (Figure 1).

Figure 1. Blowing straw on an earthen basin for odor and gas emission control.

Several commercial companies (Haybuster Products and Highline, Ltd.) were contacted and agreed to supply a machine to apply the straw and an operator to run it free of charge as a demonstration of their equipment. Both barley and wheat straw were used by the participants, with a preference to barley as indicated by past experience with straw covers in Canada (Pami, 1993). All but one (above ground tank) of the manure storage units was earthen basins and the application of straw was fairly simple and successful as shown in figure 1. The ability to get the straw evenly distributed was a function of basin size. The smallest manure storage unit to be covered in the project was an above ground tank (about 2/10 of an acre), while the largest was about 1.5 acres (Figure 2). The producer did experience some difficulty in getting this large basin completely covered.



Figure 2. Largest straw covered earthen basin (about 1.5 acres) in project

To evaluate the technical performance of the covers, air samples were collected at the surface of the manure storage unit each season (spring, summer, and fall) for odor measurement with an olfactometer. Hydrogen sulfide (H_2S) was also measured from these same air samples with either an electronic (JeromeTM) meter or colorimetric tubes.

To evaluate the economic feasibility and manageability of the covers, producers were asked to record expenses to maintain the covers during the warm weather “odor season.” This included both out-of-pocket expenses and labor costs to maintain the cover. A budget for the first year of operation was estimated. Also, responses from the producers were recorded as to the ease or the difficulty in operating or maintaining the cover.

RESULTS AND DISCUSSION

Large round bales of barley or wheat were mostly used to accommodate the application equipment and to save on shipping and handling costs. One producer did use some small square bales of straw he previously had stored at his farm. Most of the project participants were located in southern Minnesota and the straw was purchased from the northwestern (Red River Valley) area of the state, and in one case from Canada. Straw costs varied from a low of \$23 (for the

producer closest to the straw source) up to \$50 per large bale (average of 800 lbs). An application rate of roughly one large bale per 500 ft² (100 bales per acre) was suggested to the participants to obtain a 12-inch depth of straw on the manure storage units. Using an average of \$40 per bale, this would translate to a cost of about \$0.08 / ft² of storage area, which does not include the application costs. Straw application costs will range from \$0.01 to \$0.02 / ft² depending on the size of the storage. If the \$0.08/ ft² figure is used, the initial cost to cover the manure storage units in this study would vary from \$500 for the smallest (above ground storage tank) to about \$6000 for the largest (1.5 area earthen basin) in the study.

The length of time that the straw covers remained floating varied between units. One storage unit needed additional straw only six weeks after the initial application of barley straw. This unit was actually one of the smaller storage units in area and was possibly caused by a large rainfall (over 7 inches) event. Another participant had two basins covered, one with barley and one with wheat straw, and both lasted four months. Factors such as the amount of rainfall, depth of storage units, surface area, access to surface winds, and manure characteristics may explain some of the variations seen in how long straw floated on the manure storage units.

Four of the five participants agitated the full storage units in the fall with the intention to chop up the straw cover and remove it with the manure slurry. All but one of the four was successful in accomplishing this (i.e., breaking up the straw mat). The fifth producer pumped down the manure storage but did not intentionally plan to break up the straw cover and had about 50% area coverage of straw on the storage unit going into the winter. The one individual who tried to chop up the straw and was unsuccessful had the straw mat sitting at or near the bottom of the storage basin going into the winter. We don't know the extent to which this will cause problems with pumping or removing of manure from this storage units in future years.

One of the participants in the demonstration project decided to try a more permanent cover than straw and applied a geotextile material (about 1/8 inch thick) on two different manure storage basins. The cost of using this material to cover a manure storage unit ranges from \$0.15 to \$0.25 / ft² of storage area depending on the size of the storage. One of these basins had a small amount, 2 to 3 inches (5 to 8 cm) of straw blown on top of the geotextile material to aid in odor control (Figure 3).



Figure 3. Geotextile cover with thin layer of straw (2 to 3 inches) blown on top of an earthen manure storage basin.

This basin was the 2nd stage of a two stage unit (first stage was covered by just straw) and is typically not agitated and pumped directly. Instead, the level is controlled by allowing the slurry in the storage to drain back into the first stage and be removed by a standard manure pump. Because of this procedure, the geotextile material and thin layer of straw did not need to be removed for pumping manure.

The other manure storage basin cover with the geotextile material had no straw blown on top of it. This material was partially removed or “peeled back” during the pumping of the manure during the fall of 1998 and did create some additional work during the pumping process but was manageable. Both of the geotextile covers did survive the winter of 1998-99 and are still floating this summer (1999). The geotextile cover with the thin layer of straw sank slightly early this spring during some large rainfall events, but resurfaced and seems to be providing good odor and H₂S reduction although measurements have not been taken during 1999.

Odor and H₂S Reduction Data

The odor reduction performance of the straw covers was noticeable as subjectively noted by the producers, their neighbors, and others working near the units. Air samples were collected from the surface of the storage units at least twice during the summer and fall and analyzed for odor using olfactometry. Results of these measurements for odor and gas concentrations were

inconsistent due to difficulty in collecting a representative sample at the surface of the straw cover.

Even though there was difficulty in sampling from the surface of the storage units with covers, Tables 1 and 2 gives performance data from one of the earthen basin with just straw (Table 1) and one with the geotextile and straw combination (Table 2). The tables list both the surface concentrations and emissions from the surface for hydrogen sulfide (H₂S) and odor. Odor concentrations are given in odor units (o.u.) which is the number of air dilutions needed to obtain the detection threshold of the sample (the higher the number the stronger the odor). The odor emissions are given in a unit of (o.u. m³/s m²), which means the number of odor units per second (when multiplied by a flow rate of m³/s) per square meter of surface area of the manure storage unit.

Both tables show one sampling done before the covers were applied to provide some measure of effectiveness. The other data shows two or three measurements taken at different sites on the storage and in some cases using different airflow from the flux or wind tunnel hood used to collect air samples. Although not every sampling collected shows a reduction, the general trend is for lower odor and H₂S emissions from these storage basins after they were covered.

Table 1. Odor and H₂S concentrations and emissions from a manure storage basin before straw was applied (June 1998 data) and after applied (Aug. & Sept. 1998 data).

Date	H ₂ S, ppb	H ₂ S emission, µg/s/m ²	Odor units, o.u.	Odor emission, o.u. m ³ /s m ²
01-Jun-98 –No straw	200	13.6	34	1.56
04-Aug-98	72	3.33	25	0.76
10-Sep-98	17	0.79	132	4.02
10-Sep-98	39	1.8	51	1.55

Table 2. Odor and H₂S concentrations and emissions from a manure storage basin before a geotextile material with a thin layer of straw was installed (June 1998 data) and after it was applied (Aug. & Sept. 1998 data).

Date	H ₂ S, ppb	H ₂ S emission, µg/s/m ²	Odor units, o.u.	Odor emission, o.u. m ³ /s m ²
16-Jun-98- No cover	300	20.4	153	7.04
12-Aug-98	23	0.35	26	0.26
14-Sep-98	16	1.09	66	3.03

SUMMARY

This project showed that straw and a geotextile material covered with a thin layer of straw can be successfully used on outside manure storage units to provide some reduction in odor and H₂S emissions. There are application problems in applying the straw on the storage, from being able

to reach all sections of the basin or tank if it has a large surface area, to being able to judge the depth of straw on the basin during the application process. The average cost of the straw used in this project was \$0.08/ft², not including application cost, while the cost of the geotextile was approximately \$0.25/ft², which did include application. The straw stayed afloat from two to four months and did not provide much trouble when the storage units were agitated and pumped in the fall. One of the geotextile-covered basins (without a thin layer of straw) was “peeled” back during the pump-out process in the fall, which did take extra time and effort. A straw cover does offer producers a reasonably low cost solution to odor and H₂S emission problems. A geotextile cover offers a longer-term solution but for more cost and potentially greater maintenance requirements.

Further evaluation of both straw and geotextile covers on manure storage basins needs to be done to identify problems that may develop over time. Also, other more permanent floating covers (lasting longer than one year), like floating clay balls (Leca or Macrolite) or other geotextile materials, needs to be investigated.

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Covers for Manure Storage Units

Richard Nicolai and Steve Pohl, South Dakota State University, and David Schmidt, University of Minnesota

This fact sheet is one in a series intended to answer — with science-based land-grant university research — questions frequently asked by the public about issues and needs affecting agricultural growth, urban expansion, and rural community development in South Dakota.

Every livestock operation needs some kind of manure storage. Storage allows the nutrients in the manure to be applied to cropland at appropriate times in the growing cycle. Storage also allows the manure to be held when fields are frozen or snow covered when application might result in runoff that would pollute surface water.

Recommended storage capacity for manure is 6 months or more, depending on the moisture content of the manure and whether it is liquid or solid. Solid manure piles typically emit very little odor due to crusting of the pile surfaces. However, liquid manure storages can be a significant source of odor and hydrogen sulfide emissions.

Odor emissions from manure storage are typically the leading cause of nuisance complaints. Liquid manure storage tends to give off odor and gas emissions when the surface is disturbed during windy conditions or during agitation and pumping prior to land application. Spring turnover, a phenomenon that occurs when the storage warms, also increases odor and gas emissions.

Covers over the lagoons significantly reduce both odor and hydrogen sulfide emissions. Covers create a physical barrier at the liquid-air-interface, which helps retain more volatile chemical compounds in the liquid phase and minimizes emissions to the atmosphere. However, there is limited design information, and it has been difficult to evaluate performance of covers in field conditions.



South Dakota State University

College of Agriculture & Biological Sciences

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Table 1. Types of covers, effectiveness, life expectancy, and capital cost.

Type of cover	Material	Effectiveness (%)			Life expectancy	Capital cost (US\$/yd ²)	Reference
		Odor	H ₂ S	NH ₃			
Impermeable	Concrete lid	95	N/A	N/A	10-15 years	N/A	1
	Wood lid	95	N/A	95	10-15 years	N/A	1,2,3
	Inflatable plastic	95	95	95	10 years	7-15	1,4
	Floating plastic (HDPE)	60-78	90	N/A	10 years	3-5	5
Permeable	Straw	40-90	80-94	25-85	Up to 6 months	0.25-1	1,5,6,7,8,9
	Geotextile	40-65	30-90	0	3-5 years	1.25-1.6	9
	Geotextile + straw	50-80	60-98	8-85	N/A	1.5-2.6	9
	Leca®	90	N/A	65-95	10 years	15.45	3,7
	Macrolite®	60	64-84	N/A	10 years	15.45	5
References	1 Mannebeck, 1985	4 Zhang and Gaakeer, 1996		7 Bundy et al., 1997			
	2 DeBode, 1991	5 Clanton et al., 1999		8 Jacobson, 1998			
	3 Sommer et al., 1993	6 Anonymous, 1993		9 Clanton et al., 2001			

How covers work

When a cover is placed directly over the manure surface, the following processes take place:

1. Resistance to the transfer of gases is increased because of the physical barrier between the liquid and the air.
2. Gas concentrations build up under the cover.
3. The rate at which a gas diffuses out of the manure is reduced (because the concentration gradient has decreased).
4. Hydrogen sulfide, ammonia, and other volatile odorous compounds may be kept in solution, increasing the emissions of these gases when the cover is removed for land application of manure.

Most widely used covers float on the surface of the manure and are made of straw, geotextile, or a combination of both. Other types of covers on farms include impermeable plastic covers; rigid covers made with concrete, wood, and PVC material; and air-filled clay balls like Leca® and Macrolite®. Inflatable plastic covers have also been popular in Canada.

Covers are usually classified as impermeable or permeable. Impermeable covers do not allow any gases coming off the manure to be emitted to the atmosphere, while permeable covers permit transmission of some gases. Table 1 describes the effectiveness and cost of various types of covers.

Impermeable covers

Because impermeable covers trap and hold gases coming off the manure, a vent must be provided to prevent build-up of excessive pressure in the headspace and to ward off a possible

explosion (Fig 1). Odorous gases under covers are extremely corrosive or toxic. Flat, low-profile covers should be specified whenever possible to minimize headspace. Minimal headspace reduces air exchange volumes, reducing the need for odor control equipment.

Figure 1. Rigid cover (concrete, wood, PVC, etc.) or hoop structure placed on a manure storage tank and venting gases to the atmosphere.

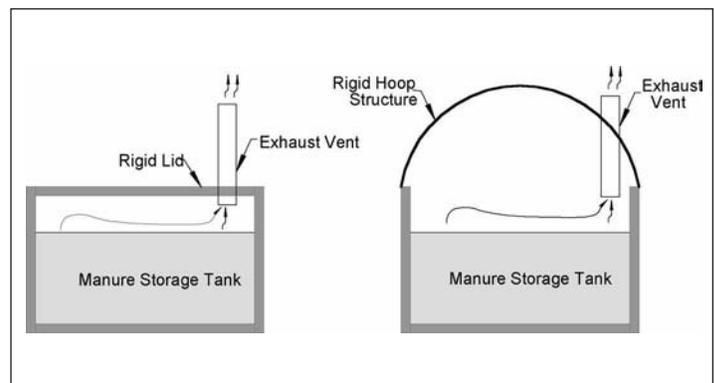
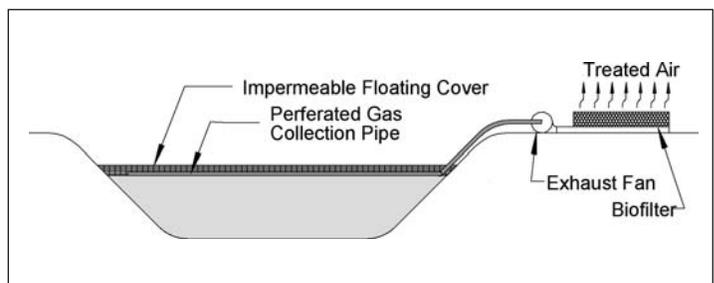


Figure 2. System to remove and treat biogas from manure storage using an impermeable cover and biofilter.



Impermeable covers need to be designed for easy access for operation or maintenance, have a minimum number of joints, and seals at all joints. The corrosive action of sulfides and sulfuric acid must be considered when selecting cover materials and concrete coatings. Overhangs, ledges, or lips on the underside of covers where condensate may collect should be avoided.

Odoriferous gases in a covered storage tank must be vented to the atmosphere to avoid pressure build-up inside the cover from the production of manure gases. Collecting and removing biogas can be done through installing perforated gas collection pipes and/or exhaust fans. Methods to reduce odor include the burning or flaring of these gases or some form of gas treatment as biofiltration or ozonation before discharge to the atmosphere (Fig 2). The design of these air treatment systems should take into account the highly odorous gas H_2S concentration (600 to 1000 ppm).

Extension Fact Sheet 925-C gives general and specific design and operating information on biofilters.

Flexible membrane covers

Flexible membrane covers are constructed of high density polyethylene. They have effectively controlled odor from industrial and municipal sites. The membranes are 20 mil minimum thickness and must be UV stabilized. Membrane covers, either permeable or impermeable, when used on an earthen basin manure storage system, are typically anchored to the manure storage perimeter with an anchor trench (Fig 3). The cover floats on the surface of the manure and partially inflates with manure gases.

If the cover is impermeable the gases must be vented to the atmosphere. This is accomplished by a variety of techniques; often, a perimeter tile is placed under the cover near the top of the berm of the manure storage and then vented through the cover. The gases are either flared or treated using some other gas treatment system. Access to the manure is typically through a large flap that can be folded back. The flap must be large enough to allow for pumping and agitation equipment.

Typical life of the covers is anticipated to be 10-15 years with an installation cost of approximately \$3-5 per square yard. This includes the venting system and is a function of the size of the area covered.

Inflatable dome system

With inflatable cover systems (Fig 4), a tarp is fastened to the tank perimeter as tightly as possible and supported by a center column with radiating straps. Air is delivered through a low-pressure blower, and the cover is maintained at a constant operating pressure (usually about 1 in H_2O , or 250 Pa). Zhang and Baakeer (1996) observed that at an operating

pressure of 0.4 in H_2O (100 Pa), air leakage was 125 cfm. This leakage is approximately equivalent to the airflow rate of a bathroom exhaust fan.

For agitation and pumping, the structure is deflated, allowing the tarp to lie over the radiating supports. Access doors are then opened to introduce pumping equipment.

Figure 3. Fastening a cover to a berm using anchor trenches.

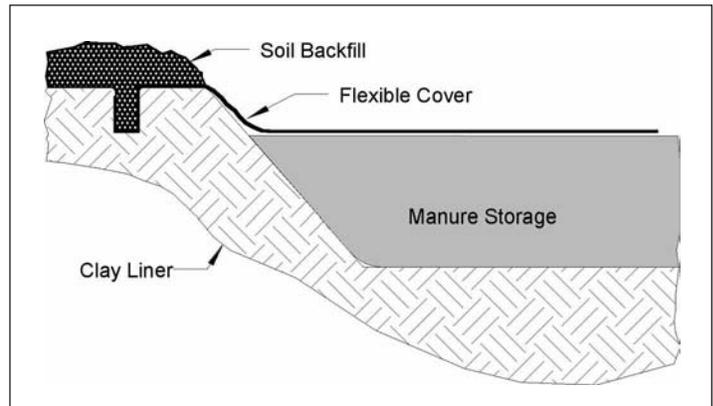


Figure 4. Inflatable dome cover and control system.

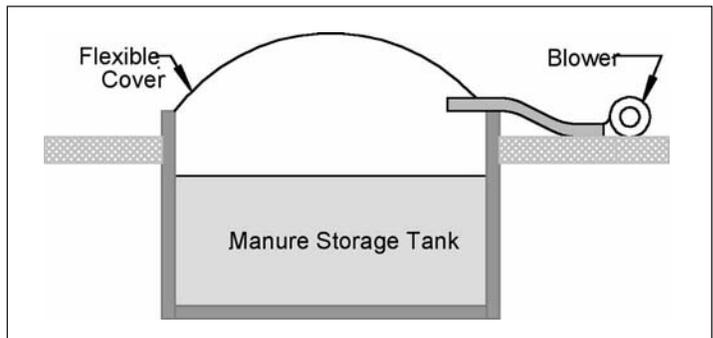


Figure 5. Geotextile floating permeable cover with closed-cell flotation.



Permeable covers

Permeable covers, such as straw, geotextile, or floating clay balls, are also effective alternatives for reducing odor from livestock manure facilities. Effectiveness of odor and gaseous emissions control is lower than with impermeable covers (see Table 1).

A biofilm may develop at the interface of cover and liquid. Some of the odorous compounds that escape to the atmosphere are broken down within the aerobic layer that is established.

Straw

Both barley and wheat straw can be used as organic floating covers; there is no significant difference between them. The straw is applied to manure storage tanks using a straw chopper/blower. The degree of odor control is not affected by the type of straw but rather the ability of the straw to float on the surface. Thus, odor reduction will vary from 90% for a thick, newly applied cover to 40% or less depending on straw thickness and uniformity. OFFSET modeling uses 50% reduction over the average life of a straw cover. Sometimes oil

is added to the straw at the time of application to increase the time the straw floats.

Straw covers usually last between 2 and 6 months depending on the amount applied (depth of straw), uniformity of application, basin size, and wind conditions during application. If the cover starts to break up or sink, additional straw must be added to retain effectiveness. Successful agitation and pumping of straw-covered storages can be accomplished by appropriate equipment (chopper pumps).

University of Minnesota researchers (Clanton, 2001) have shown that a 4-inch layer of straw alone gives 60%, 69%, and 61% reductions of odor, H₂S, and NH₃, respectively. Thicker layers of straw (8 to 12 inches) resulted in even better odor and gas reductions (70% to 90%), with the exception of ammonia reduction with a 8-in layer (about 60%). The effectiveness of straw covers apparently decreases with time.

A 12-inch depth of straw is typically recommended, since this depth has been shown to float longer than lesser depths. The amount of straw needed depends on the area of the manure storage and desired depth of the straw layer. A single large round straw bale (6 ft diameter) can cover about 500 ft² of storage (12-inch layer).

Table 2. Cover design considerations.

1. Odor and H ₂ S reduction needed:	a. If more than 50% reduction is needed, then an impermeable cover is needed. b. For 60-90% reduction geotextile or straw covers can be used.
2. Type of storage:	a. Geotextile, straw, and HDPE covers can not be easily installed on earthen basins. b. Inflatable plastic domes can not be easily installed on earthen basins. c. Concrete lids will not work with steel tanks or earthen basin. d. Straw covers will not work well on anaerobic lagoons because of the large size.
3. Size of storage:	a. Straw covers on manure storages or anaerobic lagoons over 2 acres are impractical. Wave action on these large areas will disturb the straw cover. These large surface areas have been covered by both geotextile and HDPE fabric.
4. Manure management:	a. Geotextile and HDPE fabrics are not recommended for manure storages where frequent pumping or rigorous agitation is needed. b. Covers installed on manure storages or lagoons where manure is recycled back into the barns for flushing or pit recharge is not recommended. High concentrations of dissolved gases in the manure will be released when this manure is brought back in the barn. c. Considerations should be made for evaporation and rainfall. Impermeable covers do not permit rainfall to enter storage but also restrict evaporation. Permeable covers allow rainfall to enter but may restrict evaporation.
5. Life expectancy for the solution:	a. Straw is considered an effective short term solution to an odor problem. b. HDPE has a life expectancy of 10-15 years. c. Geotextile fabrics are expected to last 3-5 years.
6. Cost:	a. Costs should include both capital investment and long term maintenance.

Geotextile

Other floating permeable covers, such as geotextile materials (non-woven fabric composed of thermally bonded, continuous polypropylene filaments), may provide a better solution than straw alone for certain types of storage basins.

Geotextile materials are self-floating and provide a physical barrier to mass transfer of gases from the liquid to the air. There is also some possibility that the geotextile helps maintain an aerobic layer of microorganisms on the manure surface, but more research is needed to verify this process. This layer would reduce the odorous gases to carbon dioxide and water.

Geotextile materials have higher initial cost than straw covers but all costs, such as installation and maintenance, must be included in the final evaluation of a cover.

One concern with geotextile or geotextile-straw covers is the ability to agitate the manure storage. This applies only in manure storage basins and tanks and not to lagoons, which are typically not agitated.

Most types of agitation equipment pump manure over the surface to help with the stirring. This is not possible with the geotextile covers. To achieve any agitation, the cover is partially removed—typically from one corner of the basin—or the cover is lifted by a cable and winch system and the agitation/pumping equipment is positioned under the cover. Neither of these options allows for vigorous agitation.

Procedures and equipment to agitate under the cover through an access is being developed.

Long-term floatation of geotextile covers was a concern when the product was first introduced. In two field situations with this early product there has been some partial sinking of the geotextile in the spring after surface ice thawed. However, in both situations, the covers came back to the surface as the system warmed.

Adding a layer of closed-cell foam between two types of geotextile materials has doubled the life of the covers and prevented sinking (Fig 5). The top geotextile layer has the ability to protect against ultra-violet radiation. Microbial buildup on the cover between the layers may increase odor reduction; more research is needed.

Management of manure covers

After a cover is installed properly, there are additional technical and operational needs. Parts of the cover may need to be removed to permit agitation and pumping when the manure is removed for land application. A permanent opening may be installed that can be sealed between pumping intervals.

Safety should **always** be considered during agitation and pumping of manure. There may be a high concentration of hydrogen sulfide or other gases under the fabric cover. Opening the flaps or lifting part of the cover must be done with caution.

Cover maintenance includes the repair of tears or punctures and removal of debris and silt accumulation on the cover surface. Geotextile covers without an additional float system may sink after the winter season and may take 1 or 2 months to float again on the manure surface. Disposing of plastic and geotextile covers after they are no longer usable may be difficult and costly depending on local hauling and landfill fees.

Straw covers may break up or sink due to high winds and heavy rain. If a straw cover starts to break up or sink, additional straw may be added to reestablish the cover's original effectiveness. Agitation and pumping of straw covered manure storages can be successful.

Manure nutrient concentration may increase after an impermeable cover is installed. More land is needed to achieve the same agronomic application rate if the manure concentration is increased.

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FLOATING COVERS TO REDUCE GAS EMISSIONS FROM LIQUID MANURE STORAGE: A REVIEW

A. C. VanderZaag, R. J. Gordon, V. M. Glass, R. C. Jamieson

ABSTRACT. Liquid manure (slurry) storages are sources of detrimental gases. Floating covers are a potential mitigation measure that can be implemented on many storage facility types. This article reviews the use of floating covers to reduce the emissions of odors, hydrogen sulfide (H_2S), ammonia (NH_3), and greenhouse gases (GHGs) including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Covers have been established with materials of natural origin (e.g. natural crusts, straw, peat, and light expanded clay aggregates), synthetic origin (e.g. geotextile, plastic, and rubber), and composites of both. Nearly all cover types have been capable of substantially reducing NH_3 emissions (compared to uncovered controls). Reductions of odor and H_2S have also been good, though fewer cover types have been assessed with respect to these parameters. When used alone, oil covers can produce foul odors and should not be used. Less information is available on the influence of covers on GHG emissions. In studies >2 weeks long, covers generally increased CH_4 and CO_2 emissions. All studies where N_2O was measured found that permeable covers increased its emission. There is some difficulty comparing laboratory and field observations, which may be due to study duration, hydrologic influences, or slurry characteristics. Principles of mass transfer are discussed with respect to the mechanisms of cover operation. Though evidence of microbial gas consumption in permeable covers exists, its relative importance is unclear. Currently, information on many cover materials is limited to one or two studies, and simultaneous assessments of the effects on all aforementioned gases is lacking for all covers.

Keywords. Ammonia, Emission reduction, Greenhouse gas, Hydrogen sulfide, Methane, Nitrous oxide, Odor control, Slurry storage.

Due to the intensification of confined livestock production, liquid manure (slurry) storage facilities have become prevalent. They can include pits beneath slatted floors, outdoor concrete pits, or earthen lagoons. They are traditionally open to the atmosphere, allowing unimpeded emissions of odors, hydrogen sulfide (H_2S), ammonia (NH_3), and greenhouse gases (GHGs) including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Mitigating these emissions is important for several reasons. Odors are the most tangible and important concern for agricultural producers by affecting their neighborly relations (Jungbluth et al., 2001). Ammonia emissions reduce the nitrogen (N) content of manure and contribute to aerosol formation and detrimental environmental effects. Greenhouse gases contribute to climate change, with CH_4 and N_2O possessing 23- and 296-times more warming potential than CO_2 , respectively (IPCC, 2001).

Many approaches to mitigating emissions from storage facilities have been investigated. These include industrial processing (Phillips et al., 1999), diet manipulation, slurry additives (Portejoie et al., 2003), equipping the storage for biogas collection (Hilhorst et al., 2001), or installing positive or negative air pressure covers (e.g. Zhang and Gaakeer, 1998; Funk et al., 2004a, b). While potentially effective, these systems tend to be expensive.

Another approach is establishing a floating slurry cover. It can be a natural crust, a layer of natural material (e.g. straw), a permeable fabric, impermeable plastic, or other alternatives. Ideally, floating covers are simple, inexpensive, adaptable, and immediately useable. Depending on the mitigation objectives, floating covers may provide a permanent solution, or an intermediate one until a better solution is feasible. Research on the effects of floating covers has been conducted sporadically since the 1980s (Meyer and Converse, 1982). Studies have been conducted on several continents, using a variety of covers at scales ranging from short-term laboratory, to multi-year field studies. The body of knowledge has grown to the point where it is beneficial to study it collectively.

The objective of this review is to bring together previous research on floating covers and their effects on emissions of odor, H_2S , NH_3 , and GHGs. Focus is placed on describing the cover types that have been studied and experimental approaches taken, then identifying areas of agreement and conflict among the results, discussing mechanisms of operation, and drawing attention to areas where further research would be beneficial. Cover types will be categorized in three groups: (i) natural origin, (ii) synthetic origin, and (iii) composites. Results for all cover types are summarized in table 1.

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The authors are **Andrew C. VanderZaag**, ASABE Member Engineer, Graduate Student, Process Engineering and Applied Science Department, Dalhousie University, Halifax, Nova Scotia, Canada; **Rob J. Gordon**, Associate Professor, Department of Engineering, Nova Scotia Agricultural College, Truro, Nova Scotia, Canada; **Vimy Glass**, Graduate Student, Land Resource Science Department, University of Guelph, Guelph, Ontario, Canada; and **Rob C. Jamieson**, Assistant Professor, Process Engineering and Applied Science Department, Dalhousie University, Halifax, Nova Scotia, Canada. **Corresponding author:** Andrew C. VanderZaag, Process Engineering and Applied Science Department (Sexton House), Dalhousie University, P.O. Box 1000, Halifax, Nova Scotia, B3J 2X4 Canada; phone: 902-893-4116; fax: 902-893-0335; e-mail: a.vanderzaag@dal.ca.

Table 1. Summary of research on floating covers and the observed effects on gas emissions from stored liquid manure.

Reference	Study Description	Manure	°C [b, c]	DM (%) [c]	pH [c]	Reps [d]	Cover Description	Percent Reduction[a]					[e]	
								Odor	H ₂ S	NH ₃	CO ₂	CH ₄		N ₂ O
Amon et al., 2006a,c	Manure was stored in 10 m ³ tanks. Fluxes measured 2x per week using a large steady-state chamber. Dairy and Swine manure were also studied, but only AD had an uncovered control.	AD-dairy	19.5	--	7	N	Summer Straw (10 cm)	--	--	44	--	-3	-6	f
Amon et al., 2006b	Same set-up as above. No uncovered control was included in the study.	Dairy	9.3	--	7	N	Winter " 100 d Winter " 140 d Summer Straw (10 cm)	--	--	19	--	-4	0	f
Balsari et al., 2006	A 79 m ³ tank was divided in half using a plastic sheet. One half was covered, the other side was the control. For six days in each season, emissions were measured simultaneously on both sides using acid traps and a funnel method.	Swine	16.7 25.5 14.2 6.4	3.5 4.1 3.2 3.1	8.1 8.0 7.8 7.9	N	Spring Leca® (10 cm) Summer " Fall " Winter "	--	--	84 87 78 73	--	--	--	f
Berg et al., 2006;	Manure was stored in 65 L open-top vessels at two laboratories. Once per week, flow-through lids were placed atop the chambers and the steady-state headspace concentration was measured. Additives were combined with the cover material prior to the study. pH was measured at the slurry surface.	Swine	19 to 22	5 [7.0] 10 [7.5]	7.0 [7.0] 7.7 [7.5]	Y	Indoor Leca® (6 cm) 162 d to Pegulit™ (6 cm) 217 d Straw (8 cm)	--	--	83* 90* 90* 75*	--	0 -13 -47 73*	-262* -280* -468*	c
Paziczki, 2006														
Bicudo et al., 2001	Earthen lagoons at 2 finishing facilities were compared. A crust formed on one lagoon, the other did not. Fluxes were periodically measured using a floating wind-tunnel.	Swine	--	2.1 (1.2)	7.7 (8.1)	N	Summer Natural Crust (vs. paired lagoon) 5 mo Natural Crust	65 46	80* 81	42 20	--	--	--	f
Bicudo et al., 2002;	Three pairs of lagoons (at a nursery, a 2000 head facility, and a 3000 head facility) were studied by covering one with a BioCap™ (Baumgartner Environments, Minnesota USA) cover and leaving the other as a control. A crust formed on the nursery and 2000 head control lagoons.	Swine	26.9 21.6 22.1	1.1 1.3 1.2	7.7 7.6	Y	2000 Geotextile (nursery) 07 - 10 Geotextile (2000 head) 2001 Geotextile (nursery) 05 - 10 Geotextile (2000 head)	24 58* 82*	67 76* 96*	53* 22 1	--	--	--	f
Bundy et al., 1997;	Fluxes measured periodically using a floating wind-tunnel. Fourteen outdoor tanks were filled with 2.3 m ³ of manure. Once per week, each tank was covered with plastic and headspace gas samples were taken. Two uncovered controls were included.	Swine	--	4 to 5	--	N	Summer Straw (7.6, 15, 25 cm) 9 wks Corn stalks (15, 25 cm) Leka rock (4, 7.6, 15 cm) Polyethylene mesh + liquid Aeration foam	>90 ~90 >90 0 >90	m m m m m	m m m m m	--	--	--	c
Li et al., 1997														
Cicek et al., 2004	Two manure storages were compared. Concentrations were measured at the outlet of a floating wind-tunnel.	Swine	--	--	--	N	Summer Straw	38	--	--	-3	-247	-8	c
Clanton et al., 1999	Twenty-one 750 L outdoor tanks were filled with manure by adding manure on 4 occasions. Gas concentrations were measured at the outlet of a wind-tunnel 24 and 48 h after manure additions.	Swine	--	2 to 5	--	Y	07/97 Straw (30 cm) to Vegetable Oil (1 cm) 10/97 Straw (30 cm) + oil Macrolite® (20 cm) PVC/rubber (impermeable) Geotextile	<78 <64 <84 <62 <78 <59	<94 <88 <94 <64 <93 <71	--	--	--	--	c
Clanton et al., 2001	Thirty-eight 160 L open-topped PVC pipes containing manure were located indoors. Manure was bottom-loaded into the columns semi-weekly. Half of the uncovered controls were stirred to prevent crust development. Headspace concentrations were measured weekly, shortly after stirring. Reductions here are vs. the stirred controls.	Swine Dairy (pooled data shown here)	room	0.7	7.4	Y	10 wk Straw (10 cm) +/- Geotextile* Straw (20 cm) +/- Geotextile Straw (30 cm) +/- Geotextile Geotextile (0.3 mm) Geotextile (1.1 mm) Geotextile (2.4 mm)	63 78 83 32 20 63	93 98 98 83 81 87	8 62 79 -4 -61 -29	--	--	--	c
DeBode, 1991	Compared to unstirred controls, reductions of Odor and H ₂ S were lower. NH ₃ higher. * The effect of Geotextile was not significant so results were pooled over all thicknesses of Geotextile (0, 0.3, 1.1, 2.4 mm) beginning of each year. Monthly flux measurements were made using a Lindvall box. Odor was reported as concentration only. For all gases, reductions in winter were lower than in summer.	Swine Cattle	--	4 - 7	7.7	N	Summer Floating foil (impermeable) 5 mo Polystyrene (impermeable) Stimulated Crust (straw added) Floating foil Polystyrene (impermeable)	28 40 43 39	--	94 85 71 86 81	--	--	--	c, f

Table 1. Summary of research on floating covers and the observed effects on gas emissions from stored liquid manure.

Reference	Study Description	Manure	°C [b, c]	DM (%) [c]	pH [c]	Reps [d]	Period	Cover Description	Percent Reduction[a]					[e]
									Odor	H ₂ S	NH ₃	CO ₂	CH ₄	
Derix and Aarnink, 1993	Two kg of slurry was stored in covered laboratory vessels. Daily average fluxes were measured using flow-through chambers. Reductions were similar for all manure types, but thicker oil layers were needed on cattle manure.	Swine Cattle Veal	room	8.1	8.0	N	1 wk	Mineral oil (2.5 – 10 mm) Vegetable oil (2.5 – 10 mm) (pooled data)	--	--	>90	--	--	f
Filson et al., 1996; PAMI, 1996	Thirty lagoons were covered with long barley straw. Testimonial evidence of perceived odor reductions was documented.	Swine	--	--	--	Y	2 yr	Straw (20 – 30 cm) Straw + oil Straw + polystyrene	m	--	--	--	--	--
Guarino et al., 2006	Nine 190 L vessels were used to store manure indoors. Cover materials (except oil) were placed on a farm tank for 30 d prior to being used in the study. Fluxes were measured 3 times using a static-chamber approach. Odor was reported as headspace concentration. Each material was tested at a different time.	Swine	15.0	2.3	7.4	Y	1 wk	Straw (7, 14 cm) Vegetable oil (3, 9 mm) Wood chips (7, 14 cm) Corn stalks (7, 14 cm) Expanded clay (7, 14 cm) Straw (7, 14 cm) Vegetable oil (3, 9 mm) Wood chips (7, 14 cm) Corn stalks (7, 14 cm) Expanded clay (7, 14 cm)	61* 52* 55* 90* 69* 83* 55* 15 84* 89*	--	86* 100* 80* 84* 75* 100* 91* 91* 60* 64*	20* -- 37* 15 35* 4 34* 21 32* -31*	28 10 26 -- 17 -- 43 -- -- 16*	c, f
Hörnig et al., 1999	Four farms with 2 or 3 concrete tanks or lagoons were used. At each farm, one storage was an uncovered control. Gas fluxes were measured using a floating static-chamber. Odor was reported as headspace concentration. A 25 d laboratory study was also conducted using 65 L containers and measuring the headspace concentrations. Vegetable oil was studied separately. The 6 mm layer performed best and is reported here.	Swine	--	--	--	N	Field	Straw (5 – 15 cm) Pegilut R (10 cm) Pegilut M (10 cm) Floating film (2 mm, impermeable)	84 94 30	--	80 91 63	--	--	c, f
Hudson et al., 2001;	In the laboratory, twelve vessels were used to hold manure (~210 L) and cover materials. Manure (<2 L) was added daily. Some covers were supported by polyethylene rods. Fluxes were determined using the steady-state equation and a flow-through headspace.	Swine	5 – 15	8.2	--	N	Lab	Straw Pegilut R (10 cm) Pegilut M (10 cm)	--	--	[25] [50]	--	--	--
Hudson et al., 2006a	Fluxes were determined using the steady-state equation and a flow-through headspace.	Swine	17 – 23	8.5	--	N	85 d	Vegetable oil (3, 6 mm)	--	--	[85]	--	--	--
Hudson et al., 2006b	36 m ² covers were deployed on a lagoon. Straw covers were supported by a lattice of polyethylene rods. Fluxes were measured 5 to 10× using a wind-tunnel. Comparisons were made against uncovered areas of the same lagoon.	Swine	--	--	7.2 to 7.6 (7.9)	Y	1 year	Straw (barley, 10cm) Straw (barley, 10cm) + support Straw (Lucerne, 10cm) + support Straw (sugar cane, 10cm) + support Polystyrene beads (10 cm)	71 to 84	--	--	-15 5 -40* -54*	0 0 0 0	f
Koppolu et al., 2005	Lab: manure was stored in 1360 L tanks. Every week, 23 L of manure was added. Concentrations and odor intensity were measured weekly at the exhaust of a floating wind-tunnel. Field: a floating equilibrium chamber was used to measure concentrations above a covered storage. Comparisons were made to the same storage prior to cover installation. The storage was agitated prior to covering.	Swine	--	[6.5] (5.6) [0.5] (0.4)	[7.1] (7.3) [8.8] (8.8)	N	Lab	Fine ground rubber (2.5 cm) Fine ground rubber (7.6 cm) Fine ground rubber (5.0 cm)	0 - 99 70 - 99 -20 - 77	m m m	[81] [<80] [16]	--	--	c
Lagué et al., 2004, 2005	Earthen manure basins at two farms were compared. Fluxes were measured on 3 days using floating chambers.	Swine	--	--	--	N	Spring - Fall	Straw (~10 cm) + support Polypropylene fabric	84 88	--	--	--	--	f
Meyer and Converse, 1982	Manure was stored in 212 L outdoor barrels. More manure was added 5 times. Covers with good floatation were assessed 5 times by odor panelists who scored them on a scale from 10 – 70. A lab study was also conducted using 18 L cylinders storing manure. Gas fluxes were measured using a flow-through lid on 11 occasions.	Swine	--	1.8 to 5.7	6.5 to 7.4	N	Field	comstalks + oil ground corncobs + oil sawdust + oil wood shavings + oil rice hulls + oil grass clippings + oil waste oil	37 42 sank 37 46 29	--	[66] [42]	--	--	c, f

COVERS OF NATURAL ORIGIN

Natural covers are made with materials such as straw, peat, clay, and minerals. They are generally non-hazardous and make beneficial soil amendments if the material is field-applied.

NATURALLY OCCURRING CRUSTS

Under certain conditions, slurries naturally form a surface crust. Although crust formation is not thoroughly understood, evidence suggests that bubbles carry particles to the surface, where they coalesce. If sufficient bubbles and dry matter (DM) are present, an appreciable crust forms. Evaporation also contributes by concentrating DM at the surface (Misselbrook et al., 2005). Crusts generally form more readily on cattle than pig slurry (Mannebeck, 1985), probably due to the presence of greater DM and fibrous material (e.g. bedding and forage). Misselbrook et al. (2005) examined how crust formation on dairy slurry was affected by bedding, diet, DM, air flow, rainfall, and labile carbon additives. The most influential factor was DM. Crusts formed on slurries containing >1% DM, and slurry with the highest DM produced the thickest crust (38 cm). Crust formation began after 10 to 20 d, and stabilized after 40 to 60 d, after which they dried and became hard. Adding labile carbon (corn starch and glucose) increased crust thickness. Webb et al. (2005) suggested that crusts form on cattle slurry with >7% DM. Smith et al. (2004) observed that the nature of DM affects crust formation (e.g. maize-fed vs. silage-fed cattle). They also found “robust” crusts (>7.5 cm thick) did not form without net evaporative loss >25 cm. De Bode (1991) noted that cattle slurry formed a natural crust after 45 d, but it was not resistant to heavy rain, so emission reduction was minimal. However, adding 4 to 7.5 kg m⁻² of chopped straw led to a “weather-resistant” crust.

Adding crust-forming slurry to non-crusting slurry can stimulate crust formation (Mannebeck, 1985). This could provide environmental benefit without additional material. However, it has generally been ineffective. Meyer and Converse (1982) added dairy manure to pig slurry but it was ineffective, providing minimal odor reduction, and eventually sinking. Similarly, Sommer et al. (2000) added cattle slurry crust to non-crusting fermented slurry but the crust disintegrated within weeks. Mannebeck (1985) suggested a mixture of >50% cattle slurry to produce a durable crust on non-crusting pig slurry. Few farms have the necessary combination of slurries, making this approach impractical.

Bicudo et al. (2001) observed that gases are held under the crust and released when it degrades or cracks, thereby delaying emissions rather than reducing them. This is an important consideration for all cover studies. Summarizing the effects of natural crusts on emissions detailed in table 1:

- Reduction of odor emissions by 40% to 65%, H₂S emissions by 80% (Bicudo et al., 2001). The highest reductions of odor (85% to 95%) are expected from a dry crust (Mannebeck, 1985).
- Reduction of NH₃ emissions by 50% to 90% (De Bode, 1991; Sommer et al., 1993; Sommer, 1997; Smith et al., 2004; Misselbrook et al., 2005). Small reductions (~20%) were observed in a short laboratory study (Williams, 2003) and from a low DM swine lagoon (Bicudo et al., 2001). Increased emissions observed by Bicudo et al.

(2001) were probably due to other differences between the lagoons.

- Reduction of CH₄ emissions by 38%, but increased N₂O emissions indicating suitable conditions for microbial N₂O production (Sommer et al., 2000). Petersen et al. (2005) found CH₄ was consumed in the presence of a crust at a rate similar to rice paddies and wetland soils. This is evidence of one mechanism by which crusts reduce emissions.

STRAW AND OTHER CROP RESIDUES

Crop residues are available on-farm at a low cost. The most frequently studied material is straw, but other materials have been studied, including cornstalks, corn cobs, alfalfa, sugarcane trash, grass clippings, and rice hulls. These materials have limited buoyancy and are susceptible to wind and rain damage. Most field studies found that straw sinks and degrades. Williams (2003) concluded it was unsuitable on pig slurry because of rapid sinking. A notable exception was Xue et al. (1999) who found a straw cover did not sink on liquid dairy manure, and NH₃ and H₂S emission reduction improved with time. They did not report the DM of the manure, but dairy DM content is typically higher than swine and may improve floatation. The performance differences among types of straw and residues have not been clear. Meyer and Converse (1982) tested many materials and found rice hulls and grass clippings performed well. Williams (2003) found barley and linseed straw sank as fast as wheat straw. However, the Prairie Agricultural Machinery Institute (PAMI) found a 15- to 30-cm layer of long barley straw was the most effective and practical for swine lagoons (Filson et al., 1996; PAMI, 1996). They found durability and buoyancy were affected by rain, wind, straw quality, and thickness. PAMI improved durability by adding oil, and using multiple straw applications when necessary. Hörnig et al. (1999) recommended >4 kg straw m⁻² to prevent wind damage. Clanton et al. (2001) recommended a layer >20 cm thick. Summarizing the effects of straw and residues on emissions detailed in table 1:

- Most experiments found odor and H₂S reductions >60% (Bundy et al., 1997; Hörnig et al., 1999; Xue et al., 1999; Clanton et al., 1999, 2001; Laguë et al., 2004; Guarino et al., 2006). Farmers and neighbors have perceived reduced odor at straw-covered lagoons (Filson et al., 1996). Guarino et al. (2006) found thicker covers performed best.
- Reduction in summer NH₃ losses were 40-100% (Sommer et al., 1993; Amon et al., 2006a, c). Lower reductions (~50% of summer) were observed in winter/spring when emission potential was low. Thick covers improved reduction in a short study (Guarino et al., 2006) but not in a longer one (Xue et al., 1999).
- Reductions of CH₄ up to 90% have been observed (Peterson et al., 2004; Laguë et al., 2004, 2005), while others found increases up to 250% (Cicek et al., 2004). Guarino et al. (2006) found a thick straw cover reduced CH₄ emissions, but a thinner cover increased them. Both increased CO₂ emissions (Hudson et al., 2001; Guarino et al., 2006) and reductions have been observed (Laguë et al., 2005; Guarino et al., 2006). Adding straw tends to increase N₂O emission, especially when the water balance is negative (Sommer et al., 2000; Laguë et al., 2005; Amon et al., 2006a,c; Berg et al., 2006).

PEAT

Peat is very porous and can adsorb up to 2.5% of its dry weight in $\text{NH}_4^+\text{-N}$ (Barrington and Moreno, 1995; Portejoie et al., 2003). This makes it an attractive cover option, but buoyancy is a challenge. Drying at high temperature causes the peat to become hydrophobic and improves floatation (Barrington and Moreno, 1995). Williams (2003) dismissed peat as a cover material because it is non-renewable. Based on an assessment of slurry N content, Barrington and Moreno (1995) found hydrophobic peat covers >10 cm thick were effective at conserving N, indicating reduced NH_3 emissions. Studies show peat reduced NH_3 emissions by 70 to 100%, and thick peat layers outperform thin layers (table 1; Sommer et al., 1993; Portejoie et al., 2003). No studies investigated other gases.

WOODCHIPS AND SAWDUST

In some locations, woodchips and sawdust are available at a moderate price. A sawdust treatment was tested outdoors but it quickly sank and a waste-oil coating did not improve buoyancy (Meyer and Converse, 1982). Guarino et al. (2006) found a thick layer (14 cm) of woodchips performed well, reducing odor, NH_3 , CO_2 , and CH_4 (table 1). A thin layer performed poorly, especially on pig slurry. This suggests woodchip covers at least 14-cm thick merit further study.

EXPANDED CLAY

Light expanded clay aggregates (LECA) are available from manufacturers, including Leca® (Leca Trading and Concessions A/S; Copenhagen, Denmark) and Macrolite® (Kinetco, Inc.; Newbury, Ohio). They are made by pretreating, heating, and burning clay particles. The resulting balls are buoyant, impervious to water, and resist degradation. Guarino et al. (2006) observed no sign of sinking or physical alteration over a 216 d outdoor test. However, LECA restricted evaporation more than other covers, increasing slurry volume and transport costs. LECA adapts to any storage shape, and is suited to circular tanks (Williams, 2003). Summarizing the effects of LECA on emissions detailed in table 1:

- Reductions of odor and H_2S from 60-90% have generally been observed (Bundy et al., 1997; Clanton et al., 1999; Guarino et al., 2006). Thick and thin cover layers performed similarly (Guarino et al., 2006).
- Reductions of NH_3 have generally been >80% (Sommer et al., 1993; Sommer, 1997; Williams, 2003; Berg et al., 2006; Guarino et al., 2006), except during winter (Balsari et al., 2006). A thicker layer provided the best results (Guarino et al., 2006).
- Generally, LECA covers had little effect on CO_2 , decreased CH_4 , and increased N_2O emissions (Berg et al., 2006; Guarino et al., 2006). Thicker layers tend to reduce CO_2 and CH_4 more (Guarino et al., 2006). The moisture status of the cover is probably an important factor affecting the N_2O emissions (Sommer et al., 2000), so studies without precipitation may tend to overestimate this effect.

PERLITE

Perlite is a volcanic glass that is heat-treated so it expands, giving it a low density. One brand that has been studied is Pegülit® (ETH/OAM International Trading & Recycling

GmbH; Hamburg, Germany), described as white, buoyant, with a density $\sim 400 \text{ kg m}^{-3}$. It is durable and re-forms a surface layer after slurry mixing (Hörnig et al., 1999). This is favorable for systems requiring agitation that would impair other materials. In the laboratory, Perlite reduced the headspace concentration of NH_3 (90%), did not change CH_4 , and increased N_2O (280%). Adding organic acids to slurry with a Perlite cover improved the reductions of CH_4 and N_2O (Table 1, Berg and Pázsiczki, 2006; Berg et al., 2006). On farm storages, Pegülit R reduced odor (30%) and NH_3 (63%), while an improved formulation Pegülit M performed better at reducing odor (93%) and NH_3 (91%) (table 1; Hörnig et al., 1999).

VEGETABLE OIL

Vegetable oil is buoyant and distributes itself across the manure surface. It is biodegradable and can safely be land-applied in small amounts. Thus it does not require special application equipment, nor pose a risk of damaging manure handling equipment. It is a candidate for slurry stored under slats within livestock buildings because excrement can pass through the oil layer from above (Pahl et al., 2002). Vegetable oil can also be added to other cover materials to enhance buoyancy. Establishing a uniform oil layer across the entire slurry surface is critical (Sommer et al., 1993; Pahl et al., 2002). Derikx and Aarnink (1993) found pig slurry had a smooth surface and required half as much oil to achieve the same NH_3 reduction as cattle slurry with a rough surface. Adding water or rainfall after oil application helps form a uniform layer (Pahl et al., 2002). Odor and GHG emission data suggest that the effect of oil changes with time, and it begins to degrade after at least one week. This is confirmed by visible changes in the oil layer after ~ 25 d (Pahl et al., 2002). Summarizing the effects of vegetable oil on emissions detailed in table 1:

- Good odor reduction was observed in a short-term study (Guarino et al., 2006), but in longer studies oil degraded and produced foul odors described as an “overpowering foul rancid odour” (Pahl et al., 2002; Williams, 2003) and a “distinctly offensive non-swine odor” (Clanton et al., 1999). Vegetable oil covers cannot be recommended unless this problem is resolved.
- Short-term reduction of NH_3 emissions were generally >90% (Derikx and Aarnink, 1993; Sommer et al., 1993; Pahl et al., 2002; Portejoie et al., 2003; Guarino et al., 2006). However, long term (>30 d) reductions have been lower and less consistent, probably due to oil degradation (Sommer et al., 1993; Hörnig et al., 1999; Pahl et al., 2002). Thicker layers perform best (Pahl et al., 2002). After repeated mixing, a 6 mm layer still reduced NH_3 emissions by $\sim 85\%$ (Hörnig et al., 1999).
- Short-term reductions of CO_2 and CH_4 have been observed (Guarino et al., 2006), but a longer study found CH_4 emission increased up to 189% due to enhanced biodegradation (Pahl et al., 2002).

AERATION FOAM

By pumping slurry through an aspirator and injector, a foam film (comprised of air bubbles and manure) can be created on the surface. Unlike aeration methods (e.g. Zhu, 1998) the slurry oxygen status is unaltered. This provides an inexpensive cover that is not an issue during homogenization

or field application. Bundy et al. (1997) maintained a foam cover by operating a pump for 5 min every 3 d. Bubbling air through solids at the bottom of the tank enhanced foam resilience. Odor detection threshold was reduced by >90%. Despite trying several aeration frequencies and durations, Pahl et al. (2002) had difficulty maintaining an effective foam layer on pig slurry with only 1.5% DM. They found NH₃ emissions were reduced by 20 to 44%. It seems this technique requires a minimum DM to maintain effective foam. Further research should identify which slurry types it works with, assess the effects on other gases, and its field-scale feasibility. Aeration foam may be useful below slatted floors, where other covers are difficult to apply.

COVERS OF SYNTHETIC ORIGIN

Synthetic covers are selected for durability and buoyancy. Although cover design often differs, there are three general groups: (i) permeable synthetic covers, (ii) impermeable synthetic covers, and (iii) petroleum-based oil.

PERMEABLE SYNTHETIC COVERS

Foam and Fabric

These covers allow water and air to pass through. Materials have been used alone and in combination, including geotextile, polyester, polystyrene foam, polypropylene foam, and polyethylene fiber. Most materials are inherently permeable, some need to be perforated. Advantages include reliable floatation and resistance to degradation. Effective covers are thick enough that gases pass through with adequate contact time to undergo aerobic breakdown (Miner et al., 2003). When covers are too thin or perforations are too large, gases can pass through rapidly without adequate breakdown (Miner and Suh, 1997). Biomass growth on the cover has been observed to decrease permeability (bio-plugging) and diminish performance by forcing gases to travel around the cover, escaping to the atmosphere at the edges (Clanton et al., 2001). Summarizing the effects of these covers on emissions detailed in Table 1:

- Reductions of odor and H₂S were generally >50% (Clanton et al., 1999; Bicudo et al., 2002, 2004; Sheffield and Thompson, 2004; Hudson et al., 2006b). Thicker covers tend to perform best, but a comparison found no statistically significant difference (Clanton et al., 2001). Reduction of H₂S emissions improved with time in one study (Zahn et al., 2001) but decreased in another (Bicudo et al., 2002, 2004).
- Effects on NH₃ emissions range from reductions (e.g. Miner et al., 2003; Portejoie et al., 2003) to increases (Clanton et al., 2001). Decreased efficacy over time was observed in the laboratory (Clanton et al., 2001) and field (Bicudo et al., 2002, 2004), possibly due to bio-plugging. In contrast, Miner et al. (2003) and Zahn et al. (2001) found efficacy improved with time, possibly due to aerobic microbial activity in the covers. These conflicting results might be explained by an initial performance improvement as aerobic microorganisms become established, followed by decreased performance due to bio-plugging.
- Increased emission of CH₄ (up to 30%) was observed by Zahn et al. (2001). Emissions increased with time and

were correlated with biomass growth. More research on GHGs is needed.

Plastic Granules

Two types of plastic granules have been examined: high density and low density. High density granules float on the slurry but are not substantially affected by wind. Low density granules are made of polystyrene or hollow plastic (often designed for insulation and packaging) and can be unevenly distributed or blown away by wind. For these reasons, Williams (2003) considered low density materials unsuitable. Williams et al. (1998) tested high density 5-cm plastic balls and found NH₃ reductions of 50% for cattle and 60% for pig slurry. Hudson et al. (2001, 2006a) tested low density polystyrene beads and found they performed as well as the other covers tested for reducing odor emissions and provided the best reduction of CO₂.

Rubber Granules

Finely ground rubber granules from recycled tires were tested in both laboratory and field settings (Koppolu et al., 2005). After 6 weeks in the laboratory some covers showed signs of degradation and were <75% intact. In the field however, the cover surface hardened and was durable for >4 months. In the field, consistent reductions of odor (up to 96%), H₂S (>99%), and NH₃ (up to 99%) were observed. Laboratory performance was variable and not as good, particularly for NH₃ where both reductions and increases were observed. Further research to provide verification and data on GHG emissions, longer-term durability, and the environmental impacts if this material is land-applied would be useful.

Hydrophobic Powder

Sakamoto et al. (2006) made a hydrophobic powder by mixing ammonium phosphate, ammonium sulfate, and hydrophobic silica. The floating powder forms a cover with high adsorption capacity. It adds nutrients and is safe to land-apply. Durability may be an issue since some dissolution was observed in the 13-d study. The cover generally reduced emissions of H₂S, NH₃, and CH₄ very well. One exception was that NH₃ emissions were not reduced from dairy slurry because emissions from the uncovered slurry were unusually low. These results should be confirmed by longer field-scale studies.

IMPERMEABLE SYNTHETIC COVERS

These covers inhibit water and air movement and have been made of PVC, foil, foam, and plastic. They reduce the emitting surface and trap gases beneath the cover. If the entire storage is covered, vents are needed to avoid pressurization from biogas (Sommer et al., 1993). Precipitation is typically kept above the cover, reducing slurry volume and transport cost, but water removal is needed to prevent damage. Wind damage has been observed with plastic bubble film (windspeed >3.5 m s⁻¹) and polystyrene sheets (windspeed >6.5 m s⁻¹) (Williams, 2003). Summarizing the effects of these covers on emissions detailed in table 1:

- Odor emission data are limited and results are inconsistent. Reductions were <50% in one study (De Bode, 1991), but between 59% and 80% in the other

(Clanton et al., 1999). Only one study evaluated H₂S, finding its concentration was usually reduced by ~90% (Clanton et al., 1999).

- There is consistent evidence that NH₃ loss is reduced >90% by plastic film covers that are secured at the edges of a storage (Sommer et al., 1993; Hörnig et al., 1999; Portejoie et al., 2003). Lower reductions have been observed in winter and using materials that do not cover the entire storage surface (DeBode, 1991; Miner et al., 2003).
- Effects on GHGs have not been reported.

PETROLEUM-BASED OIL

Petroleum-based oil shares many properties with vegetable oil, but has the advantage of being less expensive and waste oil is often available on-farm. Its use has been questioned due to potential negative impacts if land-applied (Williams 2003). Filson et al. (1996) found it enhanced straw covers and recommended investigating it because it was inexpensive. Modest odor reductions of <30% have been observed (Meyer and Converse, 1982). Better reductions of H₂S (~75%), and NH₃ (>75%) have been seen (Meyer and Converse, 1982; Derikx and Aarnink, 1993). No data on GHGs are available, though it could be expected to increase hydrocarbon emissions.

COMPOSITE COVERS

Composite covers attempt to combine the best aspects of multiple materials. This often involves using synthetic material to enhance floatation and durability of inexpensive natural material. For example, adding oil to straw, placing straw on geotextile, or peat on polystyrene. Studies on composite covers have generally used low DM manure (usually swine), where additional buoyancy is most useful. Evidence has confirmed that straw is more durable when supported by floats (Hudson et al., 2006b). Filson et al. (1996) estimated that adding oil to the first layer of straw doubled floatation time and was preferable to polystyrene or plastic bottles. For efficiency, they integrated oil addition with the straw applicator.

Are composites better than either of their components alone? In some cases composites performed better (e.g. Portejoie et al., 2003), while other studies found no advantage (e.g. Hudson et al., 2001, 2006a, b). Clanton et al. (2001) found performance of geotextile covers decreased over time (due to bio-plugging), but geotextile + straw composites performed more consistently. They hypothesized that the weight and irregular shape of straw caused the underside of the geotextile to be rough, slowing lateral movement of gas bubbles and favoring vertical movement through the cover.

Materials that do not affect buoyancy have also been used in composite covers. These include plants, chemical additives, and adsorbents. Plants have been added intentionally (Picot et al., 2001), and have grown spontaneously (Hudson et al., 2006b). There is some evidence that the plants help reduce emissions (Picot et al., 2001). Furthermore, it is possible that plants can be used to create self-renewing covers – a subject that has been explored for nutrient removal (Hubbard et al., 2004) and constructed wetlands (Hunt et al., 2007), but not emission reduction on

manure storages. Chemical additives including Fe³⁺ (Picot et al., 2001) and acidification agents (Berg et al., 2006) have been used with some success. Peat supplemented with Fe³⁺ improved H₂S emission reduction by forming insoluble ferrous sulfide (Picot et al., 2001). Adding lactic acid or saccharose decreased slurry pH and reduced CH₄ and N₂O production in some treatments, leading to reduced emissions from the covered slurries (Berg et al., 2006). Adsorbent materials like Zeolite have improved NH₃ performance (Miner et al., 2003). Zeolite has also performed well on its own, but ~10× more material was needed to achieve similar NH₃ reduction (compare Miner et al., 2003 vs. Portejoie et al., 2003). Thus, the benefits of Zeolites may be realized more economically when part of a composite. Summarizing the effects of composite covers on emissions detailed in table 1:

- Odor and H₂S emissions have generally been reduced >80% (Clanton et al., 1999; Picot et al., 2001; Hudson et al., 2006a, b), but this was not always better than simpler covers (Clanton et al., 2001; Hudson et al., 2006a,b). For odor and H₂S reduction, the best covers tested by Meyer and Converse (1982) were composites. Unlike when oil has been used alone, foul odors have not been observed when oil was mixed with straw.
- For NH₃ reduction, the best covers tested by Meyer and Converse (1982) were composites. Peat supported by polystyrene reduced NH₃ ~100% (Portejoie et al., 2003). To achieve similar results without polystyrene required twice as much peat. Permeable foam + Zeolite covers reduced NH₃ emission >80% (Miner et al., 2003). Though better than an uncovered control, acidification generally increased emissions of NH₃ compared to the same cover without acidification (Berg et al., 2006).
- Hudson et al. (2006a) found a barley straw + polyethylene composite provided a small CO₂ reduction and CH₄ emissions were unaffected. Other straw types increased CO₂ emissions. Berg et al. (2006) found CH₄ concentrations were generally reduced, and lactic acid composites performed best.

MECHANISMS OF COVER OPERATION

Understanding how covers function is paramount in developing reliable technology. The first step is to understand how gases are emitted. Emissions are the net result of gas production, consumption, storage, and transport. For most of the gases considered in this article, production is driven by anaerobic microorganisms, and consumption is driven by aerobic microorganisms and chemical equilibria or immobilization (table 2). Covers may affect gas production by changing slurry pH and equilibria; however these effects may be limited since the bulk manure remains anaerobic. Gas consumption may be enhanced by permeable covers that provide an aerobic layer at the storage surface. Nevertheless, the process probably most affected by covers is transport, which is reduced, leading to increased storage in the liquid phase.

MASS TRANSFER

Gas transport between liquid and air occurs according to the principles of mass transfer, and is driven by a concentration gradient:

$$Q = A \times k_c \times \Delta C \quad (1)$$

where Q is the emission rate (mol s^{-1}), A is the emitting surface area (m^2), k_c is the mass transfer coefficient (m s^{-1}), and ΔC is the concentration difference between the bulk liquid and bulk air phases (mol m^{-3}). This process can be described by the two-film theory, which states that when a dissolved gas moves between the bulk liquid and air phases it must move across two thin films at the air-water interface: a liquid-film and a gas-film (Macintyre et al., 1995; Basmadjian, 2007). These films are very thin and each provides a resistance to mass transfer. The resistances are additive and together they give the overall resistance to mass transfer ($1/k_c$, s m^{-1}):

$$\frac{1}{k_c} = \frac{1}{k_l} + \frac{1}{k_g} \quad (2)$$

where $1/k_l$ is the resistance in the liquid-film, and $1/k_g$ is the resistance in the gas-film (Basmadjian, 2007). The dominant resistance term depends largely on the solubility of the gas being considered. Transport of soluble gases is limited primarily by gas-film resistance (i.e. $1/k_c \approx 1/k_g$), whereas slightly-soluble gases are limited primarily by liquid-film resistance (i.e. $1/k_c \approx 1/k_l$) (Macintyre et al., 1995; Basmadjian, 2007). When a membrane is placed at the air-liquid interface, another resistance term is added, giving an overall resistance of:

$$\frac{1}{k_c} = \frac{1}{k_l} + \frac{1}{k_g} + \frac{L}{D_m} \quad (3)$$

where the resistance provided by the membrane is a function of its thickness (L , m) and its diffusivity (D_m , $\text{m}^2 \text{s}^{-1}$) (Basmadjian, 2007). Based on these principles of mass transfer, we can discuss the effect of floating covers on gas emissions.

EFFECTS OF SOLUBILITY AND COVERS ON MASS TRANSFER

Let us first consider factors specific to soluble gases (table 2) where emissions are limited primarily by the gas-film. Transport across the gas-film or boundary layer occurs by diffusion and turbulent transport. Of these, turbulent transport is generally several orders of magnitude greater (Basmadjian, 2007). Thus, factors that increase turbulence will reduce gas-film resistance and increase transport. This happens when the surface conditions are unstable because of surface heating and wind. Floating covers can therefore reduce emissions by reducing surface heating (e.g. by insulation or a high albedo) and wind at the surface. These principles agree with data on NH_3 (Olesen and Sommer, 1993; Arogo, 1999b; Ni, 1999) and H_2S (Arogo et al., 1999a) where emissions from manure storages were a function of air velocity at the surface and the temperature difference between the surface and the air above. These principles also generally agree with the results shown in table 1, where most covers effectively reduced NH_3 and H_2S , which would be expected since most covers should provide some reduction of surface air speed, and many provide some insulation. Poor performance was generally limited to NH_3 emissions from geotextile-covered storages when fluxes were measured using a wind tunnel (Clanton et al., 2001; Bicudo et al., 2002, 2004). This makes sense since the

geotextiles used were thin (little effect on surface wind) and dark (low surface albedo).

Next let us consider factors specific to slightly soluble gases (table 2) where emissions are limited primarily by the liquid film. Transport across the aqueous boundary layer occurs by diffusion, turbulence, and ebullition. The rate of diffusion depends on the concentration gradient in the aqueous boundary layer and is generally slow. The concentration gradient depends on the biological and chemical sources or sinks of a particular gas, and the transport of the dissolved gas from deeper areas to the boundary layer. Turbulence is important for transport across larger distances and occurs when eddies form that move liquids and dissolved gases to, and within, the boundary layer. This replenishes the concentration in the boundary layer and helps drive diffusion. Turbulent eddies are created primarily by surface stress (usually caused by wind, but potentially caused by experimental equipment such as flux chambers), differential heating, and convective surface heat loss. The latter two factors are particularly important when wind stress is low. For example, it has been reported that when windspeed is moderate (less than $\sim 3 \text{ m s}^{-1}$) gas transfer from water was up to 30% higher during evaporative conditions than condensing conditions (Macintyre et al., 1995). Ebullition provides a transport pathway that bypasses the aqueous boundary layer. It is especially important for CH_4 which has a very low solubility, but has wider implications because bubbles can strip other gases from the liquid and carry them to the surface. Ebullition becomes important when methanogenesis exceeds diffusive loss. In some aquatic environments without plants, ebullition accounts for over 50% of CH_4 emissions (Chanton and Whiting, 1995). It is not known how important this role is in gas transport within liquid manure storages, but anecdotal observation of bubbles suggests it may be large. How might floating covers reduce the emission of slightly-soluble gases? First, covers can reduce diffusion by providing a physical barrier or providing biological and chemical sinks that lower the concentration gradient. Second, covers can reduce turbulent transport in the liquid by minimizing convective heat loss, differential heating, and wind stress. Third, covers can reduce ebullition by stopping bubbles before they reach the surface and in permeable covers, forcing gases to travel by diffusion through the aqueous boundary layer. As shown in table 1, most studies found permeable covers increased or had little effect on CO_2 and CH_4 emissions, suggesting they are not very effective against slightly soluble gases. Large emission increases were observed when materials were used that add carbon (e.g. corn stalks, sugar cane, straw, and oil) and thereby provide more substrate for gas production and increase the concentration gradient. The largest reductions were generally found when gas production was decreased by adding lactic acid, and in short laboratory studies (<2 weeks) where ebullition may have been low because methanogenesis had not yet exceeded diffusive transport.

Let us now consider other factors related to cover function. All covers decrease A and should therefore reduce Q unless the concentration gradient between the remaining exposed area and the air increases. Gas solubility is temperature dependent and therefore if a cover can reduce the temperature in the manure it will increase solubility and allow more gas storage in the bulk liquid phase. Cover materials can change the surface pH (Xue et al., 1999;

Table 2. Properties of important gases emitted from covered liquid manure storages.

Gas	Density		Solubility		Conditions for Production (P) or Consumption (C)	Some Important General Reactions or Equilibria ^[c]
	Specific Density ^[a]	vs. Air	K ^o _H Range ^[b]	Qualitative Scale		
CH ₄ (Methane)	0.55	Lighter	9.7×10 ⁻⁴ to 9.2×10 ⁻³	Very slightly soluble	P: Anaerobic (E _H < -150 mV) ^[d] C: Aerobic	OM → acetate → CH ₄ CO ₂ → CH ₄ ^{[e],[f]} CH ₄ → CO ₂ , Org-C ^[e]
CO ₂ (Carbon Dioxide)	1.52	Heavier	3.1×10 ⁻² to 4.5×10 ⁻²	Slightly soluble	P: Anaerobic or aerobic C: Photosynthesis	OM → CO ₂ CO ₂ ↔ H ₂ CO ₃ , HCO ₃ ⁻ ^[g] CO ₂ → Org-C
N ₂ O (Nitrous Oxide)	1.52	Heavier	2.4×10 ⁻² to 2.6×10 ⁻²	Slightly soluble	P: Somewhat aerobic (E _H > +180 mV) ^[d] C: Somewhat anaerobic	NH ₄ ⁺ + Org-C → N ₂ O NO ₃ ⁻ + C → N ₂ O ^[e] N ₂ O + Org-C → N ₂ ^[e]
NH ₃ (Ammonia)	0.59	Lighter	10 to 78	Very Soluble	P: Anaerobic C: Aerobic	OM → →NH ₃ (slow) ^[h] Urea → NH ₄ ⁺ NH ₃ ↔ NH ₄ ⁺ , pKa ≈ 9.2 ^[f] NH ₄ ⁺ → →N ₂ NH ₄ ⁺ → NO ₃ ⁻ NH ₄ ⁺ → OM (rapid) ^[h]
H ₂ S (Hydrogen Sulfide)	1.18	Heavier	1.0×10 ⁻³ to 1.0×10 ⁻¹ * (* high agreement)	Somewhat soluble	P: Anaerobic C: Aerobic	OM → →H ₂ S SO ₄ ²⁻ + OM → H ₂ S H ₂ S → HS ⁻ , pKa ≈ 7.0 ^[i] H ₂ S → Org-S H ₂ S + Fe ₃ ⁺ → FeS or FeS ₂ ^[j]
CH ₃ COOH (Acetic acid)	2.07	Heavier	820 to 10000	Very Soluble	P: Anaerobic C: Anaerobic Aerobic	OM → →VFAs, VOCs ^[f] VFAs, VOCs → microbial cells → CO ₂ , CH ₄ VFAs, VOCs → microbial cells → CO ₂ ^[f]
C ₁₁ H ₂₄ (Undecane)	5.39	Heavier	5.6×10 ⁻⁵ to 5.4×10 ⁻⁴	Very slightly soluble	“	“
C ₁₂ H ₂₆ (Dodecane)	5.88	Heavier	1.4×10 ⁻⁴	Very slightly soluble	“	“

[a] Density of the gas/Density of air; air = 1.00.

[b] Henry's Law constant for solubility in water at 298.15 K, mol kg⁻¹ bar⁻¹ (Sander, 1999; NIST, 2005).

[c] This is not meant to be a comprehensive list. OM = Organic Matter; Org-C = Organic Carbon; VFA = Volatile Fatty Acid; VOC = Volatile Organic Compound.

[d] Redox potential for CH₄ and N₂O production in a flooded soil suspension (Yu and Patrick, 2004).

[e] Davidson and Schimel, 1995.

[f] Mackie et al., 1998.

[g] Macintyre et al., 1995.

[h] Sommer et al., 2003.

[i] Clanton and Schmidt, 2000; Yongsiri et al., 2005.

[j] Picot et al., 2001.

Portejoie et al., 2003), which affects the equilibria of some gases (table 2, e.g. NH₃/NH₄⁺) and can increase or decrease ΔC accordingly. Adsorbents or other binding agents can also decrease ΔC. Resistance provided by the cover is a function of L and D_m. Experimental results generally show that increasing cover thickness improves emission reduction, which agrees with this principle. Impermeable covers have a D_m ≈ 0 and therefore reduce mass transfer to near zero. Observations reflect this, with most impermeable covers providing high reductions (table 1). However, this causes the gases to build up below the cover (increased storage) and unless this causes a feedback to decrease production or increase consumption, emission reductions will be

temporary. Once the resistance is removed (e.g. cover removed or manure pumped out), the gas storage will be depleted rapidly by transport to the atmosphere driven by the high concentration gradient. This emphasizes the need for covers to either provide a sink or to reduce production in order to give lasting benefits.

MICROBIAL CONSUMPTION

This brings us to a discussion of the potential for microbial gas consumption in permeable covers or crusts. Questions have been raised about whether microbial consumption is overstated (Hudson et al., 2006a). If it is important, one would expect evidence of improved performance with time

as microbial populations develop. This has been seen in some instances (Miner et al., 2003), but in others cover efficacy diminished with time (Hudson et al., 2006a). In contrast, it has repeatedly been observed that emission reductions begin immediately after cover installation, suggesting resistance to transport is the dominant factor (Koppolu et al., 2005; Hudson et al., 2006a). While that may be true, there is evidence that microorganisms consume CH₄ in natural crusts and straw covers (Ambus and Petersen, 2005; Petersen et al., 2005; Petersen and Ambus, 2006). Furthermore, nitrification and denitrification have been quantified in permeable covers (Miller and Baumgartner, 2007), and the presence of microbes capable of catabolizing H₂S, NH₃, and CH₄ has been observed in a permeable foam cover (Miner et al., 2003). Such activity has not been found in all materials, for example no CH₄ consumption was found in Leca[®] covers (Ambus and Petersen, 2005; Petersen and Ambus, 2006). As discussed earlier, there is also evidence that microbial growth can lower cover performance due to bio-plugging (Clanton et al., 1999) and increased CH₄ emissions (Zahn et al., 2001). Quantifying reaction kinetics and consumption rates, and improving them are important areas for future study as this is a means of providing lasting emission reductions.

CONSIDERATIONS FOR ODOR AND N₂O

Odors are complex and are comprised of many gas constituents that fall into both soluble and slightly-soluble categories. In addition to H₂S and NH₃, other odorants such as volatile organic compounds (VOCs) have been measured from covered storages. For example, Bicudo et al. (2001, 2004) measured at least 10 VOCs including acetic acid, undecane, and dodecane. Of these, some are soluble while others are only slightly-soluble (table 2). Thus, overall odor emissions are affected by both soluble and slightly-soluble gas transport mechanisms. On one hand, this means ideal covers must provide both gas-film and liquid-film resistance to achieve maximum odor reductions. On the other hand, it means most covers will probably decrease odor emissions by reducing transport of a subset of the odor constituents. As shown in table 1, all cover types reduced odors, often by >50%.

Emission of N₂O is unique among the gases explored here because it is primarily produced by bacteria that do not live in anaerobic environments (Davidson and Schimel, 1995). As such, it is unlikely to be produced in manure storages unless a crust or permeable cover is present. These floating materials provide a place for N₂O producing bacteria to live that is nutrient rich and somewhat aerobic. Production is sensitive to O₂ status – maximum production by nitrifying bacteria occurs when there is enough O₂ for NH₄⁺ oxidation, but O₂ must be limiting for N₂O to be a significant end product. Similarly for denitrifying bacteria, maximum production occurs when O₂ is limited enough to promote NO₃⁻ reduction but not low enough to promote N₂O reduction (Davidson and Schimel, 1995). Given these delicate O₂ requirements, it is not surprising to find that N₂O emissions are affected by the moisture status of a crust or cover. Studies found N₂O emissions occurred when a crust or permeable cover was dry and were suppressed by precipitation (Sommer et al., 2000; Berg and Pazsiczki, 2006). Ideally, both covered and uncovered storages should emit no N₂O. However, when uncovered storages form a

crust and produce N₂O a cover may provide an emission reduction. As shown in table 1, the only cover that reduced N₂O emission was Pegulit[™] + Saccharose in a study where a crust formed on the control (Berg and Pazsiczki, 2006).

EXPERIMENTAL APPROACHES

Obtaining reliable emissions information from livestock waste facilities is challenging. Jungbluth et al. (2001) drew a distinction between “data” and “reliable data,” and summarized requirements for collecting reliable data at livestock facilities as: (i) continuous measurement of ventilation rates and gas concentrations, (ii) long-term experiments, to cover diurnal and seasonal effects, (iii) simultaneous measurement of multiple gases, and (iv) sampling area as large as possible. These targets are useful when studying manure storage covers. Meeting those targets present logistical, technical, and cost challenges – often at the expense of replication. Most studies on manure storage covers do not meet these targets but future research should strive to, especially for developing emission factors for covered manure storages.

It is important to define study objectives to determine whether only measuring concentration is acceptable. Fluxes should be measured whenever possible since they are essential for determining environmental impacts. When measuring fluxes, the influence of the method should be identified and discussed in the context of the mechanisms of gas emissions and cover operation. For example, laboratory-scale studies enable replication and the assessment of relative effects, but are unrepresentative of actual manure storages for many reasons including lack of exposure to the physical environment, and changing manure characteristics. Such conditions are certain to alter emission rates. Many studies used static chambers and flow-through headspaces where the surface is not exposed to solar heating and windspeed is low. Such conditions produce a large air boundary layer where turbulent transport is low (in such instances it is possible that gas density may affect transport; table 2). To provide a more realistic assessment, studies should assess cover efficacy when they are exposed to a range of windspeeds (Olesen and Sommer, 1993). Only a few studies have assessed cover performance under field conditions with the surfaces exposed to natural wind and energy balance (Sommer, 1997; Zahn et al., 2001). Recommendations for future experimental approaches include:

- Short-term laboratory studies are probably best suited to measuring effects on transport of gases that are already abundant in the manure (e.g. NH₃). Assessing effects on gases that are largely produced microbially while in storage (e.g. CO₂, CH₄, and N₂O) are best studied in longer experiments.
- Laboratory studies should focus on mechanisms of operation. Measuring how mass transfer coefficients are affected by covers and how they change with time and other factors would be ideal (e.g. Olesen and Sommer, 1993; Xue et al., 1999).
- Conditions of all control manure storages/containers should be clearly described. In particular, any crust that develops on the controls should be described and quantified. Studies have found cover efficacy was highest

at facilities where crusts did not develop on the control lagoon (Bicudo et al., 2002, 2004). This is presumably because natural crusts also reduced the gas emissions.

- When reductions are calculated in comparison to the same storage before cover installation this should be clearly stated and possible limitations discussed.
- Estimating emissions based on changes in manure chemistry over time has had limited success, and was deemed unreliable for odor and VOCs (Bicudo et al., 2002, 2004).
- Experiments that assess cover performance under surface conditions (water balance, energy balance, wind-speed) that are representative of on-farm conditions will provide the most meaningful results.

CONCLUSIONS AND FURTHER WORK

Considerable progress has been made in demonstrating that floating covers can reduce gas emissions from liquid manure storages. Studies have assessed a variety of cover types for effects on odor, H₂S, NH₃, and GHGs (table 1). Straw, vegetable oil, impermeable films, and expanded clays have been studied the most frequently. In terms of gases, odors and NH₃ have been monitored the most, and GHGs the least. Ammonia has been reduced the most effectively and consistently by the covers tested. When installed properly (e.g. adequate cover thickness), many cover materials can reduce NH₃ emissions by over 70%. Odors have been controlled moderately well (~40% to ~90%) by most covers, and reductions of H₂S were usually higher and more consistent. Notable exceptions are impermeable films, where it has been hypothesized that odor escapes around the edges of the covers, and vegetable oil, which can develop a displeasing odor. Strategies to optimize odor reductions and maintain them would be useful for managing odor nuisance issues. Information on GHG emissions is limited, and completely lacking for many cover types. Few studies have assessed odor, H₂S, NH₃, and GHGs simultaneously, and no study has done this in an outdoor experiment. Future research should continue to investigate new ideas (e.g. composite covers), new materials, and combining covers with other treatments. Adding to the existing data will be useful, particularly with respect to:

- Characterizing the mechanisms controlling cover function (e.g. calculating mass transfer coefficients with and without a cover; measuring cover efficacy at different windspeeds).
- Understanding, quantifying and optimizing the role of microbial activity (Petersen and Miller, 2006).
- Enhancing the ability of covers to act as a gas sink, or to decrease gas production.
- Identifying the extent to which covers delay emissions by trapping slightly-soluble gases in the slurry (e.g. measuring emissions during agitation).
- Simultaneously quantifying the effects on emissions of odor, H₂S, NH₃, and GHGs.
- Weighing the trade-off between odor and GHGs that has been observed.
- Improving on-farm use of covers such as installation and maintenance.
- Producing “reliable data” that has the potential to be widely utilized.

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PERMEABLE SYNTHETIC COVERS FOR CONTROLLING EMISSIONS FROM LIQUID DAIRY MANURE

A. C. VanderZaag, R. J. Gordon, R. C. Jamieson, D. L. Burton, G. W. Stratton

ABSTRACT. *Liquid manure storages emit greenhouse gases (GHGs) and ammonia (NH₃), which can have negative effects in the atmosphere and ecosystems. Installing a floating cover on liquid manure storages is one approach for reducing emissions. In this study, a permeable synthetic cover (Biocap™) was tested continuously for 165-d (undisturbed storage + 3-d agitation) in Nova Scotia, Canada. Covers were installed on three tanks of batch-loaded dairy manure (1.3 m depth × 6.6 m² each), while three identical tanks remained uncovered (controls). Fluxes were measured using steady-state chambers. Methane (CH₄), carbon dioxide (CO₂), and nitrous oxide (N₂O) were measured by absorption spectroscopy, and NH₃ was measured using acid traps. Results showed covered tanks consistently reduced NH₃ fluxes by approximately 90%, even though a surface crust formed on controls after about 50 days. Covers continued to reduce NH₃ flux during agitation. Covered tanks also emitted significantly less CO₂ and N₂O than the controls (p-value <0.01). However, CH₄ fluxes were not reduced, and therefore overall GHG fluxes were not substantially reduced. Short-term trends in CH₄, CO₂, and N₂O flux provided insight into cover function. Notably, bubble fluxes were a key component of CH₄ emissions in both treatments, suggesting the covers did not impede CH₄ transport.*

Keywords. *Air quality, Emissions, Floating cover, Liquid manure storage.*

In many livestock production systems, manure is handled as a liquid and stored in tanks or lagoons until land-applied. These storage systems emit greenhouse gases (GHGs) including methane (CH₄), carbon dioxide (CO₂), and nitrous oxide (N₂O) (van der Meer, 2008), and ammonia (NH₃) (McGinn et al., 2008). Reducing emissions is important for addressing environmental concerns and for improving agricultural carbon (C) and nitrogen (N) conservation. Installing floating covers on stored liquid manure is one way some producers are trying to achieve this environmental goal. Covers are intended to provide a resistance to gas mass transfer from liquid to air, and to function as a biofilter (Miner and Suh, 1997), whereby microorganisms convert undesirable gases into more innocuous forms. Covers can be added to existing farm-infrastructure, and therefore have potential to be widely used. Synthetic covers are durable and unlike natural covers such as straw, do not impede pumping of the slurry. Permeable materials allow precipitation to seep through, eliminating the need for water removal on the cover. Permeable geotextile covers also have relatively low capital

costs compared to some other permeable materials and impermeable covers (Nicolai et al., 2004).

A recent review (VanderZaag et al., 2008) identified that information about the effect of permeable synthetic covers on GHG emissions from manure storages was limited to a single study (Zahn et al., 2001). Furthermore, effects on NH₃ emissions were uncertain because some studies found NH₃ emissions were reduced (Miner et al., 2003; Portejoie et al., 2003), while others observed increased emissions (Clanton et al., 2001). Efficacy changes with time were also unclear, improving in some studies (Zahn et al., 2001; Miner et al., 2003) but worsening in others (Clanton et al., 2001; Bicudo et al., 2004). Whether gases are temporarily trapped in the liquid and subsequently released during agitation remains unclear (Bicudo et al., 2001).

Therefore, this study was conducted to assess the effect of a permeable synthetic cover (Biocap™) on GHG and NH₃ fluxes from stored liquid dairy manure. A research approach was chosen that exposes manure and covers to environmental conditions and agitation while allowing replication and frequent flux measurements. The specific objectives were to: (i) determine changes in CO₂, CH₄, N₂O, and NH₃ fluxes, (ii) characterize the effect of agitation, and (iii) evaluate short-term (minutes – hours) and long-term (days – months) flux trends.

METHODS

SITE DESCRIPTION

Liquid dairy manure was stored in six concrete tanks (surface area of 6.6 m² each, fig. 1a, b) at the Nova Scotia Agricultural College (NSAC) in Truro, Nova Scotia, Canada. Fresh manure from the NSAC dairy unit was loaded into the tanks to 1.3 m-depth (8.6 m³) on 6 May 2008. No additional manure was added during the study. The next day, floating

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The authors are **Andrew C. VanderZaag**, ASABE Member Engineer, Graduate Student, Process Eng. and Applied Sci. (PEAS), Dalhousie Univ., Halifax, Nova Scotia, Canada; **Rob J. Gordon**, Associate Professor and Dean, Ontario Agricultural College, University of Guelph, Guelph, Ontario, Canada; **Rob C. Jamieson**, Assistant Professor, Process Eng. and Applied Sci. (PEAS), Dalhousie Univ., Halifax, Nova Scotia, Canada; **David L. Burton**, Professor, and **Glenn W. Stratton**, Professor, Department of Environmental Science, Nova Scotia Agricultural College (NSAC), Truro, NS, Canada. **Corresponding author:** Andrew C. VanderZaag, Process Eng. and Applied Sci. (PEAS), Dalhousie Univ., Halifax, Nova Scotia, Canada; phone: 902-494-6791; fax: 902-893-0335; e-mail: a.vanderzaag@dal.ca.

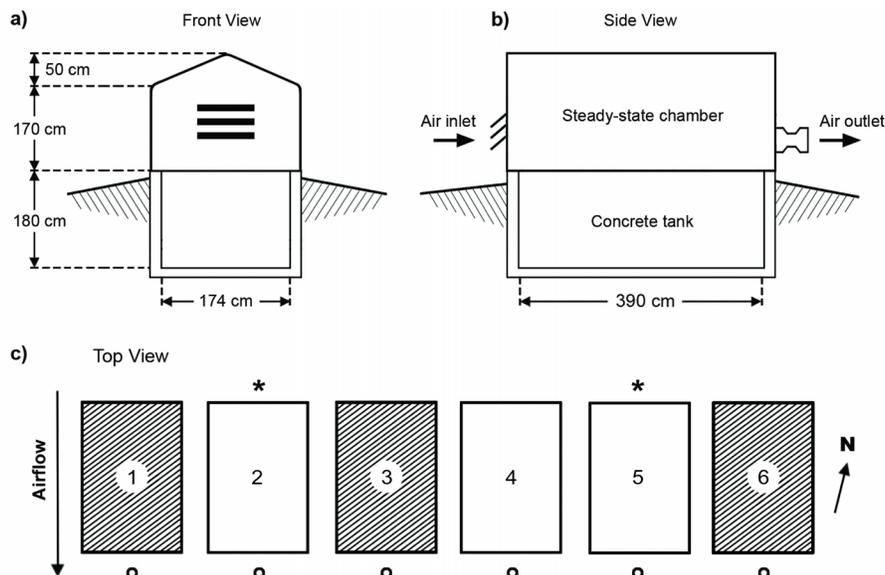


Figure 1. Diagram of the research site showing a cross-section of one manure storage tank and steady-state chamber from the front (a) and side (b), and a top view (c) of all six tanks indicating inlet (*) and outlet (o) air sampling locations. Tanks with BioCap™ covers are shaded, and control tanks are unshaded. All tanks were agitated at the end of the study. The space between tanks was 120 cm.

covers were installed in three tanks (fig. 1c). Commercially available Biocap™ covers (Baumgartner Environics, Olivia, Minn.) were used. These are a composite of approximately 1-mm acrylic-polyester geotextile-fabric adhered to 18 mm of permeable polyethylene foam (recycled, cross-linked closed cell foam). The covers were custom-made to fit tightly, and each had a small removable section (0.12 m²) to allow access for manure sampling and agitation. The other three tanks were controls, which did not receive a synthetic cover, but were allowed to develop a natural crust.

Flux monitoring was conducted from 12 May through 28 October 2008 using steady-state chambers that exclude precipitation. To maintain an approximately neutral water balance (precipitation = evaporation) and provide a surface disturbance similar to rainfall, sprinklers inside each chamber were operated twice per week (30 mm wk⁻¹) through August, and once per week thereafter (15 mm wk⁻¹). A flow meter was used to ensure all tanks received the correct amount of water. Water was taken from a groundwater well (pH 7.9, nitrate-N <2.3 mg L⁻¹, Fe <0.02 mg L⁻¹, Mn < 0.02 mg L⁻¹, sulfate 43 mg L⁻¹). To monitor the water balance, freeboard was measured continuously in tank 3 (covered) and tank 4 (control) using SR50 sonic ranging sensors [Campbell Scientific (Canada) Corp., Edmonton, AB], and confirmed by manual measurements in all tanks.

Manure was agitated at the end of the study using three remote-controlled electric trolling motors (25-kg thrust, providing up to 70-W m⁻³ manure; Johnson Outdoors Inc., Racine, Wis.). First, tank-pairs were agitated intermittently for 8 h per day on three consecutive days, during which time the Biocap™ covers remained on. Then, covers were removed and intermittent agitation continued for two days (table 1).

MANURE SAMPLES AND CHARACTERISTICS

Monthly manure samples were taken at the near-surface, middle, and bottom of each tank and were refrigerated and analyzed according to recommended methods (Peters et al.,

Table 1. Agitation schedule.^[a]

Day ^[b]	Agitation ^[c]	Day	Agitation (cover removed)
1-3	T1, T2	4-5	T1
4-6	T3, T4	7-8	T3
7-9	T5, T6	10-11	T6

^[a] There were insufficient mixers to agitate all tanks simultaneously, so each tank-pair was agitated simultaneously for 3 d (8-h d⁻¹). Afterwards, covers were removed and agitation continued in those tanks for 2 d.

^[b] T = Tank; Day 1 = 18 Oct.

^[c] Biocap™ covers on in T1, T3, and T6.

2003). Total ammoniacal N (TAN = NH₃-N + NH₄⁺-N) content was determined by distillation. Total Kjeldahl N (TKN) was determined by acid digestion. Total-C (TC) was determined using the Dumas method of combustion in a CNS analyzer (LECO Corp., St. Joseph, Mich.). Dry matter (DM) content was determined by drying manure samples (approximately 20 g) at 105°C, and volatile solids (VS) were then determined by loss-on-ignition at 550°C. The pH was measured potentiometrically using an electrode (Accumet; Fisher Scientific Inc., Waltham, Mass.). The E_H (Redox potential) of each sample was determined on-site, before refrigeration, with a calibrated electrode (Orion Star; Thermo Fisher Scientific Inc., Waltham, Mass.).

To measure crust thickness, an arrow-shaped probe was inserted through the crust, then rotated 90° and lifted until the shoulders of the probe-head met the bottom of the crust (modified from Smith et al., 2004). An average was calculated from five measurements along a central transect in each tank.

ENVIRONMENTAL MEASUREMENTS

Environmental parameters were recorded every 60 s using a data-logger [CR1000; Campbell Scientific (Canada) Corp., Edmonton, AB] that calculated hourly and 24-h averages. Air temperatures inside each chamber were measured by three

shielded copper-constantan thermocouples suspended approximately 30 cm above the manure. Manure temperature was measured in each tank at 5 cm below the surface and 10 cm above the bottom. Net radiation was measured inside chamber 2 and 5 (described later) at 1.50-m height using net radiometers [Q-7.1; Campbell Scientific (Canada) Corp., Edmonton, AB]. Periodic manual measurements of manure, crust, or cover surface temperatures (depending on the treatment and presence of a crust) were taken with a non-contact infrared thermometer (42500; Extech Instruments, Waltham, Mass.).

FLUX MEASUREMENTS

Steady-State Chambers

Six steady-state flux chambers (fig. 1a, b) were installed on the tanks and remained in place at all times except during manual measurements (e.g., manure and crust sampling) and when agitators were installed or removed. Chambers were made with transparent greenhouse plastic (0.15-mm Super Durafilm 4; AT Plastic, Edmonton, AB) on aluminum frames. Fresh air entered the chambers through three vents and exited through a 35-cm diameter exhaust fan (Leader Fan Industries, Toronto, ON). Exhaust fan speed was set to provide a nominal air-exchange rate of 2 to 3 times per min, and it was consistent among chambers and through time. Airspeed near the manure surface was measured periodically with a hot-wire anemometer at 16 locations, ranging from 0.5 to 1 m s⁻¹. Exhaust ducts had a venturi shape to promote laminar airflow in the narrow section, where exhaust airspeeds were measured every 60 s using cup anemometers (7911, Davis Instruments, Hayward, Calif.). Hourly averages were recorded by a data-logger [CR10X; Campbell Scientific (Canada) Corp., Edmonton, AB]. Flux densities were calculated using the steady-state equation (Livingston and Hutchinson, 1995):

$$F = \frac{Q}{A}(C_o - C_i) \quad (1)$$

where

- F = flux density (mg m⁻² s⁻¹)
- Q = airflow rate (airspeed in the venturi × cross-sectional area of the venturi, m³ s⁻¹)
- A = surface area of the manure tank (m²)
- C_i = gas concentration in the inlet air (mg m⁻³)
- C_o = gas concentration in the outlet air (mg m⁻³).

Inlet air was sampled at two points, 1.7 m above ground, 0.3 m in front of tanks 2 and 5 (fig. 1c). These samples were assumed to represent the inlet air of all chambers, so in calculations C_i was the average. For all gases, outlet air was sampled at the center of each exhaust duct. The chamber setup was tested before the study using a mass recovery of N₂O (Crill et al., 1995). A known mass of N₂O was added at the chamber inlets using a mass flow controller and certified standard gas (Air Liquide Canada Inc., Montreal, QC) while N₂O in exhaust air was monitored using 10-Hz data with the trace gas analyzer described later. The average recovery was 97%.

Despite their advantages, steady-state chambers alter the enclosed environment (Livingston and Hutchinson, 1995; Cole et al., 2007). As a result, absolute fluxes measured in this study have an uncertain relationship with the actual flux magnitudes that would occur without chambers. We assume

relative flux versus time and treatment are representative of actual differences. Although measured fluxes are reported, trends and treatment differences are the focus of this analysis.

CH₄, N₂O, and CO₂ Measurement

Air from each sampling location (two inlet, six outlet) traveled through 25 m of polyethylene tubing (3.2 mm i.d.) to a valve box where air from one of eight sites was directed to a high-flow air dryer and then to one of two tunable diode laser trace gas analyzers (TDLTGA, Campbell Scientific, Logan, Utah) that measured the CH₄ and N₂O concentration. While cycling sequentially through the eight sites, air was constantly drawn through all valves and tubing by sending air from the remaining valves directly to the vacuum pump (bypassing the analyzers). Airflow in each sample tube was set to 0.9 L min⁻¹ by an orifice at the intake (D-12-BR, O'Keefe Controls Co., Turnbull, Conn.). Certified reference gases (Air Liquide Canada Inc., Montreal, QC) were used in the TDLTGA reference cell. Reference gases that bracket the measurement range were used for span calibrations. Concentration data, parameters, and diagnostics from the TDLTGA were recorded by a data-logger [CR5000, Campbell Scientific (Canada) Corp., Edmonton, AB] that also controlled valves and recorded an average concentration from each location every 4 min (i.e. one cycle of eight sites at 30 s per site). When switching between sites, data were omitted during the sample crossover period. The average coefficient of variation (CV) for ambient samples during typical operation was 2.5% for CH₄ and 0.5% for N₂O.

The CO₂ concentration at each sampling location was determined using a similar set-up with the following differences: no external air dryers were used, an infrared gas analyzer (Li-Cor 6400; LI-COR Biosciences, Lincoln, Nebr.) with a N₂ reference gas measured CO₂ concentration at each site for 45 s on an 8-min cycle. The average CV for ambient samples during typical operation was 1%.

Due to power outages, equipment repairs, and maintenance, data were not obtained from: 18-19 May, 12-13 June, 20-21 July, 31 July to 7 August for CH₄; 21-27 May, 27 June to 2 July, 17-21 July, 2-4 August for N₂O; and 8-12 June, 11-15, 26-29 July, 8-17 September, 14-15 October for CO₂.

NH₃ Measurement

Air from each sampling location traveled through 25 m of polyethylene tubing to an ammonia trap. Sample air was bubbled through 100 mL of 0.005 M H₃PO₄ (Chantigny et al., 2004) using a dispersion tube (Ace Glass, Vineland, N.J.). Airflow in each tube was regulated by a 3-L min⁻¹ orifice (O'Keefe Controls Co., Turnbull, Conn.) between the suction pump and an airflow meter (Gallus 2000, Actaris Metering Systems, Greenwood, S.C.). All sample locations were monitored simultaneously using eight traps. For practical reasons, a sampling interval from 0830 h to 0830 h (the next day) was used to measure daily average NH₃ flux. Samples were typically obtained three days per week except during agitation when samples were obtained each day. The CV for ambient samples measured in the same week was 5% to 30%.

After a 24-h sampling period, a 13-mL subsample from each trap was immediately refrigerated in a capped plastic tube. The aqueous NH₄⁺-N concentration was determined by the phenate method using a Technicon AutoAnalyzer II

(Technicon Instruments Corp., Tarrytown, N.Y.). The aqueous concentration was used to calculate the average $\text{NH}_3\text{-N}$ concentration in sample air:

$$C_{\text{air}} = C_{\text{aq}} \times V_{\text{aq}} / V_{\text{air}} \quad (2)$$

where

- V_{aq} = trapping-solution volume (m^3)
- V_{air} = sample-air volume (m^3)
- C_{aq} = $\text{NH}_4^+\text{-N}$ concentration in the trapped liquid (mg m^{-3})
- C_{air} = $\text{NH}_3\text{-N}$ concentration in air (mg m^{-3}), which is either C_0 or C_i (eq. 1) depending on sample location.

DATA ANALYSES

Data processing and flux calculations were performed using MATLAB[®] (The Mathworks Inc., Natick, Mass.). Covers were randomly assigned using adjacent tank-pairs as blocks to minimize potential effects of spatial variability and micro-climates. Since flux measurements were taken across time from each manure tank, repeated measures analysis was used to compare fixed effects of cover, time, and agitation. The random effects of tank and block were also included in the model. This analysis was performed on daily average data, using PROC MIXED (SAS Institute, 2008). Repeated measurements were not equally spaced (due to data gaps), so measurements closer in time were more correlated than those that were farther apart. Covariance structures suitable for unequally spaced data were selected based on fit-statistics (Littell et al., 1998; Littell et al., 2006). Regression analysis and tests on non-repeated sample means were conducted using JMP[®] (SAS Institute, 2007).

A key assumption in flux calculations was that ambient samples represent all inlet air. When valid, the difference between ambient samples should be zero. Thus, for each gas, the concentration difference between concurrent ambient samples was calculated along with a 5-period running standard deviation (SD) of the differences. Consecutive differences not bound by $0 \pm 2\text{SD}$ were flagged and associated data were checked and manually removed. This procedure caused <2% of CH_4 , N_2O , and NH_3 data to be removed. However, many CO_2 data were removed especially during nights with low wind. This can be explained by advection of CO_2 -rich air (due to respiration) from the surrounding landscape during stable atmospheric conditions. Similar problems occur in eddy covariance CO_2 -flux measurements (Balocchi, 2003). Removing these data should not bias results because CO_2 flux did not exhibit a diurnal trend in either treatment.

RESULTS AND DISCUSSION

ENVIRONMENTAL PARAMETERS

Manure Temperature

Altering manure temperature by covering can affect fluxes through the rate of microbial gas production (Conrad, 1996). The covers had a dark surface that heats up due to insolation. However, insulating material lining the cover will reduce the transfer of heat to the manure. To investigate the potential warming effect on the manure in the tanks, infrared surface temperature was measured. The geotextile surface of covered tanks were always significantly warmer than the

surface of control tanks, especially on sunny days. For example, at mid-day on 20 June, the average IR-temperature for covered tanks was $50 \pm 5^\circ\text{C}$ compared to $29 \pm 4^\circ\text{C}$ for controls, but manure temperature at 5-cm depth was similar ($17.1 \pm 0.5^\circ\text{C}$ compared to $16.1 \pm 0.5^\circ\text{C}$). Late in the year, and on cloudy days, thermocouple data showed covered tanks had warmer near-surface manure temperatures on a daily basis (p -value <0.05; fig. 2), presumably due to insulation. This was evident in hourly thermocouple data, for instance at mid-day on 25 September, the temperature at 5 cm in covered tanks was $16.6 \pm 0.3^\circ\text{C}$ compared to $12.8 \pm 0.5^\circ\text{C}$ in control tanks.

Water Balance

The covered tanks had less evaporative losses, leading to a progressive depth increase (fig. 3). In total, 2800 L (422 mm) of water was added to each tank with sprinklers. Overall, control tanks had approximately neutral water balances, indicating a 2.6-mm d^{-1} evaporation rate; whereas depth increased in covered tanks, indicating a significantly lower evaporation rate of 1.4 mm d^{-1} (p -value <0.01; fig. 3, right-panel). Reduced evaporation observed in the present study may result from reduced convection, perhaps further reduced by particles in the manure plugging pores in the cover. Less evaporation would reduce available freeboard and increase transport costs.

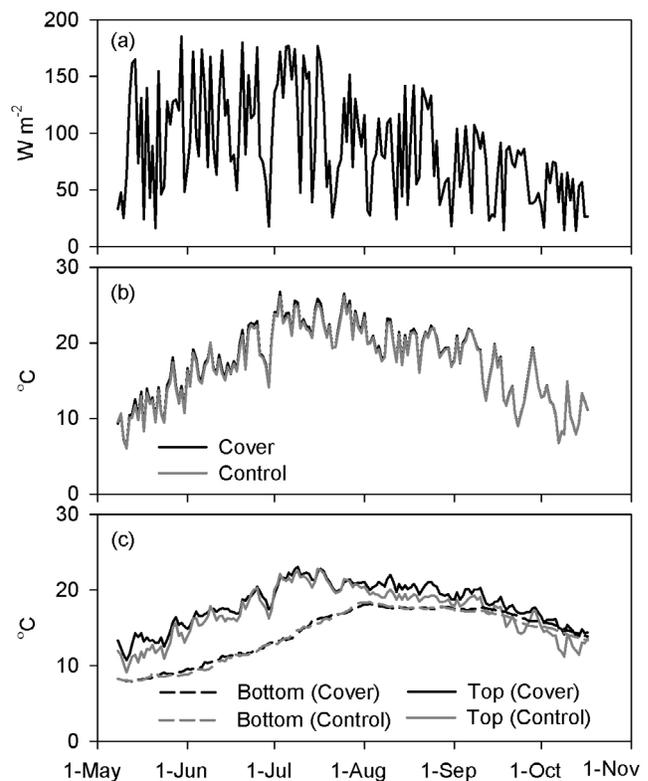


Figure 2. Daily average environmental parameters at the site: (a) net radiation, (b) air temperature (treatment average), and (c) manure temperature measured near the top and bottom of each tank (treatment average).

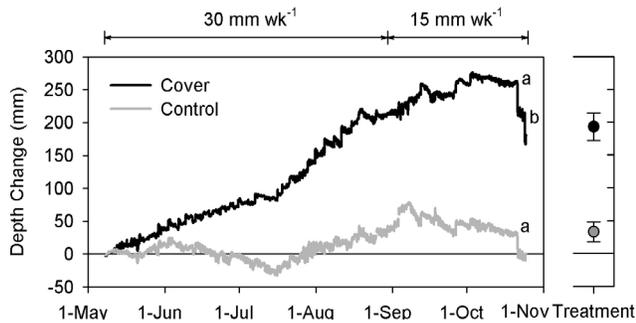


Figure 3. Cumulative depth change in tank 3 (cover) and tank 4 (control), measured hourly with sonic ranging sensors. Positive depth changes imply precipitation exceeds evaporation. Precipitation was simulated using sprinklers inside each chamber, supplying the rate shown above. Labels indicate the start of agitation (a), and cover removal (b). The right panel (treatment) shows overall depth change for each treatment based on freeboard measurements at the start and end of the study (three tanks each; mean \pm standard deviation).

MANURE CHARACTERISTICS

Manure analyses are summarized in table 2. Only results from top and bottom sample locations and the first and last sample dates are shown. Changes with time were gradual for all parameters, except TAN and TKN where most of the decrease occurred in May and June. Samples from mid-depth were similar to samples from the top. No significant treatment differences were observed for concurrent samples of any parameter at any depth, suggesting covers did not alter manure characteristics. Significant changes through time were observed within each treatment. This included decreasing all forms of N (confirming N-loss implied by flux measurements), increasing pH (favors higher NH_3 flux), and increasing E_H (less favorable to CH_4 production, though still below the +50 mV threshold for methanogenesis; Conrad, 1996).

FLUXES DURING UNDISTURBED STORAGE CH_4 , CO_2 , and N_2O Fluxes

There was no significant difference in CH_4 fluxes between treatments (table 3). Significant changes did occur with time, indicating a lag-phase of approximately 50 d before CH_4 flux increased exponentially (fig. 4). A lag is expected for fresh manure stored in clean tanks (without inoculum; van der Meer, 2008) and was comparable to the delay reported by Massé et al. (2008). There was a significant difference in CO_2 emissions between treatments (table 3). The treatment \times time interaction was also significant, reflecting that covers initially reduced CO_2 fluxes 20% to 35%, but after a crust formed on control tanks the covers no longer had an impact on CO_2 flux (fig. 4, table 4). Fluxes of CH_4 and CO_2 peaked simultaneously, coinciding with crust formation (fig. 4). Presumably, biogas ($\text{CH}_4 + \text{CO}_2$) production exceeded diffusion, causing bubbles that carried particles to the surface (Misselbrook et al., 2005). Bubbles were also visibly lifting particles in covered tanks; however, particles remained submerged due to the cover and positive water balance.

Table 3. Significance levels (*p*-values, or ** for *p*-value < 0.01) of the main effects and interactions on daily average flux of methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), and ammonia (NH_3) using repeated measures.

Source ^[a]	CH_4	CO_2	N_2O	NH_3
Treatment	0.51	**	**	**
Time	**	**	**	**
Agitation	**	**	0.66	0.08
Treatment \times Time	0.23	**	**	**
Treatment \times Agitation	**	**	0.37	0.17
Agitation \times Time	**	**	0.61	**
Treatment \times Agitation \times Time	**	**	0.48	**

^[a] Data obtained after covers were removed during agitation are not included.

Table 2. Manure characteristics at the start (9 May) and end (17 October, prior to agitation) of the study.^[a]

	Time	Control ^[b]		Cover ^[b]	
		Top	Bottom	Top	Bottom
Dry matter (DM, %)	Start	2.2 (0.3) ^{ab}	7.7 (0.4) ^{ab}	2.2 (0.3) ^b	7.3 (0.3) ^{ab}
	End	2.5 (0.5) ^{ab}	5.2 (1.1) ^{ab}	1.9 (0.2) ^b	4.2 (1.6) ^{ab}
Volatile solids (% of DM)	Start	70 (2) ^b	87 (1) ^b	71 (2) ^b	85 (2) ^b
	End	75 (7) ^b	87 (3) ^b	70 (2) ^b	86 (6) ^b
Total carbon (%)	Start	0.9 (0.1) ^b	3.4 (0.2) ^{ab}	0.9 (0.1) ^b	3.2 (0.1) ^{ab}
	End	1.0 (0.3) ^b	2.3 (0.5) ^{ab}	0.8 (0.1) ^b	1.8 (1.7) ^{ab}
Total ammoniacal N (mg L ⁻¹)	Start	1730 (287) ^a	2230 (455) ^a	1650 (144) ^{ab}	2173 (140) ^{ab}
	End	1013 (31) ^a	1063 (15) ^a	1053 (45) ^a	1117 (61) ^a
Total Kjeldahl N (mg L ⁻¹)	Start	2213 (136) ^a	2597 (169) ^a	2213 (127) ^a	2547 (189) ^a
	End	1590 (60) ^a	1727 (6) ^a	1550 (142) ^a	1783 (140) ^a
pH	Start	6.8 (0.0) ^a	6.7 (0.1) ^a	6.8 (0.0) ^a	6.7 (0.1) ^a
	End	7.5 (0.1) ^a	7.5 (0.1) ^a	7.5 (0.0) ^a	7.5 (0.0) ^a
E_H (mV)	Start	-178 (47) ^a	-147 (9) ^a	-202 (10) ^a	-145 (30) ^a
	End	-39 (18) ^a	-51 (3) ^a	-46 (3) ^a	-45 (21) ^a

^[a] Samples were taken below the cover or crust, and at the bottom. The mean of three tanks in each treatment is shown with standard deviation in parentheses.

^[b] There were no significant differences between treatments at the same time and sampling depth. For each parameter, superscripts indicate significant differences (*p*-value < 0.05) between the start and end in the same sampling location ('a'), and between depths at the same time in the same treatment ('b').

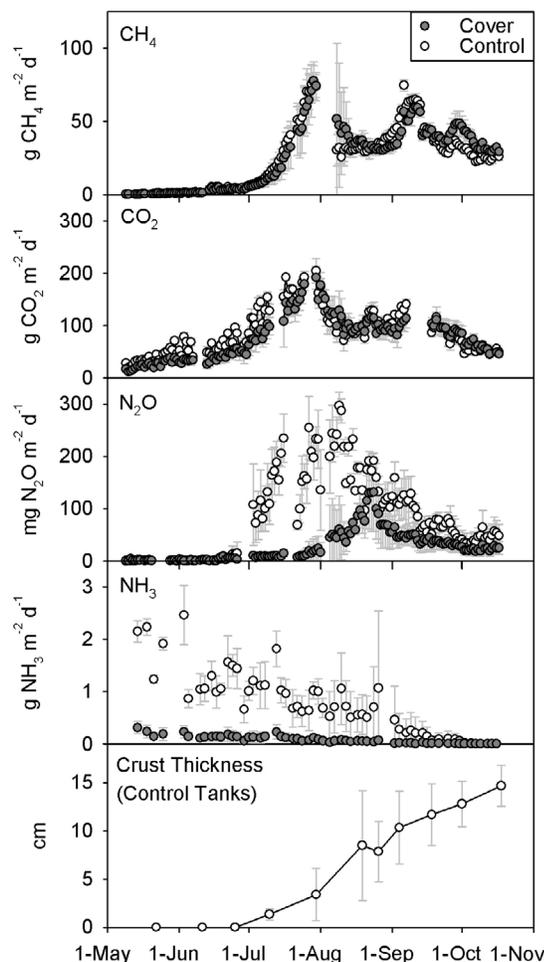


Figure 4. Daily average gas fluxes for each treatment and crust thickness on the controls during undisturbed storage (circles represent the average of 3 replicates in each treatment, whiskers are the standard deviation).

N_2O was emitted in control tanks about 1 month before fluxes were observed in covered tanks (fig. 4). A neutral or negative water balance favors N_2O production in surface crusts because of microbial activity in aerobic microsites (Sommer et al., 2000). Fluxes from covered tanks did not begin until late July, suggesting the covers were not as conducive for producing and emitting N_2O . For N_2O , effects of treatment, time, and treatment \times time were all significant (table 3), reflecting flux-reductions provided by covers after crust development (48% to 93%; table 4).

NH₃ Emissions

Ammonia flux significantly declined with time for both treatments (fig. 4; table 3), a trend observed in other batch-loaded studies (Xue et al., 1999; Misselbrook et al., 2005). A concurrent decline in TAN confirmed that N was lost, which would lead to lower NH_3 emissions. The cover treatment had significantly lower fluxes (table 3) and provided about 90% flux-reductions for most of the study (table 4) despite declining fluxes and crusts on control tanks. Surface resistance is one potential reason why the Biocap™ covers reduced NH_3 fluxes. Another is that the covers reduced evaporation, therefore diluting the manure and

decreasing TAN concentration near the surface of covered tanks. Lower flux-reductions in October (30%) coincided with cool temperatures, low fluxes, and the crusts on control tanks reaching a maximum thickness of 14 cm.

EMISSIONS DURING AGITATION

In both treatments, agitation led to significant increases in 24-h fluxes of CO_2 and NH_3 , decreased N_2O , and had no effect on 24-h fluxes of CH_4 (fig. 5). During agitation, hourly fluxes of CH_4 (in both treatments) and CO_2 (control treatment only) exhibited similar trends to what was observed in a previous study (VanderZaag et al., 2009) — spiking 2- to 5-times higher than summer maximums. However, the spikes were offset by low fluxes when mixers were off (approximately zero flux for CH_4). Thus, there was little change in the 24-h average flux of CH_4 . The possibility that agitation caused unsuitable conditions for methanogenesis was examined by frequent pH and E_H measurements, but no significant changes were observed. The N_2O fluxes declined in control tanks presumably because crusts were destroyed, eliminating N_2O production sites (Sommer et al., 2000). In comparison, our previous study found agitation had no effect on N_2O flux because N_2O emissions had already declined to zero before agitation started (VanderZaag et al., 2009). Ammonia fluxes from covered tanks were similar to pre-agitation levels in October; whereas fluxes from controls increased significantly. Thus, covers continued to provide high NH_3 flux-reductions (94%; table 4) demonstrating that surface resistance was effective even when manure was agitated. When the covers were removed, substantial increases in NH_3 and CO_2 fluxes were observed (fig. 5). In just two days, NH_3 lost from previously covered tanks was approximately 20% of total losses with the covers on (165 d). Thus, leaving the covers in place during agitation maintains NH_3 flux-reductions. It also suggests that covers were enhancing resistance to CO_2 transport.

OVERALL COVER EFFICACY

Overall, during 162 d of undisturbed storage and 3 d of agitation (with covers), Biocap™ covers provided significant ($p < 0.05$) emission reductions of CO_2 (15%), N_2O (68%), and NH_3 (89%) as shown in table 4. Total GHG emissions from both treatments were dominated by CH_4 emissions (converted to CO_2 -equivalent global warming potential; CO_2e). If CO_2 emissions are excluded from the GHG-total, then there was no difference between treatments (table 5). If CO_2 emissions are included, covers reduced GHG emissions by 2.5% (p -value < 0.05). Including indirect N_2O emissions does not change these conclusions (i.e. 1% of NH_3 -N emissions; Solomon et al., 2007; van der Meer, 2008). The observation that covers reduced three of four gases, but did not substantially reduce total GHG emissions confirms that decreasing CH_4 emissions is imperative for liquid manure.

CONTEXT FOR EMISSIONS

Fluxes of CH_4 after the lag-phase (monthly averages: approximately 23 to 35 $g CH_4 m^{-3} d^{-1}$) were comparable to fluxes from stored dairy manure (approximately 16 to 56 $g CH_4 m^{-3} d^{-1}$; Sneath et al., 2006). The cumulative CH_4 emissions were approximately 3 $kg CH_4 m^{-3}$ (4400 L CH_4 per m^{-3} manure). This corresponds to 0.14 L $CH_4 g^{-1}$ VS (assuming top, middle, and bottom samples each represent

Table 4. Average gas flux from each treatment (three replicates; standard deviation in parentheses), and flux-reduction provided by the cover treatment. Total emissions are shown at the bottom of the table.

Period	Crust ^[a] (cm)	CH ₄ Flux (g CH ₄ m ⁻² d ⁻¹)			CO ₂ Flux (g CO ₂ m ⁻² d ⁻¹)			N ₂ O Flux (mg N ₂ O m ⁻² d ⁻¹)			NH ₃ Flux (mg NH ₃ m ⁻² d ⁻¹)		
		Control	Cover	% Redn. ^[b]	Control	Cover	% Redn.	Control	Cover	% Redn.	Control	Cover	% Redn.
9-31 May	0 (0)	1 (0)	1 (0)	0	38 (2)	25 (3)	34	1 (1)	1 (2)	0	1,885 (60)	221 (94)	88
June	0 (0)	3 (0)	3 (1)	0	62 (4)	40 (8)	35	3 (4)	3 (1)	0	1,278 (130)	143 (82)	89
July	2 (1)	33 (5)	29 (9)	12	148 (4)	118 (19)	20	154 (14)	11 (8)	93	997 (264)	121 (66)	88
Aug.	8 (4)	32 (4)	36 (7)	-13	106 (1)	109 (12)	-3	174 (16)	72 (12)	59	692 (555)	55 (22)	92
Sep.	11 (3)	46 (2)	44 (3)	4	100 (9)	95 (14)	5	85 (21)	41 (17)	52	183 (228)	17 (11)	91
1-17 Oct.	14 (1)	26 (2)	35 (3)	-35	56 (6)	60 (7)	-7	44 (19)	23 (11)	48	10 (4)	7 (0)	30
Agitation	0	28 (4)	29 (5)	-4	241 (100)	78 (15)	68	15 (5)	13 (3)	8	666 (362)	41 (35)	94
Totals ^[c]	Days	(g CH ₄ m ⁻²)			(g CO ₂ m ⁻²)			(mg N ₂ O m ⁻²)			(mg NH ₃ m ⁻²)		
Undisturbed	162	3,950	4,043	-2	14,560	12,682	13	13,579	4,307	68	139,714	15,458	89
Agitation	3	84	87	-4	723	234	68	45	39	13	1998	123	94
Total:	165	4,034	4,130	-2	15,283	12,916	15	13,624	4,346	68	141,712	15,581	89
Total:													
kg CO ₂ e m ⁻²		100.9	103.3		15.3	12.9		4.1	1.3				

^[a] Crust thickness is the average (standard deviation) of control tanks.

^[b] % Reduction = $([F_{control} - F_{cover}] / F_{control}) \times 100$; where $F_{control}$ and F_{cover} are the flux in control and covered tanks, respectively.

^[c] Calculated by multiplying treatment-average flux for each period by the number of days in each period and summing. Emissions were converted to CO₂ equivalent (CO₂e) on a 100-yr time horizon using CH₄ = 25 and N₂O = 298 (Solomon et al., 2007).

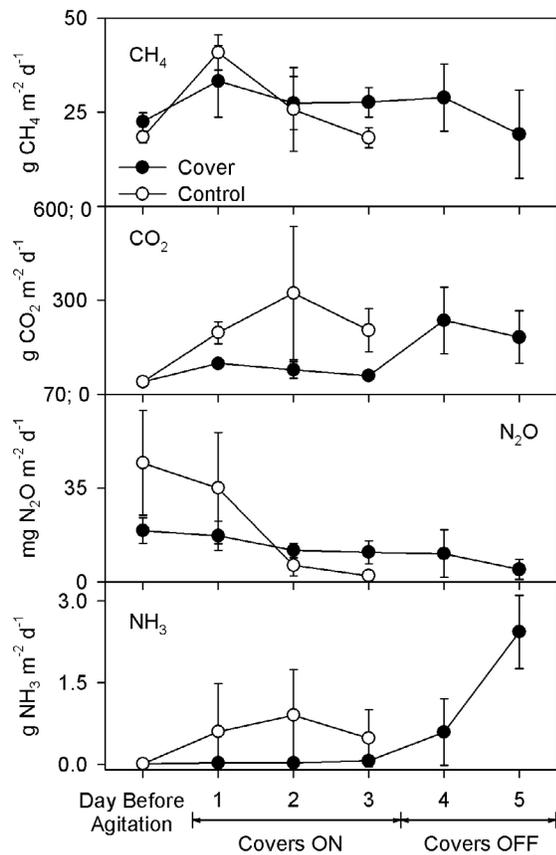


Figure 5. Daily average flux from covered and control tanks before and during agitation. Circles represent treatment means, whiskers the standard deviation. On days 1-3, covered tanks were agitated with covers in-place; whereas, on days 4 and 5 covers were removed and agitation continued. Control tanks were agitated for 3 days.

Table 5. Cumulative GHG emissions during 162 d of storage and 3 d of agitation.^[a]

	Control	Cover	Reduction ^[b]
CH ₄	100.9 (1)	103.3 (2)	n.s.
N ₂ O	4.1 (0.1)	1.3 (0.3)	68.5% *
GHG total	105.0 (1.4)	104.6 (1.7)	n.s.
CO ₂	15.3 (0.2)	12.9 (1.1)	15.5% *
GHG total including CO ₂	120.3 (1.2)	117.5 (1.2)	2.5% *

^[a] Values are the mean (standard deviation) of three tanks in each treatment (kg CO₂e m⁻²). The total GHG emissions are shown with and without including CO₂ (since it is not a net contribution to atmospheric CO₂).

^[b] % Reduction = $([F_{control} - F_{cover}] / F_{control}) \times 100$; where $F_{control}$ and F_{cover} are the flux in control and covered tanks, respectively. Only statistically significant reductions are shown (n.s. for p -values > 0.05, * for p -values < 0.05).

1/3 of the tank) and a methane conversion factor (MCF) of 55% using a B₀ value of 0.24 L of CH₄ per g of VS in the manure (Zeeman and Gerbens, 2000). This MCF is higher than default values for manure tanks in cool and temperate climates (39% and 45%; IPCC, 2000). The discrepancy could be because the IPCC defaults are average values and do not account for the warm-season monitoring period, modified climate inside the chambers, and batch-loading used in the present study.

Fluxes of CO₂ were consistent with expectations for anaerobic breakdown of organic matter, as evidenced by the approximately 50:50 CO₂-C:CH₄-C ratio (after CH₄ lag-phase; Conrad, 1996).

For N₂O, the maximum 4-min flux from a control tank was comparable to the maximum flux measured at mid-day from crusted dairy slurry (893 vs. approximately 950 mg N₂O m⁻² d⁻¹; Sommer et al., 2000). Pre-crust NH₃ fluxes from the controls were higher than one lab-scale chamber study (up to 0.75 g NH₃ m⁻² d⁻¹; Xue et al., 1999), lower than another (3.6 to 6 g NH₃ m⁻² d⁻¹; Sommer et al., 1993), and lower than

field-scale emissions (daily average: 3.6 to 8.6 g NH₃ m⁻² d⁻¹; McGinn et al., 2008).

Reductions of CH₄ and NH₃ flux can be compared to previous studies on permeable synthetic covers, but no reports were found on CO₂ or N₂O emissions. Some studies used geotextile covers, and others used Biocap™ covers. The only study on CH₄ flux found no effect initially, but after one month, the covered section of a lagoon had significantly higher fluxes than an uncovered section of the same lagoon. This increase was attributed to higher methanogenesis, although methanogenesis was not measured directly (Zahn et al., 2001). In our study, however, these treatment differences and trends were not observed. Thus, more research is needed to determine whether permeable synthetic covers tend to increase CH₄ production or perhaps could be designed to reduce CH₄ emissions by hosting methanotrophs (Petersen and Miller, 2006). Fluxes of NH₃ were reduced more (and more consistently) in our study than in previous field-studies on swine lagoons (17% to 54%, Zahn et al., 2001; 29% to 45%, Bicudo et al., 2004) and a pilot-scale study using dairy manure (geotextile did not reduce NH₃ flux; Clanton et al., 2001). A potential explanation for the enhanced performance in our study is that covers maintained 100% buoyancy, whereas others observed sinking — at least partially caused by snow accumulation (Bicudo et al., 2004).

SHORT-TERM FLUX TRENDS

Short-Term Trends in CH₄ and CO₂ Fluxes

Daily and monthly averages might suggest CH₄ fluxes from covered and uncovered tanks were nearly identical. This was not the case, however, on a short timeframe (fig. 6). Fluxes of CH₄ and CO₂ (fig. 7) were strongly influenced by short-term events, a characteristic that has been previously noted for CH₄ (Husted, 1994; Kaharabata et al., 1998; Park et al., 2006; Sneath et al., 2006). The flux-trend from any tank consisted of two main components: a baseline flux, presumably due to diffusion; and intermittent bursts, presumably due to bubble flux (ebullition). In control tanks, bubbles were periodically seen emerging through cracks in the crusts; whereas in covered tanks bubbles were not visible — even at the edges. Despite similar flux trends, there was no correlation within or between treatments. For example, high CH₄ flux observed in one tank did not predict concurrent high fluxes elsewhere. This suggests the cycle of gas production, bubble accumulation, and release, was independent of treatment and external factors. The covers might be expected to trap bubbles underneath and force more CH₄ to move by diffusion. However, data indicate that transport was still sporadic. Accounting for bubble flux is essential and may explain variability in previous studies where intermittent, short-duration measurements were taken (e.g. Husted, 1994; Sommer et al., 2000; Laguë et al., 2005). Our study suggests short measurements (minutes to hours) are inadequate for assessing CH₄ fluxes from liquid manure. Consider data from 15 to 18 August (fig. 6). A treatment comparison at one instant could show the cover was reducing CH₄ flux from -1400% to +87%. Even 20-min averages yield a range from -149% to +64%. In comparison, the treatment effect was -9% when 4-min data are averaged over 3 days. Thus, to capture the net production rate, CH₄ flux measurements must be frequent and long enough to average over stochastic transport processes — “snapshots” are

inadequate. Another implication is that a wide flux range should be expected, so outlier removal should be done carefully. Care is also warranted for high-frequency measurements, since spike-removal algorithms could remove meaningful data.

Short-Term Trends in N₂O Flux

N₂O fluxes showed a diurnal trend. For example, from 15 to 18 August (fig. 6), the coefficient of determination (r^2) between N₂O flux and chamber air-temperature-squared (T_{air}^2) was 0.88 for covered manure and 0.91 for the control (both regressions, $p < 0.001$; data during simulated rainfall was removed). Two implications are: (i) short, mid-day flux measurements (e.g., Sommer et al., 2000) will tend to overestimate the daily average N₂O flux, and (ii) cooler surface temperatures should reduce N₂O flux, thus shaded storages and reflective covers may be advantageous.

Fluxes During Rain Events

Flux events during rainfall have little effect on overall emissions, but give insight into gas production and transport (fig. 6). For example, on 7 July, CH₄ emissions from the control (tank 4) spiked when sprinklers were on. This was likely a result of bubbles released from particles at the surface (the crust was <2 cm thick, so the physical disturbance was noticeable). In contrast, CH₄ flux in covered tanks dropped to zero; presumably, because water acted as a sealant while percolating through the cover. Fluxes of N₂O also dropped in both treatments and then rapidly returned to previous trends, suggesting lower fluxes were due to restricted transport, not decreased production.

CONCLUSION

Our results, from batch-loaded, pilot-scale dairy manure tanks frequently monitored for six months, show tanks with a Biocap™ floating cover emitted significantly less CO₂ and N₂O than controls. However, CH₄ emissions were not reduced, and since CH₄ represents the largest portion of total GHG emissions, total GHG emissions were not reduced. Thus, permeable covers designed to reduce CH₄ fluxes are needed. NH₃ fluxes were consistently reduced by approximately 90%, even though a crust formed on the undisturbed controls after about 50 days (which reduced fluxes in the control tanks). Excellent flux-reductions were also observed during agitation. Removing covers before agitation, however, led to greater losses of CO₂ and NH₃. Thus, being able to agitate manure below floating covers is beneficial, and may be preferable to materials that disintegrate during mixing.

Short-term (4-min) CH₄ flux data showed that bubble fluxes were a key component of fluxes from both covered and uncovered storages. This observation suggests that the Biocap™ cover does not substantially impede CH₄ transport. Moreover, bubble fluxes emphasize that brief measurement “snapshots” are inadequate for accurately measuring CH₄ fluxes from liquid manure, or even for making valid comparisons among treatments. The N₂O flux from Biocap™-covered and naturally crust-covered storages both had a diurnal trend that was strongly correlated with air temperature.

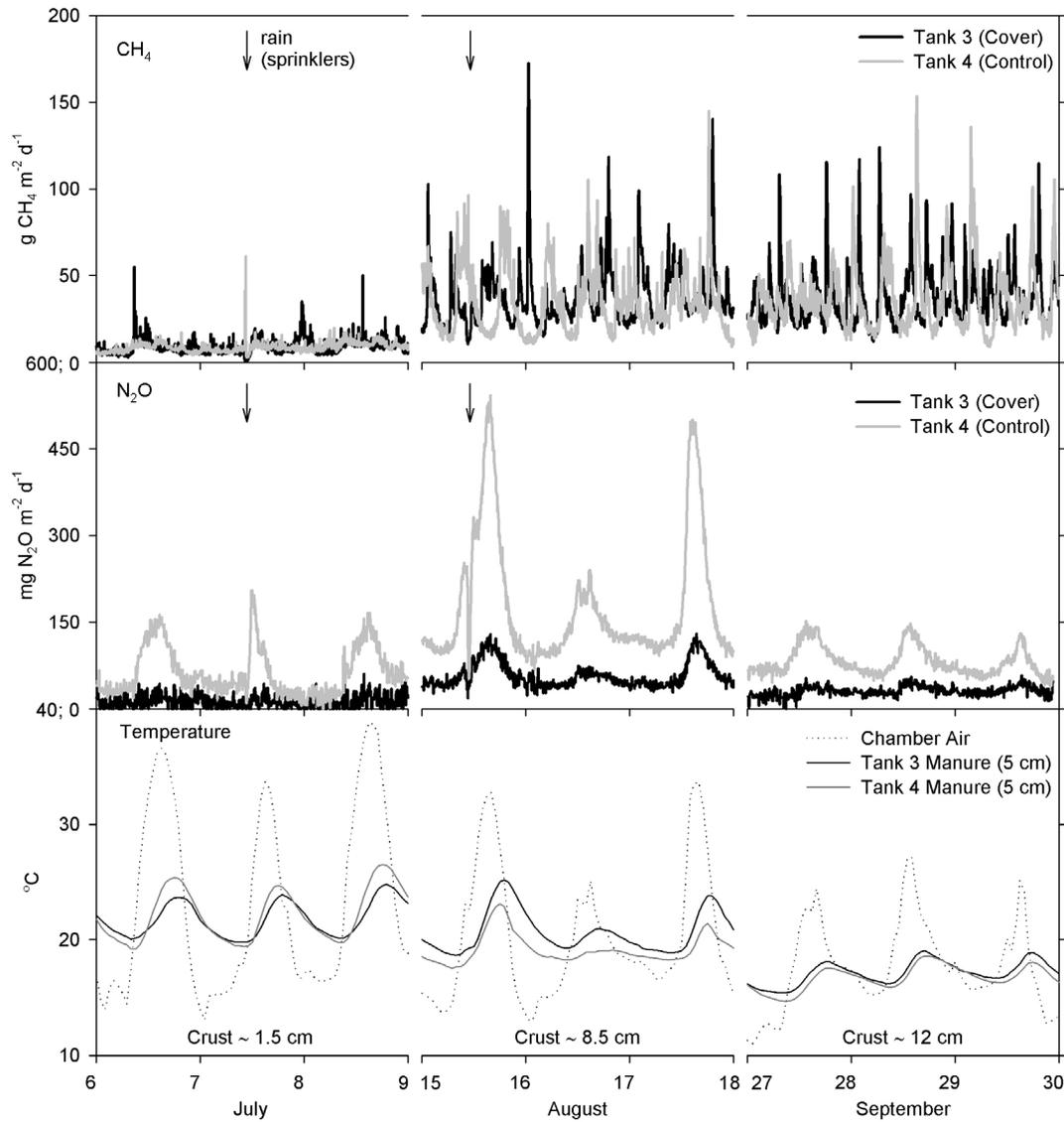


Figure 6. Fluxes of CH₄ and N₂O (4-min data, reported as d⁻¹ for ease of comparing with other figures) are shown in the top two panels for tank 3 (covered) and tank 4 (control). The bottom panel shows average air temperature in all chambers (measured 30 cm above manure), manure temperature measured approximately 5 cm below the surface, and the approximate crust thickness (treatment average). These data are shown for three days in July, August, and September. Vertical arrows indicate simulated rain events (via sprinklers in the chambers).

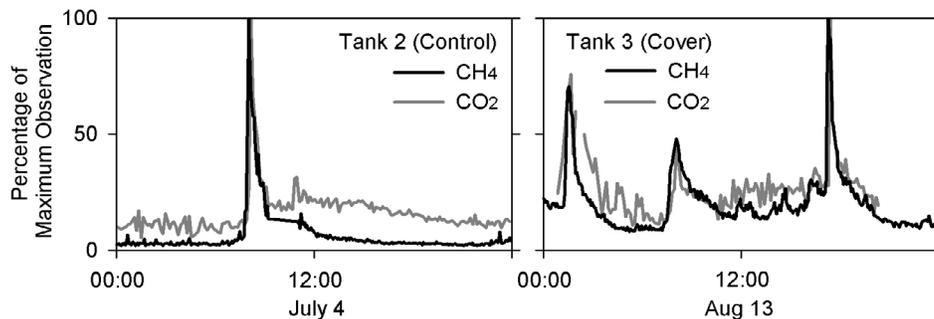


Figure 7. Fluxes of CH₄ (4-min data) and CO₂ (8-min data) showing bubble fluxes. Fluxes are shown from a control tank (left) and a covered tank (right), and each is normalized by dividing by the maximum flux of each gas.

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GAS EMISSIONS FROM STRAW COVERED LIQUID DAIRY MANURE DURING SUMMER STORAGE AND AUTUMN AGITATION

A. C. VanderZaag, R. J. Gordon, R. C. Jamieson, D. L. Burton, G. W. Stratton

ABSTRACT. *This study evaluated the effect of straw covers on emissions from liquid manure during storage and agitation. Emissions of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and ammonia (NH₃) were measured from six tanks (6.6 m² each) containing batch-loaded liquid dairy manure. This was conducted between June and October 2007 in Nova Scotia, Canada. Straw was added to four of the tanks at two thicknesses (15 and 30 cm), while two tanks remained uncovered. Gas concentrations were measured using tunable diode lasers, an infrared gas analyzer, and acid traps. Fluxes were measured using steady-state chambers. At the end of the study, one tank from each treatment was agitated. During 122 d of undisturbed storage, the covers increased emissions of CO₂ and N₂O. However, the 15 and 30 cm covers reduced CH₄ emissions by 24% and 28% and reduced NH₃ emissions by 78% and 90%, respectively. During 5 d of intermittent agitation, substantial releases of CO₂, CH₄, and NH₃ were observed from all treatments. In this period, greenhouse gas emission reductions were relatively unchanged because releases from the control and covered tanks were similar. However, emissions of NH₃ during agitation were highest from tanks that had been covered, thereby decreasing the overall emission reduction provided by the 15 and 30 cm covers to 68% and 76%, respectively. Despite elevated emissions during agitation, the results suggest that straw covers provide an overall reduction of CH₄ and NH₃ emissions compared to the control.*

Keywords. *Air quality, Emissions, Floating cover, Liquid manure storage.*

Livestock production involving completely or partially confined animals is common, and in these systems manure is often stored and handled as a liquid. Liquid manure storage systems create conditions high in organic matter and nitrogen (N), where production of greenhouse gases (methane, CH₄; carbon dioxide, CO₂; and nitrous oxide, N₂O) and ammonia (NH₃) can occur. These systems are typically open to the atmosphere, allowing unimpeded gas emissions. Mitigating emissions is important for several reasons: first, ammonia loss reduces the ultimate N content and value of the manure as fertilizer; second, in the atmosphere, ammonia contributes to aerosol formation and negative environmental effects; and third, greenhouse gases (GHGs) contribute to climate change, with CH₄ and N₂O possessing 25× and 298× more warming potential on a 100-year time horizon than CO₂, respectively

(Solomon et al., 2007). Manure management is a component of livestock production where mitigation measures can improve air quality (FAO, 2006).

Floating covers can be used to reduce emissions from liquid manure storages. Straw has been a moderately effective cover material in previous studies (VanderZaag et al., 2008) and has the advantage of being simple, inexpensive, adaptable, and readily available. A range of emission reductions have been observed for NH₃ (e.g., 40% to 100%; Sommer et al., 1993), and both reductions and increases have been observed for GHGs (e.g., -250 to +80% for CH₄; Cicek et al., 2004; Laguë et al., 2005). Therefore, further study is needed to discern what effects on air quality can be expected when straw covers are used. The amount of straw used may also affect performance. The treatments chosen in this study are based on previous research where cover durability and efficacy were assessed. Recommendations include a cover thickness of 15 to 30 cm (Filson et al., 1996), >20 cm (Clanton et al., 2001), and >4 kg m⁻² (Hörnig et al., 1999). Manure agitation is another aspect of cover use that has not been addressed in previous literature. Agitation can substantially affect emissions (Kaharabata et al., 1998; Park et al., 2006) and may release gases trapped below the covers, thereby offsetting emission reductions.

Emissions are the net result of gas production, consumption, and storage. In order for a straw cover to reduce emissions, it must decrease production, increase consumption, and/or increase storage. Storing more gas in the liquid will give the illusion of reduced emissions, but the gas will ultimately be emitted during agitation and field spreading. Thus, lasting benefits can only accrue from decreased production or increased consumption. Some aspects of production and

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The authors are **Andrew C. VanderZaag**, ASABE Member Engineer, Graduate Student, Process Engineering and Applied Science, Dalhousie University, Halifax, Nova Scotia; **Rob J. Gordon**, Professor and Dean, Ontario Agricultural College, University of Guelph, Guelph, Ontario; **Rob C. Jamieson**, Assistant Professor, Process Engineering and Applied Science, Dalhousie University, Halifax, Nova Scotia; **David L. Burton**, Professor, and **Glenn W. Stratton**, Professor, Department of Environmental Science, Nova Scotia Agricultural College, Truro, Nova Scotia. **Corresponding author:** Andrew C. VanderZaag, Process Engineering and Applied Science, Dalhousie University, P.O. Box 1000, Halifax, Nova Scotia, Canada B3J 2X4; phone: 902-494-4597; fax: 902-420-7639; e-mail: a.vanderzaag@dal.ca.

consumption, and how covers may affect them, are discussed in this section. Production of the gases investigated in this study is mainly driven by anaerobic microorganisms (except N_2O , which can also be produced aerobically). Covers may affect the production rate by altering the manure pH and equilibria near the surface. This could be important for NH_4^+ dissociation and NH_3 flux, but is probably less important for the other gases. It is likely that covers contain a variety of microsites with a range of redox potentials, some of which could be conducive for microbial N_2O production and consumption of NH_3 or CH_4 (Petersen et al., 2005). Covers may also reduce emissions by gas adsorption. Permeability and thickness should affect these processes by altering gas contact time in the cover.

Covers affect gas transport from the liquid to the atmosphere. Mass transfer of gas between liquid and air is driven by a concentration gradient, as described by the two-film theory (Basmadjian, 2007). When a dissolved gas moves between the bulk liquid and air, it crosses a liquid film and a gas film (Macintyre et al., 1995; Basmadjian, 2007). Each film provides a resistance, which combine to give the overall resistance to transport. Transport of soluble gases (like NH_3) is limited by gas-film resistance, whereas transport of low-solubility gases (e.g., CH_4 , CO_2 , or N_2O) is limited by liquid-film resistance (Macintyre et al., 1995). Therefore, floating straw should reduce NH_3 emissions by increasing the atmospheric boundary layer. However, this may not be the primary mechanism for reducing emissions of low-solubility gases. Low-solubility gases move across the aqueous boundary layer by diffusion and ebullition (bubble flux). Ebullition is particularly important because it bypasses the aqueous boundary layer and releases the gases directly to the atmosphere. Thus, straw covers could reduce emissions of CH_4 and CO_2 by trapping bubbles in the liquid, forcing the gases to move by diffusion instead, which is much slower and should increase contact time in the cover. Although bubbles are formed by low-solubility gases, soluble gases can also diffuse into them. Thus, by reducing ebullition, straw covers might also reduce NH_3 emissions (Ro et al., 2008).

The present study was conducted to assess the effect of floating straw covers on NH_3 and GHG emissions from stored liquid manure. A research approach was chosen that exposes the manure and covers to environmental conditions (range of temperatures, precipitation, solar radiation) and agitation while allowing frequent flux measurements. The specific objectives were to: (1) characterize temporal changes in emissions and identify factors affecting them, (2) determine the percentage emission reduction provided by straw covers during undisturbed storage, (3) characterize the effect of agitation on emissions from all treatments, and (4) determine whether there is a difference in efficacy between 15 and 30 cm straw covers.

METHODS

SITE DESCRIPTION

Liquid dairy manure was stored in six concrete tanks (6.6 m^2 each; figs 1a and 1b) at the Nova Scotia Agricultural College (NSAC) in Truro, Nova Scotia, Canada. Manure from the NSAC dairy was put into the tanks to a depth of 1.3 m (8.6 m^3) on 6 June 2007. On the same day, two thicknesses (15 cm = 3.3 kg m^{-2} ; 30 cm = 6.6 kg m^{-2}) of barley

straw were added on top of the manure (fig. 1c). Two tanks remained uncovered (controls). Cover treatments were randomly assigned using tanks 1 to 3 and 4 to 6 as blocks to minimize potential effects of spatial variability and microclimates.

Flux monitoring was conducted from 13 June through 17 October 2007 using steady-state chambers that block precipitation. To maintain an approximately neutral water-balance and provide a physical surface disturbance similar to rainfall, sprinklers inside each chamber were operated twice per week during the summer (30 mm per week) and once per week in the autumn (15 mm per week). This water was taken from a groundwater well (pH 7.9, nitrate-N <2.3 mg L^{-1} , Fe <0.02 mg L^{-1} , Mn <0.02 mg L^{-1} , sulfate 43 mg L^{-1}).

At the end of the study, three manure tanks (tanks 1, 2, and 3) were agitated using electric trolling motors (55 lbs thrust, providing up to 70 W m^{-3} manure; Johnson Outdoors, Inc., Racine, Wisc.) to simulate the disturbance that would occur on a farm prior to land application of manure. During agitation, the straw covers became mixed into the bulk manure. The agitators were remote controlled so emissions could be measured without human interference. This took place for 8 h per day on five consecutive days (13 to 17 October 2007). Operators attempted to maintain consistent agitation among treatments and across time; however, practical challenges made this difficult.

MANURE SAMPLES AND CHARACTERISTICS

Manure samples were taken from each tank at the start and end of the study. A sampling device enabled manure to be obtained at discrete depths. Samples were immediately refrigerated, and analyses were performed according to recommended methods (Peters et al., 2003). The following is a brief summary. Ammonium-N ($\text{NH}_3\text{-N} + \text{NH}_4^+\text{-N}$) content was determined by distillation. Total N (TN) and total C (TC) were determined using the Dumas method of combustion in a Leco model 1000 CNS analyzer (Leco Corp., St. Joseph, Mich.). Dry matter (DM) content was determined by drying manure samples (~20 g) at 105°C. The pH was determined by electrode.

During the study, a natural crust formed on the surface of the uncovered manure tanks. Crust thickness was measured by inserting a thin arrow-shaped probe until the head of the probe passed the bottom of the crust, and then rotating the probe 90° and pulling it up until the top of the arrow head was resisted by the bottom of the crust. An average thickness was calculated from five measurements taken along a central transect in the tanks.

ENVIRONMENTAL MEASUREMENTS

Environmental parameters were measured using a CR5000 datalogger (Campbell Scientific, Edmonton, Alberta) that recorded hourly and daily averages. Air temperature inside each chamber was measured by three shielded thermocouples suspended ~30 cm above the manure or straw located 0.5, 1.5, and 3.0 m from the air inlet. Manure temperature was measured by thermocouples attached to small floatation devices at ~5 cm depth in the center of each tank. Net radiation was measured inside chamber 2 and 5 at 1.5 m height above the manure or cover surface using Q-7.1 net radiometers (Campbell Scientific).

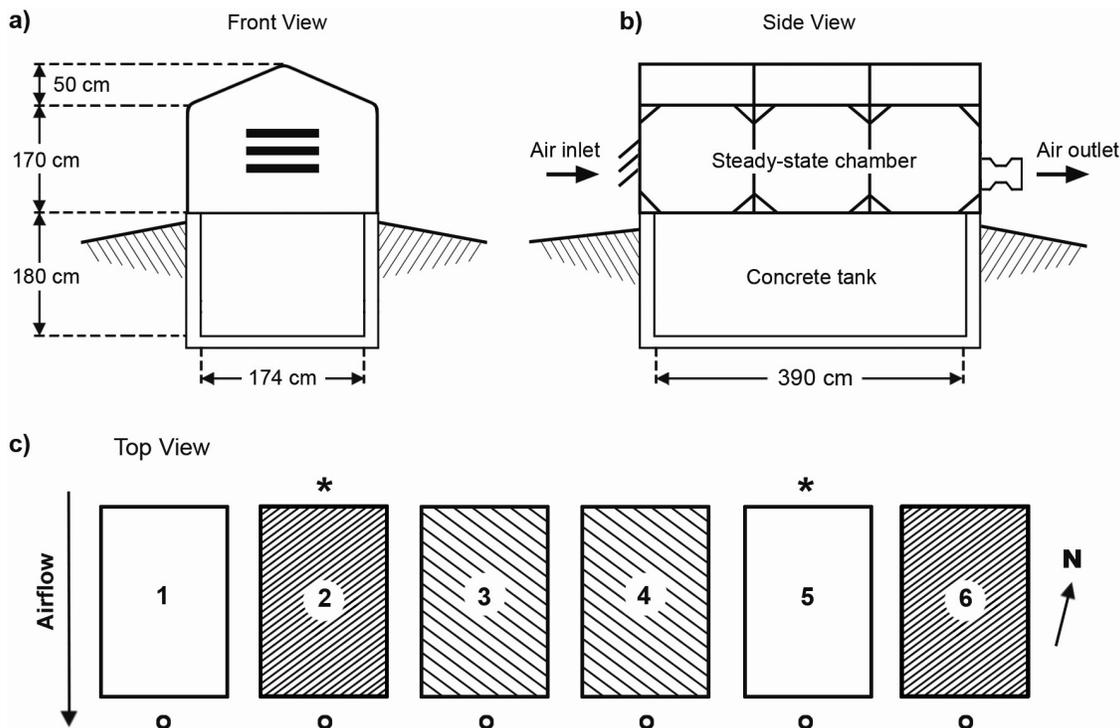


Figure 1. Diagram of the research site showing a cross-section of one manure storage tank and steady-state chamber from the (a) front and (b) side, and (c) top view of all six tanks indicating the inlet (*) and outlet (o) air sampling locations and cover treatments: dark shading = 30 cm (6.6 kg m^{-2}) straw, light shading = 15 cm (3.3 kg m^{-2}) straw, and unshaded = uncovered control. Tanks 1, 2, and 3 were agitated at the end of the study.

FLUX MEASUREMENTS

Steady-State Chambers

Six steady-state flux chambers (figs. 1a and 1b) were installed on top of the concrete tanks. The chambers were constructed with 0.15 mm (6 mil) greenhouse plastic (AT Plastic, Edmonton, Alberta) over an aluminum frame. Air entered the chambers through three vents on the inlet side and exited through a 35 cm diameter exhaust fan (Leader Fan Industries, Toronto, Ontario). Exhaust fans were always on when the chambers were in place. The speed of each exhaust fan was set to provide a nominal air-exchange rate in the chambers of $2\times$ to $3\times$ per minute. Airspeed near the manure surface was measured periodically with a hot-wire anemometer at 16 locations inside the chambers. It ranged from 0.5 to 1 m s^{-1} . The exhaust ducts had a venturi shape to promote laminar airflow in the narrow section, where exhaust airspeeds were measured continuously using cup anemometers and daily averages were recorded by a CR10X datalogger (Campbell Scientific). Flux densities were calculated using the steady-state equation (Livingston and Hutchinson, 1995):

$$F = \frac{Q}{A}(C_o - C_i) \quad (1)$$

where F is the flux density ($\text{mg m}^{-2} \text{ s}^{-1}$), Q is the flow rate of air through the chamber (airspeed in the venturi \times cross-sectional area of the venturi, $\text{m}^3 \text{ s}^{-1}$), A is the surface area of the manure tank (m^2), and C (mg m^{-3}) is the concentration of the gas in the inlet (C_i) and outlet air (C_o). Inlet air was sampled at two points, 1.7 m above ground, 0.3 m in front of tanks 2 and 5 (fig. 1c). It was assumed that these samples represented the inlet air of all six chambers, so in calculations C_i was the average of both inlet samples. For all gases,

outlet air was sampled at the center of each exhaust duct. The integrity of the chamber setup was tested using a mass recovery of N_2O (standard addition; Crill et al., 1995). A known mass of N_2O was added at the chamber inlets using a mass flow controller and a certified standard gas (Air Liquide Canada, Inc., Montreal, Quebec), while N_2O in the exhaust air was monitored using 10 Hz data with the trace gas analyzer described in the next section. The average recovery was 97%.

Despite their advantages, steady-state chambers alter the environment at the emission source (Livingston and Hutchinson, 1995; Cole et al., 2007). As a result, the absolute fluxes measured in this study have an uncertain relationship with the actual flux magnitudes that would occur without the chamber. We assume that the relative emissions versus time and treatment represent the actual differences. Thus, although we report the measured fluxes, the reader is urged to focus on treatment differences and temporal trends.

CH_4 , N_2O , and CO_2 Measurement

Air from each sampling location (2 inlet, 6 outlet) traveled through 25 m of polyethylene tubing to a valve box where air from one of the eight sites was directed to a high-flow air dryer and then to one of two tunable diode laser trace gas analyzers (TDLTGA, Campbell Scientific) that measured the concentration of CH_4 and N_2O . Certified reference gases were used (Air Liquide Canada, Inc.). The TDLTGA computer controlled the valves and recorded appropriate data from each sampling location, so an average concentration from each location was recorded every 4 min.

The concentration of CO_2 at each sampling location was determined using a similar setup with the following differences: no external air dryers were used, an infrared gas analyzer (Li-Cor 6400, Li-Cor Biosciences, Lincoln, Neb.) with

an N₂ reference gas measured the concentration at each site on a 20 min cycle. Further data processing was done using MATLAB (The Mathworks, Inc., Natick, Mass.).

NH₃ Measurement

Air from each sampling location traveled through 25 m of polyethylene tubing to an ammonia trap. Sample air was bubbled through 100 mL of 0.005 M H₃PO₄ (Chantigny et al., 2004) using a dispersion tube (Ace Glass, Vineland, N.J.). Airflow was regulated by a 3 L min⁻¹ inline orifice (O'Keefe Controls Co., Turnbull, Conn.) between the suction pump and an airflow meter (Gallus 2000, Actaris Metering Systems, Greenwood, S.C.) that recorded the volume of air sampled. All sample locations were monitored simultaneously using eight traps.

At the end of every sampling period, a 13 mL subsample from each beaker was placed in a plastic tube, capped, and refrigerated immediately. The aqueous NH₄⁺-N concentration in the subsample was determined by the phenate method using a Technicon AutoAnalyzer II (Technicon Instruments Corp., Tarrytown, N.Y.). This concentration (*C_{aq}*, mg NH₄⁺-N L⁻¹) was used to calculate the average concentration of NH₃-N in the sample air (*C_{air}*, mg NH₃-N m⁻³) during the sampling interval as:

$$C_{air} = \frac{C_{aq} \times V_{aq}}{V_{air}} \times \frac{1000 \text{ L}}{\text{m}^3} \quad (2)$$

where *V_{aq}* is the final volume of trapping solution, and *V_{air}* is the volume of sample air that bubbled through the solution. Depending on the sample location, *C_{air}* represents either *C_o* or *C_i* (eq. 1). For practical reasons, a sampling interval from 0830 h to 0830 h (the next day) was used to measure daily average flux. Samples were typically obtained three days per week, except during agitation when samples were obtained every day.

DATA ANALYSES

Due to power outages and vacuum pump repair, data were not obtained from 22 to 25 June and from 15 to 19 August for CO₂, and from 11 to 23 August for CH₄ and N₂O. For these periods, daily average data were interpolated using the linear or spline procedure and the INTERP1 function in MATLAB. The same function was used to interpolate between NH₃ sampling periods.

RESULTS AND DISCUSSION

ENVIRONMENTAL PARAMETERS

Environmental measurements during the study are shown in figure 2. Generally, net radiation peaked in mid-June and then gradually declined. Ambient air temperature increased until late July, peaking near 24°C, and then gradually decreased to a daily minimum near 10°C in October. The near-surface manure temperature varied among treatments and across time. Initially, the near-surface temperature was control > 15 cm straw > 30 cm straw. This can be explained by the insulation and high surface albedo provided by the straw covers in contrast to the low albedo (dark) manure, an important difference when solar radiation was high. However, later in the study when solar radiation was lower and the control treatment developed a surface crust (the temperature sensors were just beneath the crust), the near-surface temperature of

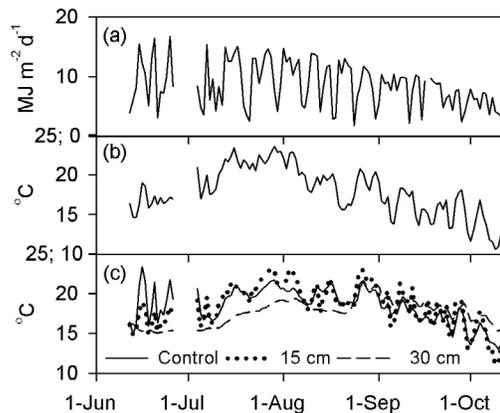


Figure 2. Daily environmental parameters at the site: (a) net radiation (average of chambers 2 and 5), (b) air temperature (average of all chambers), and (c) near-surface manure temperature (treatment average).

the control treatment was similar to the 15 cm straw treatment. At the end of the study, the 30 cm straw cover treatment had the warmest near-surface temperature, presumably due to insulation provided by the cover.

MANURE CHARACTERISTICS

The initial liquid manure characteristics were determined on 12 June 2007, six days after the manure was delivered to the research site. At that time, stratification was already apparent, as indicated by the dominant partitioning of DM and TC at the bottom of the tanks (table 1). As the study progressed, changes were observed in the manure characteristics. Decreases in ammonium-N and TN were found in all treatments, which suggested that N was being lost from the systems (as confirmed by the gas measurements). Increased pH was also observed in all treatments, which would favor increased NH₃ volatilization. In the control treatment, DM and TC became concentrated at the top of the tank as the study progressed. This was reflected by the surface crust that formed in early August (fig. 3). The crust development in this study was comparable to Misselbrook et al. (2005) where after 43 d, liquid dairy manure with 5.0% and 6.6% DM developed ~14 and ~30 cm crusts, respectively.

GAS EMISSIONS DURING UNDISTURBED STORAGE

Daily average flux densities (fig. 3) and cumulated emissions (fig. 4) show that emission rates changed temporally and differed among treatments. Fluxes of CO₂ were initially low, gradually increased to a maximum in mid-August, and subsequently declined. This trend generally followed changes in the near-surface manure temperature, except that autumn emission rates were higher than spring rates despite lower temperatures. This was possibly due to warmer sludge temperatures, but such data were not available. In August, cumulative CO₂ emissions from the 30 cm straw treatment were clearly higher than both other treatments and this difference increased in subsequent months. Fluxes of CH₄ were low for the first month and then began to increase rapidly in late July and early August. After peaking in August, emissions declined until early September, after which fluxes from the controls were stable or increasing while both straw treatments continued to decline slightly. Similar to the trend observed for CO₂, CH₄ fluxes in autumn were >5× higher than in the

Table 1. Manure characteristics at the start (12 June) and end (12 October) of the undisturbed storage period.

Parameter	Date	Treatment and Sample Location ^[a]					
		Control		15 cm Straw		30 cm Straw	
		Top	Bottom	Top	Bottom	Top	Bottom
Dry matter (%)	Start	1.8	6.4	1.6	6.0	1.8	5.5
	End	2.4	4.4	1.8	4.5	1.9	4.9
	% Change ^[b]	+30%	-31%	+15%	-24%	+5%	-11%
Ammonium-N (mg L ⁻¹)	Start	1,043	1,045	853	1,140	979	999
	End	815	895	920	985	950	935
	% Change ^[b]	-22%	-14%	+8%	-14%	-3%	-6%
Total N (mg L ⁻¹)	Start	2,500	1,930	1,845	2,190	2,455	2,505
	End	1,705	1,500	1,290	1,665	1,315	1,390
	% Change ^[b]	-32%	-22%	-30%	-24%	-46%	-45%
Total C (%)	Start	0.8	2.4	0.6	2.3	0.8	2.1
	End	1.0	2.0	0.8	2.0	0.8	2.2
	% Change ^[b]	+31%	-17%	+21%	-14%	+3%	+5%
pH	Start	6.8	6.9	6.8	6.8	7.0	6.9
	End	7.3	7.3	7.2	7.2	7.3	7.2
	% Change ^[b]	+7%	+7%	+5%	+7%	+4%	+4%

[a] Averages for each treatment are reported. Top \approx 10 cm below the surface cover or crust. Bottom \approx 10 cm above the bottom of the tank.

[b] % Change = [(end - start) / start] \times 100.

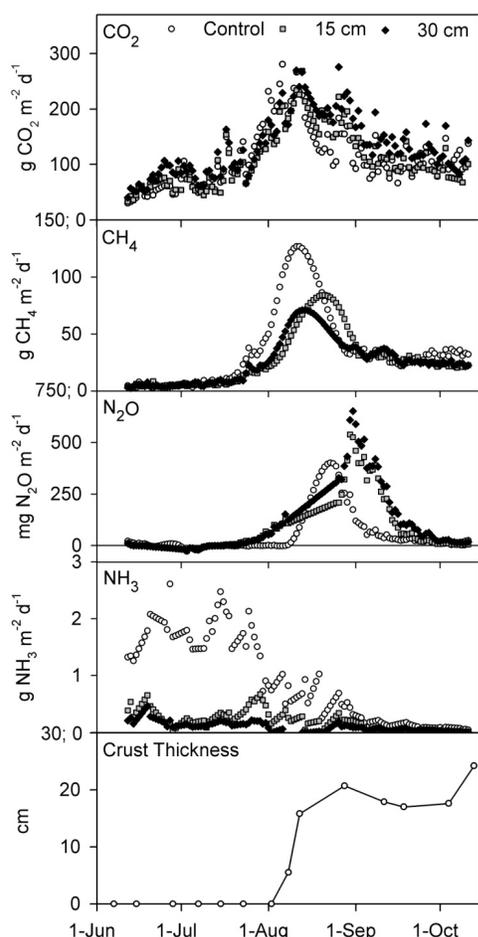


Figure 3. Daily average gas fluxes for each treatment and the average crust thickness on the controls during undisturbed storage.

spring. Cumulative CH₄ emissions from the control treatment were clearly higher than from both straw cover treatments, due primarily to the high August fluxes. Fluxes of

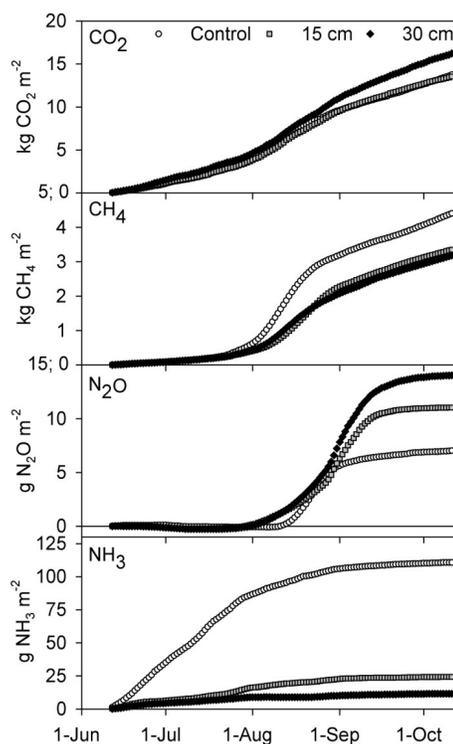


Figure 4. Cumulative emissions of CO₂, CH₄, N₂O, and NH₃ during undisturbed storage (treatment average).

N₂O were negligible before increasing in late July and early August. Fluxes from both straw treatments began to increase about three weeks before the control emissions increased. Peak emissions from both straw treatments were also higher and occurred later. Cumulative N₂O emissions were highest from the 30 cm straw treatment, followed by the 15 cm and control treatments, respectively. Fluxes of NH₃ were highest during the first six weeks, and then gradually declined. Fluxes from the control treatment were much higher than both covered treatments, especially in June and July. In all

treatments, NH₃ fluxes were lower in autumn than in the spring. Cumulative emissions from the control treatment were substantially higher than from the straw treatments, and the 30 cm straw treatment had the smallest losses.

Surface crusts formed on the control tanks in early August, coinciding with rapidly rising fluxes of CH₄ and CO₂ (fig. 3). This supports the explanation of crust formation described by Misselbrook et al. (2005), who suggested that crusts develop when gas bubbles (CH₄, CO₂) carry particles to the surface. Ebullition is important when gas production exceeds diffusion (Macintyre et al., 1995). Thus, this period of maximum CH₄ flux probably coincided with maximum ebullition and transport of solids to the surface. After about two weeks, crust thickness stabilized while CH₄ and CO₂ fluxes peaked and N₂O emissions began. This suggests that the crust was reducing CH₄ and CO₂ flux while enabling N₂O production. At the same time, NH₃ flux decreased. Taken together, these findings suggest that crust development can have a negative feedback on high emissions of CH₄ and CO₂, reducing emissions of multiple gases by acting as a physical barrier (e.g., CO₂, CH₄, and NH₃) and providing a site for microbial consumption (e.g., CH₄), but facilitating production of N₂O. This agrees with previous research on the effects of crusts on emissions (Sommer et al., 2000; Petersen et al., 2005; VanderZaag et al., 2008). Similar trends in the covered tanks suggest that solids may have also been brought up underneath the straw

covers, decreasing CO₂ and CH₄ flux by further reducing ebullition.

Treatment Effects on GHG Emissions

To compare the overall treatment effect on GHG emissions from undisturbed storage, monthly average flux data, cumulative emissions, and % reductions are provided in table 2. Emissions of CH₄ and N₂O have been converted to CO₂ equivalent global warming potential (CO₂e) using a 100-year time horizon (Solomon et al., 2007). These CO₂e results are summarized in table 3. Emissions of CO₂ are included in the table with the recognition that emissions from manure and straw are not net contributors to atmospheric CO₂ since the carbon was previously sequestered from the atmosphere.

First, consider the treatment effects on each gas separately (table 2). The highest CO₂ fluxes were observed from the 30 cm straw treatment in August, which contributed to cumulative CO₂ emissions 18% higher than the control. The 15 cm straw treatment had nearly identical CO₂ emissions to the control treatment. For CH₄ emissions, the control treatment had the highest fluxes in August, and overall the straw cover treatments provided 24% (15 cm straw) and 28% (30 cm straw) emission reductions. For N₂O emissions, the 30 cm straw treatment had the highest fluxes in August, and the straw covers increased cumulative emissions by 57% (15 cm straw) and 100% (30 cm straw). These observations reflect

Table 2. Average daily gas fluxes for each month and cumulative emission reduction provided by the straw cover treatments during undisturbed storage.

	Month / Parameter ^[a]	Control	15 cm Straw	30 cm Straw
CO ₂ Flux (g CO ₂ m ⁻² d ⁻¹)	June (13 - 30)	51.2	59.4	74.2
	July	97.5	82.4	98.7
	August	177.7	184.8	206.6
	September	100.6	106.3	137.7
	October (1 - 12)	110.9	86.3	110.4
	Total emission (g CO ₂ m ⁻²)	13.7 × 10 ³	13.6 × 10 ³	16.2 × 10 ³
	% Reduction ^[b]	n/a	1%	-18%
CH ₄ Flux (g CH ₄ m ⁻² d ⁻¹)	June (13 - 30)	4.4	4.7	4.3
	July	15.9	9.7	10.7
	August	83.3	59.5	52.4
	September	29.3	28.9	29.3
	October (1 - 12)	33.3	22.3	23.8
	Total emission (g CH ₄ m ⁻²)	4.4 × 10 ³	3.3 × 10 ³	3.2 × 10 ³
	Total emission (kg CO ₂ e m ⁻²)	110.1	83.7	79.5
% Reduction ^[b]	n/a	24%	28%	
N ₂ O Flux (mg N ₂ O m ⁻² d ⁻¹)	June (13 - 30)	5.9	-5.1	-5.7
	July	-6.4	6.6	3.4
	August	180.5	184.8	233.5
	September	45.1	171.2	220.0
	October (1 - 12)	14.5	6.1	18.7
	Total emission (g N ₂ O m ⁻²)	7.0	11.0	14.0
	Total emission (kg CO ₂ e m ⁻²)	2.1	3.3	4.2
% Reduction ^[b]	n/a	-57%	-100%	
NH ₃ Flux (g NH ₃ m ⁻² d ⁻¹)	June (13 - 30)	1.75	0.32	0.23
	July	1.69	0.32	0.15
	August	0.64	0.21	0.04
	September	0.14	0.05	0.05
	October (1 - 12)	0.69	0.02	0.02
	Total emission (g NH ₃ m ⁻²)	110.7	24.3	11.6
	% Reduction ^[b]	n/a	78%	90%

^[a] CO₂ equivalent global warming potential (CO₂e) calculated using the following conversion factors: CH₄ = 25, N₂O = 298 (Solomon et al., 2007).

^[b] % Reduction = [(control emission - covered emission) / control emission] × 100.

Table 3. Total GHG emissions from each treatment and the emission reduction provided by each straw cover treatment during undisturbed storage. CO₂ equivalent global warming potential (CO₂e) calculated using: CH₄ = 25, N₂O = 298 (Solomon et al., 2007).

Emission	Control (kg CO ₂ e m ⁻²)	15 cm Straw (kg CO ₂ e m ⁻²)	30 cm Straw (kg CO ₂ e m ⁻²)
CO ₂ [a]	13.7	13.6	16.2
CH ₄	110.1	83.7	79.5
N ₂ O	2.1	3.3	4.2
Total	125.9	100.6	99.9
% Reduction[b]		20%	21%

[a] CO₂ is included with the recognition that emissions from manure and straw are not net contributors to atmospheric concentrations.

[b] % Reduction = $([\text{control emission} - \text{covered emission}] / \text{control emission}) \times 100$.

the multiple roles that straw covers play. As a physical barrier, they reduce mass transfer and impede ebullition, but they also add carbon and provide a site for aerobic microbial activity. The thickness of the cover affects the balance among these roles. In this case, the 30 cm cover may have reduced transport more than the 15 cm treatment (therefore lowering CH₄ losses), but the additional carbon increased CO₂ loss and the increased surface area may have facilitated more N₂O production.

Now, consider the treatment effects when all three GHGs are combined (table 3). During the four months of undisturbed storage, the control treatment had the highest cumulative GHG emissions. Straw covered tanks emitted less, and the 15 and 30 cm treatments had nearly identical totals. Thus, although the two straw cover treatments had different effects on each GHG individually, when taken together they both provided about 20% reduction of GHG emissions. The reductions were due to reducing CH₄ emissions, and were offset by increased emissions of CO₂ and N₂O.

To confirm that interpolation did not alter the conclusions drawn from the data, the results were also analyzed using only measured data. The results were similar. If interpolated data were not included, then the 15 cm straw treatment provided an 18% overall GHG reduction, and the 30 cm straw treatment provided a 15% reduction. These overall reductions are lower than 20% because most of the missing data occurred in late August when emissions were high and the covers were most effectively reducing CH₄. Additionally, the 3% difference between the two straw treatments was mainly due to higher CO₂ emissions from the 30 cm treatment.

Treatment Effects on NH₃ Emissions

Straw covers were effective at reducing NH₃ fluxes throughout the study (table 2). In most months, NH₃ flux increased in order of decreasing straw thickness: 30 cm straw < 15 cm straw < control. Covers were most effective early in the study when fluxes were highest. At the end of the 122 d of undisturbed storage, cumulative emissions were reduced 90% by 30 cm straw covers and 78% by 15 cm straw covers.

GAS EMISSIONS DURING AGITATION

At the end of the four-month storage period, three tanks were agitated. This disturbance had a substantial effect on the fluxes of CO₂, CH₄, and NH₃ (fig. 5) but had little effect on N₂O. Hourly data for CO₂ and CH₄ show that fluxes increased dramatically when agitation began. The maximum fluxes from agitated tanks were highest on the first day, but it is difficult to discern whether flux trends and maxima on

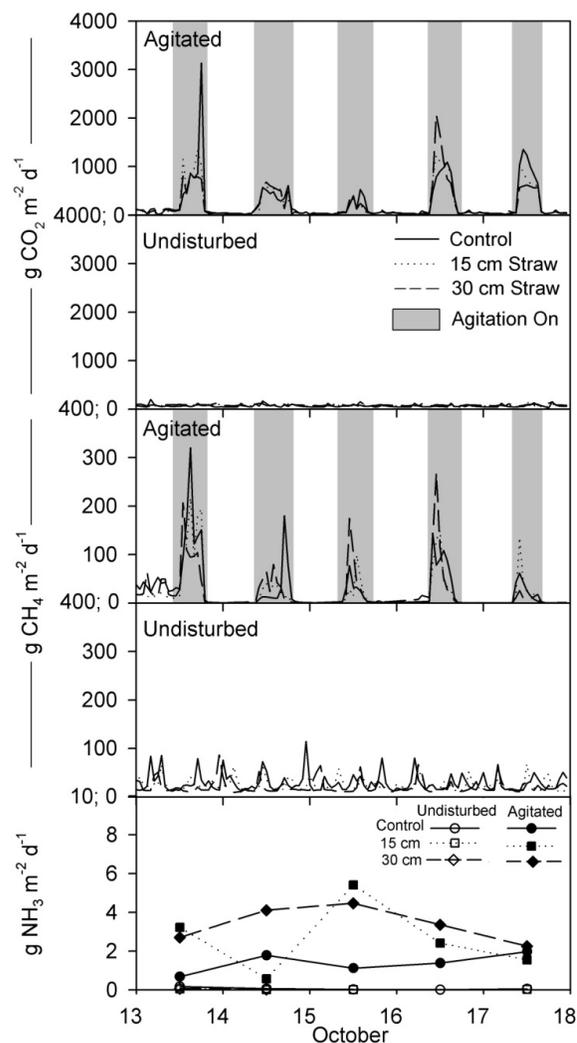


Figure 5. Fluxes of CO₂, CH₄, and NH₃ during the 5 d agitation period (agitation had little effect on N₂O, thus it is not shown). Hourly average data are shown for CO₂ and CH₄ (expressed in units of d⁻¹ for ease of comparing magnitudes to fig. 3). Daily average data are shown for NH₃ (data points are placed at 1200 h on the day obtained). Where hourly data are given, shaded areas indicate when agitation was taking place. Emission spikes from undisturbed tanks are due to ebullition (based on visual observation).

subsequent days were due to treatment differences, changes in dissolved gas storage, or other factors. When the agitators were turned off, the flux of CO₂ and CH₄ quickly dropped below pre-agitation levels, and below the level in undisturbed tanks. In fact, CH₄ emissions in all agitated treatments approached zero when the agitators were off. Daily average NH₃ flux data show that agitation increased emissions in all tanks, with the largest increases in covered treatments. Unlike CO₂ and CH₄ emissions, NH₃ fluxes reached a maximum on the third day in the straw treatments and the fifth day in the control tank.

The lack of agitation effect on N₂O flux is expected since N₂O is produced near the manure-air interface, so the amount of dissolved N₂O in the bulk manure would be minimal. In contrast, CO₂ and CH₄ are produced in the bulk manure and therefore accumulate as dissolved gas and bubbles. In particular, CH₄ has a very low solubility, and its transport is limited by liquid-phase resistance. When the manure is agitated, CH₄

Table 4. Emissions from each treatment during agitation and undisturbed storage.

	Control		15 cm Straw		30 cm Straw	
	Agitated	Undisturbed	Agitated	Undisturbed	Agitated	Undisturbed
GHGs	(kg CO ₂ e m ⁻²)					
CO ₂	1.3	0.5	1.2	0.4	1.1	0.6
CH ₄	3.0	3.6	2.4	3.1	2.6	2.5
N ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
Agitation period ^[a]	4.3	4.1	3.7	3.5	3.7	3.2
Undisturbed period ^[b]	125.9	125.9	100.6	100.6	99.9	99.9
GHG total	130.2	130.0	104.3	104.1	103.6	103.1
% During agitation	3%	3%	4%	3%	4%	3%
% Reduction ^[c]	N/A	--	20%	--	20%	--
NH ₃	(g m ⁻²)					
Agitation period ^[a]	6.9	0.3	13.2	0.0	16.9	0.0
Undisturbed period ^[b]	110.7	110.7	24.3	24.3	11.6	11.6
NH ₃ total	117.6	111.0	37.5	24.3	28.5	11.6
% During agitation	6%	0%	35%	0%	59%	0%
% Reduction ^[c]	N/A	--	68%	--	76%	--

^[a] Each cover treatment had two replicates. During the agitation period, one replicate was agitated, and the other was undisturbed.

^[b] The average for each cover treatment is used here. Results were similar when data from each tank were used. The % during agitation was nearly identical for GHGs (3%) and was higher for NH₃ (44% and 66% for 15 and 30 cm covers, respectively). For NH₃, this decreased the % reduction from agitated tanks to 54% and 61% for 15 and 30 cm covers, respectively.

^[c] % Reduction = [(agitated control emission - covered emission) / agitated control emission] × 100.

is rapidly emitted as trapped bubbles are released. Dissolved CH₄ is also released as the turbulent liquid contacts the air. When agitation stops, the liquid-phase resistance is restored. The concentration gradient between the manure and air has diminished, so emissions decline. Agitation may also decrease CH₄ production because the turbulent liquid is exposed to oxygen, which could increase the redox potential enough to inhibit methanogenesis. Factors affecting CO₂ are similar, except that CO₂ has a higher solubility and is in equilibrium with carbonate. Thus, there may be more dissolved CO₂ (due to solubility), and what is lost during agitation can be replenished by the equilibrium and microbial production. The differences in solubility and equilibria may explain why CO₂ continued to be emitted when the agitators were off, whereas CH₄ was not. This may also explain why CO₂ emissions on the final two days of agitation were similar to the first day, while CH₄ emissions declined. With respect to CH₄ and CO₂, these data show that agitation causes a substantial release of dissolved gas and trapped bubbles. However, releases from covered and control treatments were similar, suggesting that the covers did not trap more gas in the manure. This observation might be confounded by crusting on the control causing more gas accumulation than would otherwise occur.

Ammonia is a soluble gas, and its transport is limited by gas-phase resistance. Furthermore, NH₃ is in equilibrium with aqueous NH₄⁺, so when lost to the atmosphere it can be quickly replenished. When a straw cover or crust is destroyed during agitation, the primary resistance to emission is reduced. Thus, fluxes will increase until limited by other constraints, and eventually decrease as the concentration of NH₄⁺ declines. As shown in figure 5, NH₃ fluxes increased from all treatments when agitated. Emission rates from the agitated cover treatments were, on average, higher than the control. This may be due to higher concentrations of ammonium-N in the covered tanks (table 1), which is consistent with the low NH₃ emissions previously observed in those treatments. In other words, covered tanks retained more ammonium-N while covered, but had more to lose when agi-

tated. These data show that agitation led to increased loss of NH₃, with substantially higher losses from covered tanks in comparison to the agitated control.

Now consider this agitation period (5 d) in the context of the entire manure storage period (127 d) to determine whether agitation negated any benefits from the straw covers observed during the previous 122 d. Agitated tanks emitted ~2× to 3× more CO₂ than undisturbed tanks of the same treatment (table 4). Due to extremely low emissions while the agitators were off, CH₄ emissions from agitated tanks were similar to undisturbed tanks. For all treatments, agitation contributed 3% to 4% of the total storage (undisturbed + agitation) GHG emissions. Thus, agitation did not change the benefits accrued during undisturbed storage (20% to 21% GHG reduction). However, the same is not true for NH₃. Cumulative NH₃ losses during agitation were ~2× higher for straw treatments than the agitated control. Since emissions from both straw treatments during undisturbed storage were low, the high fluxes during agitation represented 35% and 59% of the total storage losses for the 15 cm and 30 cm straw cover treatments, respectively. Put another way, more NH₃ was emitted from the 30 cm straw treatment during 5 d of agitation than during 122 d of undisturbed storage. Thus, the benefits of NH₃ emission reduction using straw covers were diminished when agitation was included. Over the total storage period, NH₃ reduction was 68% with 15 cm straw covers and 76% with 30 cm straw covers in comparison to the agitated control.

CONCLUSION

During the 122 d period of undisturbed manure storage, the 15 cm and 30 cm straw cover treatments reduced GHG emissions by 20% and 21%, respectively, compared to the uncovered control (a surface crust formed on the controls after ~60 d). This reduction was due to lower CH₄ emissions from covered storages, as the straw covers generally increased emissions of N₂O and CO₂. The 30 cm straw covers

had lower CH₄ emissions but higher emissions of N₂O and CO₂ than the 15 cm covers. During the same period, the 15 cm and 30 cm cover treatments reduced NH₃ emissions by 78% and 90%, respectively.

During the subsequent 5 d period of intermittent agitation, substantial releases of CO₂, CH₄, and NH₃ were observed from all agitated tanks. The high fluxes of CO₂ and CH₄ were offset by low fluxes between agitation sessions. Thus, agitated tanks only emitted slightly more than undisturbed tanks. Overall, the agitated straw treatments both still provided a 20% GHG emission reduction (after 127 d of storage, compared to the agitated control). However, agitation did affect NH₃ emissions. The agitated 15 and 30 cm straw cover treatments emitted ~2× more NH₃ than the agitated control. For the 30 cm treatment, this was more NH₃ than had been emitted during the 122 d undisturbed storage period. Thus, the overall reduction of NH₃ emissions provided by the 15 cm and 30 cm straw cover treatments declined to 68% and 76%, respectively, in comparison to the agitated control.

Considering the entire storage period including agitation, these data suggest that straw covers can provide reductions of CH₄ and NH₃ emissions from liquid dairy manure. Thicker covers provided greater reductions of CH₄ and NH₃, but increased N₂O and CO₂ emissions, negating some benefits. Agitation in autumn increased overall emissions of NH₃, but caused negligible increase in GHG emissions. Furthermore, agitation increased NH₃ losses more from straw covered tanks than from the control, but affected CH₄ emissions from covered and control tanks similarly. This suggests that the covers did not merely trap CH₄ temporarily, but must have reduced its production or increased its consumption. Had no crust formed on the controls, the emission reductions probably would have been greater. Batch-loading used in this study may limit the application of these results to other situations; further research to compare batch versus continuous loading would be useful.

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