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Abstract
Carbonaceous and nitrogenous gases are produced during storage of livestock manure, with the magnitude of production being affected by the chemical properties of the manure and the physical conditions of storage. This lab-scale study quantifies the emission rates of ammonia (NH₃), nitric oxide (NO), and greenhouse gases (GHG), i.e., methane (CH₄), carbon dioxide (CO₂), nitrous oxide (N₂O), from biogas digester effluent (BDE) stored at different depths of 1.0, 1.5, and 2.0 m in dynamic emission vessels (DEVs). The selected storage depths were reflective of the typical depth range of on-farm BDE storage in China. The static storage was held at a relatively constant media temperature of 15°C and an air exchange rate of 11.5 air changes per hour (ACH) for 78 days. Each depth regimen was replicated four times using four DEVs (12 DEVs total). The results showed that the mean (±SE) daily gaseous emission rates per volume of BDE stored at 1.0, 1.5, and 2.0 m depths, in g gas m⁻³ d⁻¹, were, respectively, 9.1 (±0.7), 10.1 (±0.6), and 10.1 (±0.4) for CH₄ (p = 0.39); 38.0 (±2.2), 34.5 (±1.3), and 30.7 (±0.6) for CO₂ (p < 0.05); 1.9 (±0.11), 1.3 (±0.08), and 0.9 (±0.03) for NH₃ (p < 0.05); and 6.7 (±0.5) × 10⁻³, 5.0 (±0.8) × 10⁻³, and 3.4 (±0.2) × 10⁻³ for N₂O (p < 0.05). Nitric oxide (NO) emissions were negligible. The overall GHG (CH₄ + N₂O + CO₂) emissions were dominated by CH₄, which accounted for more than 85% of the CO₂-equivalent emissions for all three storage depths. The CH₄ emissions peaked during the early storage period, with the first 20-day cumulative emissions accounting for 56% to 58% of the total 78-day storage emissions. The results reveal that storage of BDE at 2.0 m depth yielded lower CO₂, NH₃, and N₂O emission rates but similar CH₄ emission rates compared to the 1.0 and 1.5 m depths.

Keywords
Ammonia, Biogas digester effluent (BDE), Carbon dioxide, Methane, Nitrous oxide, Storage depth

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AMMONIA AND GREENHOUSE GAS EMISSIONS FROM BIOGAS DIGESTER EFFLUENT STORED AT DIFFERENT DEPTHS

Y. Wang, H. Dong, Z. Zhu, T. Li, K. Mei, H. Xin

ABSTRACT. Carbonaceous and nitrogenous gases are produced during storage of livestock manure, with the magnitude of production being affected by the chemical properties of the manure and the physical conditions of storage. This lab-scale study quantifies the emission rates of ammonia (NH₃), nitric oxide (NO), and greenhouse gases (GHG), i.e., methane (CH₄), carbon dioxide (CO₂), nitrous oxide (N₂O), from biogas digester effluent (BDE) stored at different depths of 1.0, 1.5, and 2.0 m in dynamic emission vessels (DEVs). The selected storage depths were reflective of the typical depth range of on-farm BDE storage in China. The static storage was held at a relatively constant media temperature of 15°C and an air exchange rate of 11.5 air changes per hour (ACH) for 78 days. Each depth regimen was replicated four times using four DEVs (12 DEVs total). The results showed that the mean (±SE) daily gaseous emission rates per volume of BDE stored at 1.0, 1.5, and 2.0 m depths, in g gas m⁻³ d⁻¹, were, respectively, 9.1 (±0.7), 10.1 (±0.6), and 10.1 (±0.4) for CH₄ (p = 0.39); 38.0 (±2.2), 34.5 (±1.3), and 30.7 (±0.6) for CO₂ (p < 0.05); 1.9 (±0.11), 1.3 (±0.08), and 0.9 (±0.03) for NH₃ (p < 0.05); and 6.7 (±0.5) × 10⁻³, 5.0 (±0.8) × 10⁻³, and 3.4 (±0.2) × 10⁻³ for N₂O (p < 0.05). Nitric oxide (NO) emissions were negligible. The overall GHG (CH₄ + N₂O + CO₂) emissions were dominated by CH₄, which accounted for more than 85% of the CO₂-equivalent emissions for all three storage depths. The CH₄ emissions peaked during the early storage period, with the first 20-day cumulative emissions accounting for 56% to 58% of the total 78-day storage emissions. The results reveal that storage of BDE at 2.0 m depth yielded lower CO₂, NH₃, and N₂O emission rates but similar CH₄ emission rates compared to the 1.0 and 1.5 m depths.

Keywords. Ammonia, Biogas digester effluent (BDE), Carbon dioxide, Methane, Nitrous oxide, Storage depth.

Anaerobic digestion of livestock manure converts organic matter into biogas, a mixture of methane (CH₄, typically 60% to 70%) and carbon dioxide (CO₂, 30% to 40%) and other trace gases, which can be used as a fuel source for production of heat and/or electricity. In addition to the economic benefits of creating renewable energy, anaerobic digestion systems are attractive because they help in reducing odors, recycling organic nutrients, improving the utilization of manure as fertilizer, and reducing greenhouse gas (GHG) emissions when the biogas is harvested (Umetsu et al., 2005; IPCC, 2006). For these reasons, anaerobic digesters have been widely used in China. As of 2012, China maintained over 91,600 biogas digesters that use animal manure and agricultural residues, with a total digestion volume of 13.5 million m³ (China Ministry of Agriculture, 2013). However, operation of biogas digesters produces a large volume of digested effluent that requires proper management to further alleviate potential environmental impact.

Biogas digester effluent (BDE) is generally stored in uncovered tanks before land application as crop or orchard nutrients. Because of its high concentrations of organic matter, BDE storage has been shown to be an important source of GHG emissions (Sommer et al., 2000; Clemens et al., 2006; Hansen et al., 2006; Menardo et al., 2011). Anaerobic fermentation also increases the ammonium ion (NH₄⁺) concentration in BDE, which facilitates ammonia (NH₃) emissions during storage (Sommer, 1997; Sommer et al., 2000; Clemens et al., 2006). Furthermore, nitrous oxide (N₂O) and nitric oxide (NO) are produced from the processes of nitrification and/or denitrification (Chadwick et al., 2011). Because NH₄⁺ is the substrate for nitrification, increasing NH₄⁺ concentration leads to higher N₂O emissions (Sommer et al., 2000; Amon et al., 2006). However, negligible N₂O emissions during slurry storage were observed in some studies (Clemens et al., 2006).

Several studies have been conducted concerning gaseous emissions from BDE storage. The residual biogas potentials of anaerobically digested waste can vary widely (Hansen et al., 2006), depending on the anaerobic digestion (AD) op-
erating parameters such as feedstock type and quality, organic loading rate, and hydraulic retention time (Lindorfer et al., 2007; Menardo et al., 2011). Gaseous emissions from BDE storage are also affected by management practices and storage environment, such as storage temperature (Kaparaju and Rintala, 2003), air velocity over the slurry surface (Balsari et al., 2007), solar radiation (Sommer, 1997), presence or absence of storage cover (Clemens et al., 2006), solid-liquid separation of BDE (Kaparaju and Rintala, 2008), and dissolved oxygen (DO) level in the storage effluent (Molodovskaya et al., 2008).

Storage depth is one of the key parameters affecting methane (CH$_4$) production in the septic tank storage process (IPCC, 2006). A shallow septic tank (<1 m deep) often possesses an aerobic environment, producing little or no CH$_4$. Septic tanks with depths of 2 to 3 m are usually anaerobic and are expected to produce greater amounts of CH$_4$ (IPCC, 2006). Emissions of CH$_4$, CO$_2$, and NH$_3$ from piggery wastewater stored at different depths (0.15, 0.40, and 0.65 m) in deep pits were studied by Ye et al. (2011a, 2011b, 2011c). Those studies showed no strong correlation between the NH$_3$ emission rate and the piggery wastewater depth, and the shallowest depth produced higher CH$_4$ and CO$_2$ emissions per volume of media. Methane emissions from liquid cattle manure storage with different depths (0.3, 0.6, 0.9, and 1.2 m) were studied by Massé et al. (2008). The authors reported that reducing the depth of the liquid manure in the tank from 0.6 to 0.3 m reduced CH$_4$ emissions by 26%. In comparison, CH$_4$ emissions increased by 52.4% when the storage manure depth increased from 0.6 to 1.2 m.

As outlined above, all studies on storage depth have focused on storing raw manure. Limited data are available concerning emissions of NH$_3$, GHG (CH$_4$, N$_2$O, and CO$_2$), and nitric oxide (NO) from BDE at different storage depths. Therefore, the objective of this lab-scale study was to investigate the effects of storage depth on gaseous emission rates of NH$_3$, CH$_4$, N$_2$O, NO, and CO$_2$ from BDE. The results will help in identifying the storage depth or range of depths that will lead to reduced gaseous emissions from BDE storages, and hence reduce the overall environmental impact of animal production.

**MATERIALS AND METHODS**

**BDE AND STORAGE DEPTH OPTIONS**

BDE was collected from a commercial swine farm in suburban Beijing, China. To improve productivity of the biogas digester in winter, flush water mixed with solid manure (collected with scrapers) from the pig barns at an average volume ratio of 6:1 was used for the influent of the biogas digester. The biogas digester operated under mesophilic conditions (35°C) with a hydraulic retention time of approximately 20 days. The BDE used in this experiment was fresh effluent from the biogas digester, and it was transported (in insulated containers) to our research lab in Beijing within 2 h after collection at the farm.

Storage depths of 1.0, 1.5, and 2.0 m were selected to reflect the typical depths of on-farm BDE or liquid livestock manure storage in China. Homogenized through vibration/motion of the transport vehicle, the media was quickly pumped into the storage vessels (described below), where it was held for 78 days at a relatively constant temperature of 15°C ±2°C (SD). Each storage regimen was replicated four times.

**DYNAMIC EMISSION VESSELS (DEVs)**

Twelve Plexiglas column-shaped DEVs were constructed and used in the study, with four identical DEVs assigned to each storage depth regimen, hence four replicates per regimen. The DEVs had the same inside diameter of 0.4 m but different heights of 1.25, 1.75, and 2.25 m to achieve the same headspace of 0.25 m and corresponding BDE storage depths of 1.0, 1.5, and 2.0 m, respectively. Each DEV had an air inlet and outlet on the lid. In addition, a Plexiglas guiding tube (9.4 cm inside diameter × 40 cm length) was partially inserted from the lid into the BDE (15 cm) for media sampling (fig. 1). A custom-made device for stratified media sampling was used to assess the vertical profile of the BDE with minimal agitation of the media (fig. 2). The liquid sampling device was fabricated at the Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, Beijing, China, and was made of stainless steel tubing with a 20 mm outside diameter, 26 cm length, and 50 mL capac-
ity. The sampler had an open top end and was fitted with a ball check at the bottom. When the device was lowered into the BDE through the 40 cm guiding tube, a liquid sample of the desired depth region was taken into the bottom of the device, and the sample of the upper portion overflowed from the top of the device. This design eliminated the need for installing faucets in the column wall.

The BDE storage temperature was set at 15°C to simulate the annual mean temperature under production conditions in Beijing. During the 78 consecutive days of storage from January to March, the ambient temperature of the storage lab varied from 10°C to 15°C. To maintain the desired storage temperature, an on/off controlled electric heating cable (on at setpoint – 1°C, off at setpoint + 1°C) was wrapped around the aluminum foil-covered outer wall of each vessel. The aluminum foil enhanced the heat distribution of the heating cable. The heating cable was then covered with 2 cm of foam thermal insulation to help maintain the desired storage temperature in the DEV. The BDE temperature was recorded at the center of the DEV every hour throughout the experiment period using a TidbiT v2 temp logger (Onset Computer Corp., Bourne, Mass.). The stored BDE had a surface area of 0.1256 m² per vessel. The air exchange rate of the head space was set and maintained at 6 L min⁻¹ (via a calibrated airflow meter/controller), yielding 11.5 air changes per hour (ACH). A schematic and photograph of the experimental setup are shown in figures 3 and 4, respectively.

**GAS SAMPLING AND ANALYSIS SYSTEM**

A photoacoustic multi-gas analyzer (Innova 1412i, LumaSense Technologies, Ballerup, Denmark) and a NO-NO₂-NOx analyzer (model 42i, Thermo Fisher Scientific, Inc., Waltham, Mass.) along with a multichannel sampler (fabricated at the Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, Beijing, China) were used to sample and analyze air samples from the 12 DEV outlets and one fresh air inlet. Before measurements, the gas analyzers were checked and calibrated, as needed, using individual CO₂, CH₄, N₂O, NH₃, NO, and nitrogen gas (N₂) standard calibration gases procured from the National Standard Material Center in Beijing, China. The gas analyzers were checked every 1 or 2 weeks during the experiment with the zero and span gases to ensure that deviations in the measured readings were within 5% of the reference values; otherwise, the gas analyzer was recalibrated. For each of the 12 outlets and the fresh air inlet, the air samples were analyzed for ten 1 min cycles with the Thermo 42i analyzer and for five 2 min cycles with the Innova 1412i analyzer. The difference in sample analysis cycle times between the two instruments was due to their different response times, with the Innova 1412i analyzer taking longer to become stabilized. The readings associated with the last sample for each of the analyzers were taken as the measured values, while the previous cycles were used for stabilization of the readings. Thus, 130 min were required to complete one system sampling cycle. A total of 11 measurements were made per
Determination of Gaseous Emission Rate

Concentrations of CO$_2$, CH$_4$, N$_2$O, NH$_3$, and NO in the inlet air and exhaust air were automatically measured and recorded. With a known airflow rate and surface area, the gaseous emission rates from the storage vessels were calculated using the following equations:

$$\text{ERA} = \left( C_i - C_o \right) \times V \times R + A$$  

$$\text{ERV} = \left( C_i - C_o \right) \times V \times R + V$$

where $\text{ERA}$ and $\text{ERV}$ are the emission rates by area and by volume (mg m$^{-2}$ h$^{-1}$ and mg m$^{-3}$ h$^{-1}$, respectively), $C_i$ is the gas concentration of the inlet air (mg m$^{-3}$), $C_o$ is the gas concentration of the outlet air (mg m$^{-3}$), $VR$ is the ventilation rate (m$^3$ h$^{-1}$) at standard temperature and pressure (STP, 0°C and 101.325 kPa), $A$ is the surface area of stored BDE in the DEV (m$^2$), and $V$ is the volume of stored BDE (m$^3$).

Media Sample Collection and Analysis

Two representative (500 mL) BDE samples were collected from each DEV before and after the storage period, respectively, after mixing the media for homogeneity. Total solids (TS), volatile solids (VS), total nitrogen (TN), total ammonia nitrogen (TAN), and chemical oxygen demand (COD) contents were determined following the China National Standards (CNS) (China National Environmental Protection Agency, 2002). The analytical methods of the CNS for determining the chemical and nutrient properties of water and wastewater parallel the APHA Standard Methods (APHA, 2005). The TS and VS contents were determined by oven-drying the sample at 105°C for 24 h and using a muffle furnace at 550°C for 2 h, respectively. The COD content was determined by the dichromate method following CNS GB11914-89. The TAN concentration was determined by the distillation-neutralization titration method following CNS HJ537-2009 with a distillation unit (B-324, Büchi AG, Flawil, Switzerland). The TN concentration was measured with the alkaline potassium persulfate digestion UV spectrophotometric method using an ultraviolet spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan). The collected samples were centrifuged and filtered through 0.45 μm membrane filters (Gelman type Supor-450, Pall Corp., Ann Arbor, Mich.) before analysis for contents of total oxidized nitrogen (NO$_x$--N), dissolved organic nitrogen (DON), and dissolved organic carbon (DOC). The NO$_x$--N and DON contents were monitored with a flow injection analyzer (FIAstar 5000, Foss, Hillerød, Denmark), while the DOC content was measured with a non-dispersive...
infrared total organic carbon (TOC) analyzer (Apollo 9000, Teledyne Tekmar, Mason, Ohio).

The BDE samples from the middle layer of the DEVs were collected each week using the sampling device described previously, and the pH value was measured with a calibrated pH meter (Easy pH, WTW GmbH, Munich, Germany). The DO level was measured directly with a DO probe (HI9146, Hanna Instruments, Woonsocket, R.I.) inserted into the middle layer of the BDE through the media sampling port.

**Statistical Analyses**

Statistical analyses of the gaseous emissions data and the BDE property parameters were performed by analysis of variance (ANOVA) using ProcGLM in SAS 9.2 (SAS Institute, Inc., Cary, N.C.), followed by Duncan’s multiple means comparison. Differences between the treatment means were considered significant at p < 0.05.

**RESULTS AND DISCUSSION**

**Chemical Properties of BDE during Storage**

The chemical properties of stored BDE at all three depths showed similar temporal trends during the 78-day storage period (table 1). The organic matter was decomposed continually with storage time, resulting in lower COD, DOC, TN, and DON contents at the end of the storage at all three depths. As a substrate for NH3 emission, TAN content in all three regimens showed a marked increase at the end of storage. The increased TAN content might have been caused by decomposition of the abundant organic matter content, with the ending TAN content at the greatest (2.0 m) depth being highest. The pH of the BDE media also increased significantly at the end of the storage period, with the largest pH increase occurring at the shallowest (1.0 m) depth. An elevated pH would accelerate the process of bacterial ammonification (uric acid → NH4+/NH3) and gaseous NH3 production and thus result in the majority of nitrogen loss as NH3 in the stored manure (Elliott and Collins, 1982). Hence, different TAN and pH levels jointly affected NH3 emission rates from the different storage regimens.

**Table 1. Chemical properties of the biogas digester effluent (BDE) at the start and end of 78-day storage at depths of 1.0, 1.5, and 2.0 m and a relatively constant temperature of 15 ± 2°C (values are means ± SE; n = 4).**

<table>
<thead>
<tr>
<th>Chemical Property(^{[a]})</th>
<th>1.0 m Storage Depth</th>
<th>1.5 m Storage Depth</th>
<th>2.0 m Storage Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start</td>
<td>End</td>
<td>Start</td>
</tr>
<tr>
<td>pH</td>
<td>7.9 ±0.0 d</td>
<td>8.4 ±0.0 a</td>
<td>7.9 ±0.0 d</td>
</tr>
<tr>
<td>DO (mg L(^{-1}))</td>
<td>0.28 ±0.00</td>
<td>0.42 ±0.13</td>
<td>0.47 ±0.20</td>
</tr>
<tr>
<td>COD (mg L(^{-1}))</td>
<td>23,623 ±203 bc</td>
<td>20,653 ±577 d</td>
<td>23,918 ±358 bc</td>
</tr>
<tr>
<td>DOC (mg L(^{-1}))</td>
<td>320 ±22 a</td>
<td>260 ± b</td>
<td>301 ±23 ab</td>
</tr>
<tr>
<td>TN (mg L(^{-1}))</td>
<td>2610 ±92 a</td>
<td>2312 ±48 b</td>
<td>2655 ±56 a</td>
</tr>
<tr>
<td>TAN (mg L(^{-1}))</td>
<td>1679 ±19 d</td>
<td>1790 ±41 c</td>
<td>1724 ±48 cd</td>
</tr>
<tr>
<td>DON (mg L(^{-1}))</td>
<td>365 ±27 b</td>
<td>67 ±10 c</td>
<td>392 ±14 ab</td>
</tr>
<tr>
<td>TS (% w.b.)</td>
<td>3.2 ±0.1 ab</td>
<td>2.8 ±0.1 c</td>
<td>3.3 ±0.2 ab</td>
</tr>
<tr>
<td>VS (% w.b.)</td>
<td>1.80 ±0.0 a</td>
<td>1.5 ±0.1 b</td>
<td>1.9 ±0.2 a</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Means within each row followed by different letters are significantly different (p < 0.05).

\(^{[b]}\) w.b. = wet basis.

**Figure 5. Daily CH4 emission rate (mean ±SE) of biogas digester effluent (BDE) stored at depths of 1.0, 1.5, and 2.0 m.**

**Gas Emissions from BDE during Storage**

**CH4 Emissions**

Temporal profiles of the emission rates and cumulative emissions of CH4 from the BDE storage at different depths are shown in figures 5 and 6. The CH4 emission rate per m3 of stored BDE showed no significant differences among the three depths during the 78 d storage period (p = 0.39) and averaged (mean ± SE) 9.1 ± 0.7, 10.1 ± 0.6, and 10.1 ± 0.4 g m⁻³ d⁻¹ for the 1.0, 1.5, and 2.0 m depths, respectively. Massé et al. (2003) reported higher CH4 emission rates (19.1 to 21.4 g CH4 m⁻³ d⁻¹) for swine manure slurry storage (VS = 83 g L⁻¹) under similar storage conditions (15°C storage temperature) and with a longer storage period (180 d). The primary reason for this difference could be the drastically different nutrient properties of BDE and swine manure. Swine manure generally contains much higher VS content, which is responsible for CH4 emissions.

During the storage process in the current study, the CH4 emission rate was higher and fluctuated more during the early period, and then decreased and became stabilized after approximately 20 days. The CH4 emission rate for the 1.0 m depth was in the range of 5.8 to 55.8 g m⁻³ d⁻¹ (mean of 20.7 g m⁻³ d⁻¹) during the first 20 days. In comparison, the CH4 emission rate for the 1.5 m depth ranged from 9.2 to 40.0 g m⁻³ d⁻¹ (mean of 21.0 g m⁻³ d⁻¹). The corresponding range and mean value for the 2.0 m depth were 8.9 to 56.7 g m⁻³ d⁻¹ and 22.4 g m⁻³ d⁻¹, respectively. The CH4 emissions during the first 20 days were the main source of the emissions over the entire storage period, accounting for...
58%, 57%, and 56% of the 78-day CH$_4$ emissions for the 1.0, 1.5, and 2.0 m depths, respectively. Similar results were obtained by Sommer et al. (2000), who reported that the CH$_4$ emission rate of fermented cattle slurry stored at 15°C peaked at 9.6 to 12 g m$^{-2}$ d$^{-1}$ during the initial storage period, and then decreased gradually in the later period and stabilized at 1.44 g m$^{-2}$ d$^{-1}$. The authors stated that the fermented slurry was a pool for fermentable organic material, and the rich methanogenic bacteria remaining in the fermented slurry contributed to the decomposition of the easily fermentable organic material, thus causing the high CH$_4$ emission rates during the early storage stage. In the case of BDE, a portion of the biogas (mostly CH$_4$ and CO$_2$) was dissolved in it and was released during the early stage of the subsequent storage.

**CO$_2$ Emissions**

The daily emission rates and cumulative emissions of CO$_2$ for the three storage depths are shown in figures 7 and 8. The daily emission rate of CO$_2$ exhibited a pattern similar to that of CH$_4$. Once again, the emissions were higher with greater fluctuations during the early period and became stabilized afterward (fig. 7). The CO$_2$ emission rates (mean ±SE) for the 1.0, 1.5, and 2.0 m depths were 38.0 ±2.2, 34.5 ±1.3, and 30.7 ±0.6 g m$^{-2}$ d$^{-1}$ (p < 0.05), respectively, indicating that the shallow storage depth had a higher CO$_2$ emission rate. This result was comparable to the study by Ye et al. (2011c), who reported that a shallow depth (0.15 m) of piggery wastewater storage emitted higher CO$_2$ per volume of media as compared to 0.40 and 0.65 m depths.

**N$_2$O and NO Emissions**

Profiles of emission rates and cumulative emissions of N$_2$O at different storage depths are shown in figures 9 and 10. The N$_2$O emission rates (mean ±SE) for the 1.0, 1.5, and 2.0 m depths were 6.7 ±0.5, 5.0 ±0.8, and 3.4 ±0.2 mg m$^{-3}$ d$^{-1}$ (p < 0.05), respectively. The NO emissions were negligible, less than 0.04 μg m$^{-3}$ d$^{-1}$ for all storage depths (data not shown). Blanes-Vidal et al. (2008) reported that completely anaerobic storage of pig slurry did not emit N$_2$O; however, Amon et al. (2006) reported an average N$_2$O emission rate of 356 mg m$^{-3}$ d$^{-1}$ from storage of digested cattle slurry (DM = 5.6% wet basis) at 17°C. In addition, Wang et al. (2014) reported a much higher N$_2$O emission of 3330 mg m$^{-3}$ d$^{-1}$ from storage of digested pig manure effluent (COD = 1053 mg L$^{-1}$) at 30°C, and the observed NO$_x$-N content was as much as 201.9 mg L$^{-1}$ at the end of storage. Those differences in N$_2$O emissions could be attributed to different storage environments and characteristics of the media. Higher storage temperature and lower COD/N ratios of the effluent are deemed to be more suitable for N$_2$O production. Antoniou et al. (1990) suggested that high storage temperatures (30°C to 35°C) increase the nitrification rate. Wu et al. (2009) compared

![Figure 7. Daily CO$_2$ emission rate (mean ±SE) of biogas digester effluent (BDE) stored at depths of 1.0, 1.5, and 2.0 m.](image1)

![Figure 8. Cumulative CO$_2$ emissions (mean ±SE) from biogas digester effluent (BDE) stored at depths of 1.0, 1.5, and 2.0 m.](image2)

![Figure 9. Daily N$_2$O emission rate (mean ±SE) of biogas digester effluent (BDE) stored at depths of 1.0, 1.5, and 2.0 m.](image3)

![Figure 10. Cumulative N$_2$O emissions (mean ±SE) from biogas digester effluent (BDE) stored at depths of 1.0, 1.5, and 2.0 m.](image4)
the effects of five COD/N ratios (0:1, 2:1, 5:1, 10:1, and 20:1) on N\textsubscript{2}O emissions from microcosm wetlands and found that the total N\textsubscript{2}O emissions for COD/N ratios of 0:1 and 2:1 were 4 to 6 times greater than for COD/N ratios of 5:1 and 10:1. In the current study, the storage temperature was low at 15°C, and the COD/N ratio was high at 9:1 or greater. Thus, there were nearly no NO\textsubscript{x} ions, and extremely low N\textsubscript{2}O emissions were observed during the entire storage.

N\textsubscript{2}O emissions peaked at 21.3 to 32.4 mg m\textsuperscript{-3} d\textsuperscript{-1} during the first week of storage. As N\textsubscript{2}O emissions are mainly sourced from nitrification and denitrification processes, the DO level is one of the key parameters affecting N\textsubscript{2}O emissions. In this study, the transport and handling of the BDE from the farm to the laboratory might have introduced oxygen into the BDE, thus causing the relatively high DO level of 1.2 to 1.4 mg L\textsuperscript{-1} during the first week of storage (fig. 11). During the following two weeks, the DO level dropped from 1.2 to 0.6 mg L\textsuperscript{-1}, and the N\textsubscript{2}O emissions decreased quickly and almost ceased in all treatments. Park et al. (2000) reported comparable results for a biological wastewater treatment system with intermittent aeration, where nearly zero N\textsubscript{2}O emissions occurred as the DO level decreased from 4 to 0 mg L\textsuperscript{-1} in the anoxic phase. The authors observed a slight increase of dissolved N\textsubscript{2}O in the wastewater, which might explain the nil N\textsubscript{2}O emissions during the anoxic phase. From the 21st day of the storage, a membrane of sludge became visible on the surface of the stored BDE, as Sommer et al. (2000) also reported. This membrane, in contact with the supply air, facilitated growth of bacteria that are conducive to nitrification and denitrification, and hence the release of N\textsubscript{2}O.

NH\textsubscript{3} Emissions

Profiles of emission rates and cumulative emissions of NH\textsubscript{3} from BDE storage at different depths are shown in figures 12 and 13. Among the three depths, NH\textsubscript{3} emission rate remained highest at the 1.0 m depth during the entire storage period and fluctuated most in the early stage. The NH\textsubscript{3} emission rate for the 2.0 m depth was lowest throughout the storage period but displayed a more stable trend. From day 57 to day 78 (February 27 to March 17), NH\textsubscript{3} emissions from the three depths all showed similar trends in fluctuations: increasing firstly, followed by decreasing, and then increasing again. The fluctuations of NH\textsubscript{3} emissions coincided with the fluctuations of water temperature during the last 21 days (fig. 12). The fluctuations of water temperature (15°C ±2°C) during the latter storage stage were caused by the warmer ambient temperature in spring followed by some extreme weather events, including unexpected heavy snow on March 10. This result is consistent with previous studies about temperature being a key influencing factor on NH\textsubscript{3} emissions (Sommer, 1997; Ye et al., 2011b).

The NH\textsubscript{3} emission rates (mean ±SE) for the 1.0, 1.5, and 2.0 m depths were 1905 ±111, 1315 ±81, and 921 ±30 mg
Ammonia release from stored effluent depends on the chemical equilibrium, which relates to the pH value and CO2 emissions. Hafner et al. (2012) reported that CO2 emissions cause an increase of pH in slurry storage, and the rising pH then contributes to an increase of NH3 emissions. In the current study, the BDE stored at the shallowest depth emitted the maximum amount of CO2 (fig. 7) and had the highest pH level during the entire storage period (fig. 14), which explained the associated highest NH3 emissions. Li and Xin (2010) reported similar results for chicken manure stored at depths of 5, 10, 20, and 40 cm for 40 days, with shallower storage depths having higher NH3 emissions per kg fresh manure. The NH3 emission levels observed in the current study are comparable with the findings of Scotford and Williams (2001), who reported an NH3 emission rate range of 880 to 1280 mg m⁻³ d⁻¹ for a pig slurry lagoon with a storage temperature of 16°C to 18°C and storage depth of 2.0 m. Sommer (1997) reported a higher mean NH3 emission rate of 9.04 g NH3-N m⁻² d⁻¹ with an annual emission rate range of 0 to 30 g NH3-N m⁻² d⁻¹ for farm tanks containing anaerobically digested animal slurry. The high emissions of NH3 reported by Sommer (1997) might have been due to warm temperatures (20°C to 25°C) and solar radiation during the summer field test.

**CONTRIBUTIONS OF INDIVIDUAL GHGS TO OVERALL GLOBAL WARMING POTENTIAL**

During the 78 consecutive days of storage, the total GHG (CH4 + N2O + CO2) emissions (mean ± SE) were 20.9 ± 1.5, 22.5 ± 1.3, and 22.2 ± 0.7 kg CO2-eq m⁻³ for BDE stored at 1.0, 1.5, and 2.0 m depths, respectively (p = 0.65). GHG emissions from the BDE storage were dominated by CH4, which accounted for 85.1%, 87.5%, and 88.8% of the total GHG emissions for the 1.0, 1.5, and 2.0 m depths, respectively. The GHG emissions per unit volume of BDE were independent of the storage depth, leading to a positive relationship between GHG emission rate per unit surface area and storage depth (fig. 15).

**SUMMARY AND CONCLUSION**

Emissions of CH4, CO2, N2O, NO, and NH3 from BDE stored at three depths of 1.0, 1.5, and 2.0 m were quantified using dynamic emission vessels over a 78-day storage period at 11.5 ACH and a relatively constant temperature of 15°C. The daily mean gaseous emission rates for the 1.0, 1.5, and 2.0 m depths were, respectively, 9.1, 10.1, and 10.1 g CH4 m⁻³ d⁻¹ (p = 0.39); 38.0, 34.5, and 30.7 g CO2 m⁻³ d⁻¹ (p < 0.05); 1905, 1315, and 921 mg NH3 m⁻³ d⁻¹ (p < 0.05); 6.7, 5.0, and 3.4 mg N2O m⁻³ d⁻¹ (p < 0.05). The NO emissions were negligible, less than 0.04 μg m⁻³ d⁻¹, for all storage depths. The cumulative GHG emissions for the 1.0, 1.5, and 2.0 m depths over the 78-day storage period were, respectively, 20.9, 22.5, and 22.2 kg CO2-eq m⁻³ (p = 0.65). Methane accounted for more than 85% of the total GHG emissions for all storage depths. Methane emissions peaked during the early storage period, with the cumulative CH4 emitted during the first 20 days accounting for 56% to 58% of the total CH4 emissions during the entire 78-day storage period.

The 2.0 m storage depth produced lower CO2, NH3, and N2O emissions but similar CH4 emissions compared to the 1.0 and 1.5 m depths. Hence, for typical BDE storage depths in China, the greater storage depth of 2.0 m would be more conducive to mitigating gaseous emissions, especially NH3, CO2, and N2O emissions.

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