Mechanism of Gas Release from Liquid Swine Wastes

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Abstract.
Releases of ammonia (NH₃), hydrogen sulfide (H₂S), carbon dioxide (CO₂), and sulfur dioxide (SO₂) from swine manure in 138-L laboratory reactors at 20° C were studied with high frequency sampling (one sample per min) for 260 d. Release behaviors of these gases were investigated under transient conditions with sudden disturbance of the manure by manure addition or mixing, and reactor shaking, and under steady state conditions with different ventilation rates. Different mechanisms were discovered in the releases of various gases. Convective mass transfer, controlled by profiles of concentration, velocity, and temperature, governed NH₃ release and influenced H₂S release. A new model of “bubble release” is proposed to explain release behavior characteristics. Bubble release controlled releases of H₂S, CO₂, and SO₂ when manure was disturbed. Bubble release is believed to be responsible for previously discovered “H₂S burst releases” that were defined as sudden increases of release by more than 100% as compared with previous release in less than one hour. Solubility of gases probably played an important role in the releases. Moreover, there was a dynamic interaction among different gases via their effect on the pH of surface manure.

Keywords. Air quality, Ammonia, Hydrogen sulfide, Carbon dioxide, Sulfur dioxide, Odor
Introduction

There are more than 130 major and minor gases derived from animal manure decomposition (Hartung & Phillips, 1994). Ammonia (NH₃), hydrogen sulfide (H₂S), carbon dioxide (CO₂) and sulfur dioxide (SO₂) are among the major gases (Muehling, 1970; Ni et al., 2000c; Heber et al., 2001). Knowledge about release/emission mechanisms of these gases is important for modeling and predicting pollutant emission, improving measurement, developing abatement technologies, and improving farm safety.

Release of NH₃ from liquid manure is generally considered a process of convective mass transfer across aqueous-gaseous interface that is affected by profiles of concentration, velocity, and temperature (Rachhpal-Singh and Nye, 1986; Jayaweera and Mikkelson, 1990; van der Molen et al., 1990; Zhang et al., 1994; Ni, 1999). The co-release of CO₂ greatly accelerates NH₃ release but does not alter the convective mass transfer (Ni et al., 2000d; 2000e).

However, only a few studies about release behaviors of H₂S, CO₂ and SO₂ are available in the literature. Arogo et al. (1999) attempted to determine the mass transfer coefficient of H₂S release from manure. The authors found that it was affected by air temperature, manure temperature and air velocity under laboratory conditions. Ni et al. (1998; 1999a) related emission of H₂S to temperature, ventilation, and animal size under field conditions. Ni et al. (2000a; 2000b) discovered a phenomenon of H₂S burst releases in commercial swine buildings. Ni et al. (1999b) and Lim et al. (1999) investigated the quantity of CO₂ produced in swine buildings with direct measurement of CO₂ emission. The CO₂ release was related to ventilation rate, animal size, and temperature. Only one report of SO₂ from manure was available (Ni et al., 2000c).

A laboratory study, sponsored by the National Pork Board (Des Moines, IA), to test the effectiveness of 35 commercial manure additives for reducing air pollution from swine manure was conducted at Purdue University with a state-of-the-art test installation. A large quantity of high frequency gas release data was recorded during the study. Data were also collected during weekly addition of manure into the reactors, and when the rate of airflow through reactors changed dramatically. Recorded data during manure-disturbing additions and step changes of airflow rate provided unique information and insight about gas release behavior. A follow-on test of two reactors used in the manure additive project evaluated gas release caused by shaking the reactors, and also by thoroughly mixing the contents. The investigation of release mechanisms started on day 14 of the last replication of the manure additive study and extended beyond its completion on day 42 for 218 more days.

The overall objective of the study was to evaluate mechanisms of NH₃, H₂S, CO₂, and SO₂ release from manure. The specific objectives were to:

1. test the effect of manure disturbance on gas release;
2. evaluate the effect of different airflow rates on gas release and manure pH change, and
3. propose a model of bubble gas release to explain observed phenomena.

Materials and Methods

Setup

Tests were conducted in two manure reactors, hereafter referred to as Reactors A and B, that served as controls in a large manure additive study consisting of 39 identical reactors. The two reactors received the same treatment during the entire 260-d test. Reactor A was continuously
monitored after day 43 for gas releases, while reactor B was occasionally monitored to check and verify the test condition. All data presented in this paper were from Reactor A, unless otherwise indicated.

The reactors were housed in a continuously ventilated environmental control room with a constant temperature of 20 °C. Each reactor was 122 cm tall and 38 cm in diameter. They were made of white PVC, with the headspace lined with Tedlar film. The total volume of each reactor was 138 L.

A stainless steel air pipe was installed in the center of the top cap of the reactor (fig. 1). There was a baffle at the pipe outlet to deflect the fresh incoming air horizontally. An exhaust air outlet and a manure addition port were installed on either side of the top cap. The manure port, normally closed with a stainless steel plug, was only open during manure addition.

![Figure 1. Schematic of the test setup.](image)

Note: F, air filter; FM, mass flow meter; P, pump. The H₂S and CO₂ analyzers had internal pumps. The manure pipe and funnel were only installed during 3-min manure additions. The positions of the manure pipe and air pipe were adjustable (shown with double-ended arrows).

A compressor continuously supplied fresh air to the reactor through an air supply system consisting of some filters and pressure regulators at a mean rate of 7.0 and 9.3 L/min before and after day 83, respectively. Exhaust air was conducted to three gas analyzers through Teflon tubing, Teflon® filters, a mass flow meter, and a Teflon manifold.

**Manure**

Manure was collected from a nearby commercial swine finishing farm in Indiana and was transported in a plastic tank to the laboratory. On day 0 of the test, the reactor was charged with 75.4 L of manure to a depth of 66 cm. The reactor received 5.8 L of fresh manure in each additional charge, which added 5.1 cm manure depth, on days 7, 14, 21, 28, and 35. The maximum manure depth in the reactor was 92 cm after day 35.

Samples of source manure were obtained during the initial charging and each additional charge. On day 43, one manure sample was taken from each reactor after the manure was thoroughly
mixed with a motor-powered propeller (15 cm diameter) for about three minutes. On day 261, one manure sample was taken from the surface manure and another was taken at 15 cm from the bottom of the reactor using a Colwisa probe sampler (Animal Environment Specialists, Rossville, IN). Samples were analyzed in the Purdue Animal Sciences Waste Management Laboratory. The characteristics of six batches of source manure and three samples of reactor manure are listed in table 1.

Table 1. Characteristics of source manure (days 0-35) and reactor manure (days 43 and 261) samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Volume†, L</td>
<td>75.4</td>
</tr>
<tr>
<td>Sample n</td>
<td>6</td>
</tr>
<tr>
<td>DM, %</td>
<td>4.49</td>
</tr>
<tr>
<td>Ash‡, %</td>
<td>1.09</td>
</tr>
<tr>
<td>TKN‡, mg/L</td>
<td>5,741</td>
</tr>
<tr>
<td>NH₄-N‡, mg/L</td>
<td>4,746</td>
</tr>
<tr>
<td>P, mg/L</td>
<td>1,465</td>
</tr>
<tr>
<td>K, mg/L</td>
<td>5,313</td>
</tr>
<tr>
<td>COD, g/L</td>
<td>84.6</td>
</tr>
</tbody>
</table>

Note: *Test days 261s and 261b were surface and bottom samples, respectively; †Volume of manure added to the reactor; ‡Wet base.

Tests

Tests on days 14, 21, 28, and 35 were combinations of airflow changes and manure disturbances that were caused by manure additions (table 2). The ventilation air was shut off several hours before manure addition. The air inlet pipe was left open to the reactor room and the manifold exhaust was closed. Three analyzer pumps, one external for the NH₃ analyzer and two internal for the H₂S and CO₂ analyzers, together exhausted a total of 1.6 L/min of air from the reactor, providing a low airflow rate for several hours.

The manure addition port was opened just before manure addition. The stainless steel manure pipe (2.4 cm ID) was screwed into the manure addition port and a funnel was inserted at the top of the pipe (fig. 1). The lower end of the pipe was kept at 15 cm above the manure surface before addition and was not re-adjusted during addition. The air inlet pipe was raised to the top of the reactor. Manure (5.8 L) was poured into the funnel, causing disturbance of the manure inside the reactor for about one minute. The total time required to add manure to each reactor was about three minutes. The manure pipe was removed and the plug was reinserted immediately after manure addition. The air inlet pipe was adjusted to keep the baffle at a distance of 15.2 cm above the manure surface.

The manure addition on day 14 was conducted with low airflow. On days 21, 28, and 35, the airflow rate was restored to 7.0 L/min before the manure additions. However, the ventilation was shut off during the 3-min manure addition on all test days.
On day 41, disturbance of manure was provided by manually shaking the reactor, during which the reactor was tilted at about 9° and suddenly returned to its original upright position once every second five times. Ventilation was maintained during the shaking procedure.

On day 43, the manure was thorough mixed with the reactor's top cap removed. The reactor was re-capped and sealed, and ventilation was restarted five minutes after mixing stopped.

On day 260, manual shaking of the reactor identical to the day 41 procedure was repeated twice. Airflow rate was kept at 9.2 L/min, but the baffle of the air inlet pipe was located 53.2 cm above the manure surface.

Table 2. Summary of test conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>14</th>
<th>21</th>
<th>28</th>
<th>35</th>
<th>41</th>
<th>43</th>
<th>260</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manure, cm</td>
<td>76</td>
<td>81</td>
<td>86</td>
<td>92</td>
<td>92</td>
<td>92</td>
<td>67</td>
</tr>
<tr>
<td>Manure, L</td>
<td>86.4*</td>
<td>92.2*</td>
<td>97.9*</td>
<td>103.7*</td>
<td>103.7</td>
<td>103.7</td>
<td>76.0</td>
</tr>
<tr>
<td>Headspace, cm</td>
<td>45.8</td>
<td>40.7</td>
<td>35.6</td>
<td>30.5</td>
<td>30.5</td>
<td>30.5</td>
<td>55</td>
</tr>
<tr>
<td>Headspace, L</td>
<td>51.6*</td>
<td>45.8*</td>
<td>40.1*</td>
<td>34.3*</td>
<td>34.3</td>
<td>34.3</td>
<td>62.0</td>
</tr>
<tr>
<td>Disturbance</td>
<td>Addition</td>
<td>Addition</td>
<td>Addition</td>
<td>Addition</td>
<td>Shaking</td>
<td>Mixing</td>
<td>Shaking</td>
</tr>
<tr>
<td>Air supply, L/min</td>
<td>1.6/7.0</td>
<td>1.6/7.0</td>
<td>1.6/7.0</td>
<td>1.6/7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>9.2</td>
</tr>
<tr>
<td>Gases measured†</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Air pipe position, cm</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>53.2</td>
</tr>
</tbody>
</table>

Note: *After manure addition; †Four gases included NH₃, H₂S, CO₂ and SO₂. Three gases included H₂S, CO₂ and SO₂.

**Measurement**

Gas concentrations (NH₃, H₂S, CO₂, and SO₂) and airflow rate in the reactor exhaust air were continuously measured during all disturbance tests and from days 43 to 96, except for day 260 when NH₃ was not measured due to maintenance problems with NH₃ analyzer.

Ammonia concentration was measured with an NH₃ Analyzer (Model 17C, Thermo Environmental Instruments (TEI), Franklin, MA), after the NH₃ was converted to nitric oxide (NO) by a converter unit at 875° C. The measurement range of the NH₃ analyzer was set at 0-200 ppm. The precision of the analyzer was <1.0% of full scale or 2 ppm. It had a lower detectable limit of 1 ppb. The response time (time to reach 90% of a step input from zero) for the NH₃ measurement system was 125 s.

Hydrogen sulfide and SO₂ concentrations were measured with a SO₂ analyzer (TEI Model 45) combined with a H₂S converter (TEI Model 340). Hydrogen sulfide in the sample air was first converted to SO₂ with the converter. The converted SO₂ plus the actual SO₂ in the sample air was measured with the SO₂ analyzer and the total sulfur (TS, sum of H₂S and SO₂) concentration was obtained. When the converter was by-passed, the concentration of SO₂ in the sample air was measured with the SO₂ analyzer. This instrument switched between measurements of H₂S and SO₂ automatically and subtracted SO₂ from TS to obtain H₂S concentration. It had a data averaging time of 60 s and a precision of <1.0% of full scale. Its sample flow rate was 1.0 L/min. The response time of the system was 150 s. The H₂S analog signal output was adjusted at 0–20,000 ppb, while the visual readout of the instrument had a
limit beyond 20,000 ppb. Thus, H$_2$S concentrations above 20,000 ppb were read visually and recorded manually every minute during the manure disturbance tests.

Carbon dioxide concentration was measured with a photo-acoustic infrared CO$_2$ monitor (Model 3600, Mine Safety Appliance Company, Pittsburgh, PA). The response time of the CO$_2$ monitor was 20 s. The noise of the monitor was < ±0.5% of full scale.

All gas instruments were calibrated twice a week with certified zero air, 23.4 ppm nitric oxide (NO) in nitrogen (N$_2$), 165 ppm NH$_3$ in air, 2.7 ppm SO$_2$ in N$_2$, 16.5 ppm H$_2$S in N$_2$, and 3,990 ppm CO$_2$ in N$_2$. Calibration frequency was reduced to weekly or biweekly after day 50.

Reactor incoming gas concentrations were measured within 6 h prior to manure additions on days 14, 21, 28, 35, and 41, and one day after the test on day 260. Concentrations of NH$_3$, H$_2$S and SO$_2$ were negligible, while CO$_2$ ranged from 510 to 550 ppm.

Exhaust airflow rates were measured with a Model 50S-10 mass flow meter (McMillan Company, Georgetown, TX). Reactor room temperatures were measured at eight locations at 1.0 m above the floor using AD592 sensors (Computer Boards, Inc., Mansfield, MA). The mean temperature was used to convert gas from volumetric to mass concentration.

Gas concentration, airflow rate and temperature data, acquired every 2.0 s, were averaged every minute, and recorded to the PC by a data acquisition system.

On days 51, 55, 57, and 58, surface manure pH at different depths (0.5-1 cm, 5 cm and 7 cm) in the two reactors was measured with a pH meter (Model 130, Corning Science Products, Medfield, MA). The pH probe was inserted into the reactor through the manure addition port. The measurements were conducted for different ventilation situations: 1) continuous airflow for past several days or hours, and 2) no airflow for several days.

**Calculation**

Volumetric gas concentrations obtained from the gas analyzers were converted into mass concentrations with the ideal-gas law by using the mean reactor room temperature and assuming one atmosphere pressure.

Gas release in this paper is defined as the process of gas transferring from the surface of liquid manure into the free air stream of the reactor headspace. Gas emission is defined as the process of gas emanating from the reactor into the outdoor atmosphere. Gas release does not equal gas emission under transient conditions, although it does under steady-state conditions. The rate of gas emission from a reactor was calculated with Eq. (1).

$$Q_{Ge} = (C_{Gex} - C_{Gin}) Q_v$$

where: $Q_{Ge}$ is gas emission rate, mg/min; $C_{Gex}$ is exhaust gas concentration, mg/L; $C_{Gin}$ is inlet gas concentration, mg/L; and $Q_v$ is reactor airflow rate, L/min.

To obtain gas release rates, the rates of change in gas mass in the reactor headspace was considered using Eq. (2).

$$Q_{Gr} = Q_{Ge} + \frac{dC_{Gh}}{dt} V_h$$

where: $Q_{Gr}$ is gas release rate, mg m$^{-2}$ min$^{-1}$; $C_{Gh}$ is gas concentration in the headspace, mg/L; and $V_h$ is headspace air volume, L. In this paper, we assumed $C_{Gh}$ was equal to $C_{Gex}$ at all times.

To use the sampled data obtained in the tests, Eq. (2) was discretized as Eq. (3).
\[ Q_{Gr}(k) = Q_{Ge}(k) + \frac{C_{Gh}(k+1) - C_{Gh}(k)}{\Delta t} V_h \]  

(3)

where: \( \Delta t \) is sampling interval, min; and \( k \) is sampling number with \( k = 0, 1, 2, \ldots \)

Gas release flux was calculated with

\[ q_{Gr} = \frac{Q_{Gr}}{A} \]  

(4)

where: \( q_{Gr} \) is gas release flux, mg m\(^{-2}\) min\(^{-1}\); and \( A \) is area of reactor manure surface, m\(^2\).

**Results**

**Manure Addition during Low Airflow**

The gas release patterns during ventilation adjustment and manure addition on day 14 are shown in fig. 2. Manure was added about 90 min after reducing airflow. Immediate increases in \( \text{H}_2\text{S} \), \( \text{CO}_2 \) and \( \text{SO}_2 \) releases were detected following the disturbance caused by manure addition. The maximum release fluxes of \( \text{H}_2\text{S} \), \( \text{CO}_2 \) and \( \text{SO}_2 \) during the test are given in table 3.

![Figure 2](image)

Figure 2. Airflow rate (per min) and gas release fluxes (per m\(^{2}\) per min) on the day 14 test. The arrow indicates the time of manure addition. The symbol “\(-\)” indicates missing hydrogen sulfide data from 2:14 to 2:36 and from 2:54 to 3:21.

The release patterns of the three gases were quite different. After a peak release from 1:29 to about 1:45, two \( \text{H}_2\text{S} \) release peaks occurred at 2:16 to 2:36 and 2:54 to 3:21. The magnitudes of the two peaks exceeded the upper limit of the analog signal output of the \( \text{SO}_2 \) analyzer, but were not manually recorded because they had not been expected. The decay of \( \text{CO}_2 \) was smoother than \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) but was not exponential. There were wide variations of high \( \text{SO}_2 \) release, which lasted for about two hours, after the initial peak induced by the manure addition. However, the \( \text{NH}_3 \) release remained unchanged despite the manure disturbance.
The 7.0 L/min airflow rate was suddenly restored about three hours after the manure addition. This induced an immediate increase in the releases of all four gases, which gradually reached equilibrium in about one hour. The release patterns exhibited exponential decay for NH₃ and CO₂, and quasi-exponential decay for SO₂. However, a follow-up peak of H₂S release was detected about 20 min after the airflow increase.

Table 3. Maximum release fluxes of hydrogen sulfide, carbon dioxide, and sulfur dioxide induced by manure disturbances.

<table>
<thead>
<tr>
<th>Test day</th>
<th>H₂S, µg m⁻² min⁻¹</th>
<th>CO₂, mg m⁻² min⁻¹</th>
<th>SO₂, µg m⁻² min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1,698*</td>
<td>288</td>
<td>60</td>
</tr>
<tr>
<td>21</td>
<td>4,068</td>
<td>389</td>
<td>49</td>
</tr>
<tr>
<td>28</td>
<td>4,176</td>
<td>403</td>
<td>45</td>
</tr>
<tr>
<td>35</td>
<td>4,953</td>
<td>508</td>
<td>70</td>
</tr>
<tr>
<td>41</td>
<td>6,160</td>
<td>610</td>
<td>150</td>
</tr>
<tr>
<td>260 (first disturbance)</td>
<td>5,364</td>
<td>53</td>
<td>51</td>
</tr>
<tr>
<td>260 (second disturbance)</td>
<td>3,832</td>
<td>44</td>
<td>46</td>
</tr>
</tbody>
</table>

Note: *This might not be the highest value because there were lost values that might be higher than this one. Maximum releases during manure mixing on day 43 could not be recorded due to opening of reactor top cap.

**Manure Additions during High Airflow**

All three tests on days 21, 28 and 35 were conducted first by lowering the airflow rate to 1.6 L/min for 3 to 4 h, during which NH₃ release fluctuated at the beginning and stabilized after about 2 h (figs. 3, 4 and 5). The release of SO₂ tended to increase during the time of low airflow on day 21. The other two gases, H₂S and CO₂ appeared relatively stable.

Figure 3. Airflow rate (per min) and gas release fluxes (per m² per min) on the day 21 test. The arrow indicates the time of manure addition.
The restoration of 7.0 L/min airflow caused sudden increases in releases of NH₃, CO₂ and SO₂ in all three tests. However, the peak H₂S release occurred about 20 to 30 min later. The decay of SO₂ releases was not as smooth as CO₂ during all three tests.

Releases of H₂S, CO₂ and SO₂ appeared to have reached steady state, but NH₃ release was still decreasing 1.8 h following high airflow restoration on day 21 (fig. 3). The time between the high airflow restorations and manure additions on days 28 and 35 were only 40 and 15 min, respectively, so gas releases were not yet stabilized.

Manure additions caused immediate sharp increases in H₂S, SO₂ and CO₂ releases followed by exponential decays whereas the opposite occurred with NH₃. Ammonia decreased and then slowly increased for about 30 min. On day 35, small SO₂ release peaks were detected 15 min after the manure addition (fig. 5). The brief ventilation shutoff due to system check only caused a small increase in releases, but did not change the overall release patterns.

**Reactor Shaking**

Immediate increases in H₂S, SO₂, and CO₂ releases occurred after reactor shaking on day 41 (fig. 6). The unusual flat top of the H₂S release curve followed shaking was probably due to the upper limit of the SO₂ analyzer. The greater lag of release peaks of SO₂ and H₂S as compared with CO₂ was due to the longer response time of the SO₂ analyzer. There was a slight decrease in NH₃ after shaking followed by a gradual increase, similar to the manure addition tests at high airflow (figs. 3–5).

Releases of all four gases appeared to have reached steady state about 80 min after the shaking. Maximum release fluxes of H₂S, SO₂, and CO₂ were higher during this shaking test as compared with the manure addition tests (table 3).

The manure volume in the reactor was 76 L on day 261, and lost about 27.7 L compared with the day of last manure addition (day 35), due to evaporation (table 2). The release peaks on day...
induced by the second shaking were 71, 83, and 90% of the first shaking for H$_2$S, CO$_2$ and SO$_2$, respectively (fig. 7 and table 3). The total mass released during the 15 min after the second shaking were 77, 90 and 86% of those after the first shaking for H$_2$S, CO$_2$ and SO$_2$, respectively.

Figure 5. Airflow rate (per min) and gas release fluxes (per m$^2$ per min) on the day 35 test. The first arrow at 3:15 indicates time of manure addition. The second arrow at 3:45 indicates a short time shut-off of ventilation for system check.

Figure 6. Airflow rate (per min) and gas release fluxes (per m$^2$ per min) on the test day 41. The arrow indicates the time of reactor shaking.

The means of the maximum releases of H$_2$S and SO$_2$ during the two shakings were similar to those during manure additions on days 21, 35, and 41. However, the mean of those for CO$_2$ on day 260 was only 11% of the mean of those of CO$_2$ after three manure additions on days 21, 35, and 41.
Figure 7. Airflow rate (per min) and gas release fluxes (per m² per min) during the day 260 test. The arrows indicate times of reactor shaking.

**Thorough Mixing**

Gas releases stabilized about 25 min following reactor re-sealing and ventilation restoration after the thorough mixing on day 43. The release fluxes (mass per m² and per min) for NH₃, H₂S, CO₂ and SO₂ at the end of the day were 4.9 mg, 0.0 µg, 49.7 mg and 2.1 µg, respectively. Two days later (day 45), releases of NH₃, CO₂ and SO₂ increased by 52, 132 and 44% respectively. The NH₃ release from day 55 to day 96 exhibited a steady increase from 2.3 to 4.0 mg m⁻² min⁻¹. However, CO₂ decreased steadily from 78 to 52 mg m⁻² min⁻¹ during the same period. The SO₂ release rose quickly from 1.1 to 4.9 µg m⁻² min⁻¹ from day 58 to day 61 and remained around 5.0 µg m⁻² min⁻¹ through day 96, except for a valley on day 64 and a peak on day 72.

The release of H₂S dropped suddenly to zero the day after thorough mixing and stayed very low (about 1.5 µg m⁻² min⁻¹) for 10 days (days 44–54), before appearing again on day 55. A relatively rapid increase in release rate was then observed for 20 days (days 55–74). Thereafter, the H₂S release showed a less stable pattern as compared with other gases.

**Effect of Airflow on Gas Release and Manure pH**

Gas releases at steady state or quasi-steady state during the manure disturbance tests are compared in table 4. Ammonia release at high airflow during the first four tests was about 2.5 times as high as under low airflow. Hydrogen sulfide demonstrated a similar characteristic, with releases during high airflow about 2–5 times as high as those during low airflow. Airflow apparently did not affect CO₂ and SO₂ release. The releases of H₂S, CO₂ and SO₂ under steady state decreased by factors of 3 to 5 times after 260 d of storage.

The pH values in top manure (0-7 cm depth) under the effect of ventilation are listed in table 5. A pH gradient was clearly shown in the two reactors when ventilation was continuously provided at 7.0 L/min. In the five measurements with ventilation "always on" (> 10 d), the mean pH of the
surface manure layer (0.5-1 cm depth) was 8.5. The pH decreased in deeper layers. At 7 cm below the surface, the mean pH was 7.2.

Figure 8. Gas release fluxes (per m² per min) after manure was thoroughly mixed on day 43. The arrow indicates the time of mixing.

Note: Data for days 41 and 42 were means of 3 samples/day, 3 min of measurement each sample. Data from day 43 to 96 were averages of one hour/day of continuous measurement. Most of the hour-data were measured from 11:00 PM to midnight. Data on day 49 were missing due to a data acquisition error.

When ventilation was shut off for 4 and 6 d, the pH gradient between different manure layers disappeared. However, when ventilation was restored for four hours, the pH gradient reestablished itself and the pH values at different layers were similar to those measured under "always on" conditions.

Discussion

Ammonia Release and Convective Mass Transfer

Ammonia exists in the liquid manure in the form of ammonium ions (NH₄⁺) and free ammonia (NH₃). The physical insight related to the NH₃ formation in manure and its release understood so far is summarized and illustrated in fig. 9. Some of the NH₃ in manure is generated from biomass by means of enzymatic and microbial activities. The NH₃ in bulk manure can be transferred by mass diffusion if there is a concentration gradient. An NH₃ molecule binds a proton to form a NH₄⁺ ion. This can be expressed by the dissociation constant, Kₐ, and association constant, Kₐ⁻. Henry's constant, Kₜ, describes the equilibrium of free NH₃ in the aqueous and gaseous phases. With convective mass transfer, the gaseous NH₃ at the liquid manure surface is released into the free air stream (Ni, 1999).

The transfer of NH₃ from liquid manure into the free air stream requires overcoming major resistances offered by the liquid and gaseous phases. The transfer inside liquid manure is by diffusion and is concentration and temperature dependent. The transfer of gaseous NH₃ from the manure surface to the free air stream is essentially the process of NH₃ release. Mass transfer due to convection involves transfer between a moving fluid and a surface or between
two relatively immiscible moving fluids. This transfer depends both on the transport properties and on the dynamic characteristics of the flowing fluid (Welty et al., 1984). It is usually expressed by Eqs (5) or (6).

\[ q_{Ar} = h_m(C_{Ag,0} - C_{Ag,\infty}) \]  

\[ Q_{Ar} = Ah_m(C_{Ag,0} - C_{Ag,\infty}) \]

where: \( q_{Ar} \), flux of NH\(_3\) release, g m\(^{-2}\) s\(^{-1}\); \( h_m \), mass transfer coefficient, m/s; \( C_{Ag,0} \), NH\(_3\) concentration on the liquid surface, g/m\(^3\); \( C_{Ag,\infty} \), NH\(_3\) concentration in free air stream, g/m\(^3\); \( Q_{Ar} \), rate of NH\(_3\) release, g/s; \( A \), area of NH\(_3\) release, m\(^2\).

Table 4. Comparison of gas release fluxes under steady state or quasi-steady state with different airflow before and after disturbances.

<table>
<thead>
<tr>
<th>Day</th>
<th>Time*</th>
<th>Disturbance</th>
<th>Airflow L/min</th>
<th>NH(_3) release mg m(^{-2}) min(^{-1})</th>
<th>H(_2)S release µg m(^{-2}) min(^{-1})</th>
<th>CO(_2) release mg m(^{-2}) min(^{-1})</th>
<th>SO(_2) release µg m(^{-2}) min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0:05</td>
<td>Before</td>
<td>7.0</td>
<td>3.5</td>
<td>221</td>
<td>79</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1:00</td>
<td>Before</td>
<td>1.6</td>
<td>1.2</td>
<td>113</td>
<td>64</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>4:30</td>
<td>After</td>
<td>1.6</td>
<td>1.3</td>
<td>161</td>
<td>62</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>6:30</td>
<td>After</td>
<td>7.0</td>
<td>3.4</td>
<td>417</td>
<td>69</td>
<td>12</td>
</tr>
<tr>
<td>21</td>
<td>0:03</td>
<td>Before</td>
<td>7.0</td>
<td>3.0</td>
<td>401</td>
<td>75</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>3:50</td>
<td>Before</td>
<td>1.6</td>
<td>1.6</td>
<td>113</td>
<td>88</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>5:30</td>
<td>Before</td>
<td>6.9</td>
<td>3.9</td>
<td>370</td>
<td>76</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>6:55</td>
<td>After</td>
<td>6.9</td>
<td>3.8</td>
<td>518</td>
<td>85</td>
<td>14</td>
</tr>
<tr>
<td>28</td>
<td>0:10</td>
<td>Before</td>
<td>7.0</td>
<td>3.3</td>
<td>222</td>
<td>73</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>3:00</td>
<td>Before</td>
<td>1.6</td>
<td>1.5</td>
<td>58</td>
<td>71</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>5:00</td>
<td>After</td>
<td>7.0</td>
<td>3.7</td>
<td>309</td>
<td>89</td>
<td>11</td>
</tr>
<tr>
<td>35</td>
<td>0:10</td>
<td>Before</td>
<td>7.0</td>
<td>3.7</td>
<td>160</td>
<td>97</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>2:45</td>
<td>Before</td>
<td>1.6</td>
<td>1.5</td>
<td>68</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>4:35</td>
<td>After</td>
<td>7.0</td>
<td>3.6</td>
<td>263</td>
<td>99</td>
<td>11</td>
</tr>
<tr>
<td>41</td>
<td>0:05</td>
<td>Before</td>
<td>7.0</td>
<td>3.5</td>
<td>247</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1:20</td>
<td>After</td>
<td>7.0</td>
<td>4.2</td>
<td>95</td>
<td>68</td>
<td>8</td>
</tr>
<tr>
<td>260</td>
<td>0:05</td>
<td>Before</td>
<td>9.3</td>
<td>---</td>
<td>44</td>
<td>19</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>6:00</td>
<td>After</td>
<td>9.2</td>
<td>---</td>
<td>28</td>
<td>19</td>
<td>3</td>
</tr>
</tbody>
</table>

Note: *Test time corresponds to the time shown in figs. 2-7.

There are two theories used to explain the mechanisms of NH\(_3\) release: the Two-film theory and the Boundary Layer theory (Ni, 1999). Both theories are essentially convection mass transfer models, which have been used previously to study NH\(_3\) releases from manure. The mass transfer coefficient, \( h_m \), in these NH\(_3\) models was always empirically determined as a function of air velocity and temperature (Srinath and Loehr, 1974; Olesen and Sommer, 1993; Svensson and Ferm, 1993; Zhang et al., 1994; Cumby et al., 1995; Arogo et al., 1996; Ni et al., 2000d).
Table 5. Manure pH at different depth and under the influence of ventilation in the two reactors.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Ventilation</th>
<th>Day</th>
<th>Number of measurements</th>
<th>pH at different manure depth</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5-1 cm</td>
</tr>
<tr>
<td>A</td>
<td>Always on*</td>
<td>57</td>
<td>1</td>
<td>8.9</td>
</tr>
<tr>
<td>A</td>
<td>Always on*</td>
<td>58</td>
<td>1</td>
<td>8.4</td>
</tr>
<tr>
<td>B</td>
<td>Always on*</td>
<td>51</td>
<td>3</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>Weighted Mean</td>
<td></td>
<td></td>
<td>8.5</td>
</tr>
<tr>
<td>B</td>
<td>Off for 4 d</td>
<td>55</td>
<td>1</td>
<td>7.4</td>
</tr>
<tr>
<td>B</td>
<td>Off for 6 d</td>
<td>57</td>
<td>1</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td></td>
<td>7.4</td>
</tr>
<tr>
<td>B</td>
<td>On for 4 h*</td>
<td>58</td>
<td>1</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Note: *Ventilation refers to status before measurement. Ventilation was shut off momentarily during measurement.

Free air stream \( C_{Ag,\infty} \) \[\rightleftharpoons\] NH₃ released

Manure surface

Gaseous NH₃ \( C_{Ag,0} \) \([NH_3]_g\)

Convection mass transfer

\( [NH_3]_g \) \[\rightleftharpoons\] \( [NH_4^+] + [H^+] \)

Chemical change

\( [NH_4^+] \) \[\rightleftharpoons\] \( [NH_3] \)

Diffusion mass transfer

Liquid manure

\( K_a \)

\( [NH_4^+] + [NH_3] \)

Enzymatic and microbial generation

Biomass

Fig. 9. Mechanism of ammonia formation and release. Source: Ni (1999).

Note: \([NH_3]_g\), free NH₃ in gaseous phase at manure surface; \([NH_3]\), free NH₃ in aqueous phase; \( C_{Ag,0}\), mass concentration of free NH₃ in gaseous phase at manure surface; \( C_{Ag,\infty}\), mass concentration of NH₃ gas in free air stream; \( K_a\), association constant; \( K_d\), dissociation constant; \( K_h\), Henry’s constant. The free NH₃ in gaseous phase at manure surface is either expressed in mole concentration, \([NH_3]_g\), or in mass concentration, \( C_{Ag,0}\).

Results obtained in this study revealed three interesting characteristics of NH₃ release behavior. Firstly, NH₃ release was apparently unaffected by manure disturbance, which forced gas bubbles to be released from liquid manure, compared with H₂S, CO₂ and SO₂. The disturbance tests demonstrated that NH₃ is not a major component of the gas bubbles. Since gas bubbles, or biogas, are the product of microbial digestion under anaerobic conditions, it can be concluded that the formation of NH₃ in swine manure is not mainly controlled by anaerobic microbial activities. Chemical activity in the manure dominates the generation/formation of NH₃.
Secondly, NH₃ release was largely affected by airflow rate. A clear difference in dependence on airflow occurred between NH₃ and CO₂ under steady state or quasi-steady state conditions (table 4). Airflow rate changed the gas concentration in free air stream in the reactor headspace and thus changed the concentration difference expressed in Eq. (5). It also influenced air velocity over manure surface. Concentration and air velocity changes together influenced the convection mass transfer process [Eq. (5)]. This may explain the increase in gas release at a higher airflow rate. Therefore, convective mass transfer governed the release process of NH₃.

Lastly, manure disturbances brought in a unique NH₃ release pattern, a slight decrease at the beginning followed by a gradual increase that lasted for more than 30 min (figs. 3–6). According to a field study by Ni et al. (2000e), the co-release of CO₂ from manure was related to this NH₃ release behavior. Further discussion on this will be in the section “Interaction among Gas Releases”.

**Burst and Bubble Releases of Hydrogen Sulfide**

Ni et al. (2000a; 2000b) previously described a new phenomenon of burst releases of H₂S, which lasted from one to several hours, in commercial swine buildings. The burst release of H₂S was defined as a sudden increase (100% or greater) of H₂S release measured during any period (< 1 hour) compared with the previous period, under relatively constant ventilation rate and indoor room temperature. Burst H₂S release was considered a unique behavior as compared with NH₃ and CO₂ release from liquid manure.

Concentrated gas bubbles of different sizes (ranging from several mm to several cm in diameters) were seen released when the reactor was charged with manure on day 0 and when manure was mixed on day 41 using a motor-driven propeller. Most of the bubbles broke up and the gases they carried entered into the reactor headspace immediately during the manure disturbances. Some small bubbles stayed on the manure surface for a while after the manure disturbance. The sudden increases of H₂S detected by the analyzers were evidently caused by these bubble releases. Therefore, it is logical to believe that such bubbles contain concentrated H₂S. The mechanism of H₂S release during burst release or manure disturbance appeared to be different from that of NH₃.

Under anaerobic conditions, bacteriologic decomposition of protein and other sulfur-containing organic matter is responsible for H₂S production (Smith et al., 1979). Manure in the reactor was under anaerobic conditions except for the surface manure that was exposed to the flowing air. Based on current understanding of H₂S production in anaerobic conditions and the results of this study, a model of bubble release is proposed (fig. 10).

Hydrogen sulfide produced from biomass as a component of biogas dissolves in the liquid manure. When more and more biogas is produced, dissolved H₂S becomes supersaturated and micro air bubbles (MAB) are formed. The slow movement of MABs, due to heterogeneity of manure, temperature difference, etc., induces collision and agglomeration of the MABs that result in larger air bubbles. When the air bubbles reach a critical size, they gain in speed, \( S_b \), due to buoyant force, which moves them upward. Ascending air bubbles absorb other MABs and air bubbles on their way toward the surface. They gradually gain in size with the snowball effect and thus accelerate their ascending speed. The bubbles finally reach the manure surface and release the gases that they carry to the air in manure surface. The rate of H₂S bubble release is determined by the air volume of bubbles, \( V_b \), and the concentration of the gas (H₂S) in the bubbles, \( C_{g,b} \).

The external mechanical force, which causes disturbance of the manure, produces a higher speed, \( S_x \), of the air bubbles. The disturbance thus accelerates the gas collision and release.
through bubbles. This process results in a sharp increase of H$_2$S concentration above the manure surface.

![Diagram](image)

Figure 10. Proposed model of bubble release.

Note: $C_{g,\infty}$ gas concentration in free air stream; $C_{g,0}$ gas concentration at liquid surface; $C_{g,b}$ gas concentration in bubbles; $q_r$ flux of gas release; $V_b$ volume of bubble; $S_b$ speed of ascending bubble movement; $S_x$ speed of bubble movement relative to liquid caused by disturbance.

Bubble releases can be visually observed in many manure storages, such as lagoons, manure pits, etc. Bubble releases do not occur uniformly over time and over the surface of manure storage under field conditions. Irregularly temporal and spatial distribution of bubble release could be the direct cause of the burst H$_2$S release. This aggravates the temporal and spatial variation of gas concentrations on the surface of manure storages and in animal confinement buildings.

Released bubbles should contain a mixture of different gases, in which H$_2$S is a major one. Since manure gases are components of odor, bubble releases of manure gases may have an effect on the strength and character of odor emitted from manure.

It requires several days to build up the MABs with concentrated H$_2$S in the liquid manure before bubbles reach critical sizes and begin release. Although the quantity of H$_2$S release was not measured during the mixing on day 43, it was believed that H$_2$S MABs in the reactor were completely depleted. Within 10 days (from day 43 to day 52) after the mixing, the H$_2$S release from the reactor dropped to almost zero, though NH$_3$ and CO$_2$ release remained almost the same magnitudes, and SO$_2$ still kept releasing as they were before the mixing (fig. 8). The H$_2$S release fluxes did not reach 100 and 400 µg m$^{-2}$ min$^{-1}$ until 11 and 27 days after the mixing, respectively.

However, convection mass transfer also participated in the H$_2$S release. This was demonstrated by the fact that H$_2$S release fluxes changed proportionally with airflow rates during the tests on days 14–35 (table 4). Hydrogen sulfide is soluble in water and in several solvents, and water
solutions are not stable (Smith et al., 1979). The convection mass transfer of H₂S is related to the dissolved H₂S and MABs of H₂S in the surface manure. Emission of H₂S from animal buildings was proportionally correlated to temperature and ventilation rates in some studies (Ni et al., 1998; 1999a). However, results shown in table 4 did not agree with the study of Arogo et al. (1999), who found that the H₂S mass transfer coefficient increased as liquid temperature increased and decreased as the air velocity and air temperature increased. Arogo et al. (1999) studied H₂S mass transfer coefficient by measuring the total sulfur remaining in the manure.

**Carbon Dioxide Release**

Carbon dioxide is the second major component of biogas, which usually consists of 35–45 % CO₂. The rest of the biogas is methane (CH₄) and other tracer gases including H₂S. Hammad et al. (1999) showed that the percentage of CH₄ in the biogas produced from different animal manure ranged from 57 to 65%.

Increases in CO₂ release were observed immediately after manure disturbances and were followed by typical exponential decays in all tests (figs. 2–7). Release of CO₂ in bubbles must have been involved in disturbance tests. However, patterns of CO₂ release were different from those of H₂S and SO₂, which sometimes contained irregular rises and falls after manure disturbances (figs. 2, and 4-6). These irregularities were probably caused by follow-up bubbles released shortly after the disturbance. These later bubbles might have had different gas composition and might have contained a higher proportion of H₂S and SO₂ as compared with other bubbles. Thus, it was possible that the bubbles did not have uniform gas compositions, and their release sequence under disturbance was related to their compositions.

Data in table 4 show that CO₂ release under steady state conditions was probably not affected by airflow rate. This was different from field studies, in which CO₂ emission from swine buildings was correlated to building ventilation rate (Lim et al., 1999; Ni et al., 1999b). The reason was perhaps that ventilation rate in swine buildings was dependent on building temperature. Greater CO₂ production by anaerobic digestion is expected at higher room temperatures.

The CO₂ release behavior, different from NH₃, H₂S and SO₂, might be related to solubilities of the gases. Carbon dioxide is the least soluble in water among the four gases studied. Most of the CO₂ generated inside the manure might come out of the manure more quickly than other gases. Only a relatively small amount of CO₂ was retained in the manure “reservoir.” In other words, CO₂ release might be largely dependent on its production process. This could probably explain the smooth decay of CO₂ after disturbances and ventilation changes (figs. 2–7), and the steady release under steady state conditions (fig. 8). The CO₂ release peak following the mixing shown in fig. 8 might have been caused by better mixing of the microorganisms and substrate, hence better anaerobic fermentation. Mixing is a technique adapted in many biogas digesters to improve anaerobic fermentation. However, other CO₂ release mechanisms may also exist and may need to be explored in future studies.

Data on day 260 (table 4) show that CO₂ release was greatly reduced whether it was under steady state conditions or under manure disturbance as compared with H₂S and SO₂, whose releases were reduced under steady state but were as strong as before day 35 under manure disturbance on day 260. It appeared that when manure increased its age, its capacity of CO₂, H₂S and SO₂ production decreased. However, its capacity as a reservoir to retain gaseous CO₂, H₂S and SO₂ did not change. These characteristics were demonstrated in their release behaviors.
**Sulfur Dioxide Release**

Release patterns of SO$_2$ were more similar to those of H$_2$S than to NH$_3$ and CO$_2$ during the disturbance tests. However, apparent differences between SO$_2$ and H$_2$S releases can also be observed (figs. 2 and 4–6). The SO$_2$ release in the second test did not decrease as much as H$_2$S compared with the first test on day 260 (fig. 7). Moreover, SO$_2$ release at steady state conditions was not affected by airflow rates. It appeared that convection mass transfer had little influence on SO$_2$ release.

The SO$_2$ release did not decrease to zero as H$_2$S did after mixing (fig. 8), indicating that SO$_2$ might be produced and retained in manure in different ways than H$_2$S. Sulfur dioxide is more soluble in water than H$_2$S and CO$_2$, but less soluble than NH$_3$. Ni *et al.* (2000c) reported that variations of the SO$_2$ release were smaller as compared with H$_2$S release from the same manure source. Available information about SO$_2$ from animal waste is still very limited. More knowledge about SO$_2$ release from manure will depend on future investigations.

**Interaction among Gas Releases**

Although gas release is a physical process of mass transportation, it causes chemical changes in manure when different gases are coming out of the manure. One of its known chemical impacts is on the acidity of manure, especially that of the surface manure.

Acidity is defined in terms of the pH scale, where pH is the negative logarithm of the hydrogen ion concentration (Eq. 7).

$$pH = -\log[H^+]$$

Data presented in table 5 clearly indicate that, 1) there is a pH gradient inside the manure, and 2) this gradient was affected by ventilation of the reactors. Because change of ventilation airflow through the reactor effectively influenced the gas releases (figs. 2–5 and table 4), it was essentially the changes in gas release that altered the pH in the surface manure.

The existence of the pH gradient, with surface pH higher and bottom pH lower, was in good agreement with the study of Zhang and Day (1996), who reported that the pH in top layers of settled manure was 0.5 and 0.9 higher than the pH of bottom layers for the manure initially having 1.8% and 3.3% total solids in a laboratory study. However, data in table 5 showed a greater pH difference (ΔpH=1.3) between top manure at 0.5–1 cm and deeper manure at 7 cm.

The relationship between gas release and pH change has been discussed in some reports. Rachpall-Singh and Nye (1986) indicated that manure pH would be influenced by release of gases. In liquid animal manure, pH is also influenced by buffer systems. Husted *et al.* (1991) found that HCO$_3^-$ and NH$_4^+$ were the dominating buffer components. Olesen and Sommer (1993) discussed the possible influence on pH by the release of gases after an investigation of stored pig slurry. They assumed that the pH in the slurry surface increases initially as more CO$_2$ than NH$_3$ is lost, because the water solubility of CO$_2$ is 200 times lower than that of NH$_3$. Thereafter, the pH is expected to decrease due to NH$_3$ losses. They demonstrated that loss of CO$_2$ increases the pH [Eq. (8)] and loss of NH$_3$ decreases the pH [Eq. (9)].

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$  \hspace{1cm} (8)
Sommer et al. (1991) found that immediately following application of pig slurry (initial pH 7.6), the pH in the slurry surface increased to 8.4. Stevens and Cornforth (1974) reported that the surface aeration of manure caused an increase of pH value during the first two days. The pH went back to neutral in the next two days. In a laboratory study with cattle slurry, Husted et al. (1991) reported that when the samples were agitated and aerated, the pH rose very quickly within one hour and reached its maximum in about 20 h.

Measurement in this study showed a uniform pH in different manure layers after 4 and 6 d of ventilation shut-off. The pH gradient in manure was re-established after about 4 h of ventilation. Ni et al. (2000d) assumed that in order for the pH to reach the uniformity in surface manure, a “repose time” was required. During the repose time, the air velocity over manure surface was very low due to low or no ventilation. The convective mass transfer as well as the releases of gases from manure was very low. The repose time allowed the mass concentration gradient inside the manure to reach equilibrium via diffusion mass transfer.

The pH value is an indication of the partition of free ammonia (NH₃) and ammonium (NH₄⁺) in liquid manure. Vlek and Stumpe (1978) stated that the concentration of NH₃ in aqueous phase increases approximately 10-fold per unit increase in pH up to pH 9. The pH values obtained when ventilation was “always on” (table 5) were in dynamic equilibrium under continuous releases of different gases. This raised pH could have accelerated NH₃ release greatly (Ni et al., 2000e).

The pH in surface manure at steady state during the tests should have been in dynamic equilibrium. The manure disturbances during the tests caused some gases to be released more than others, thus breaking the dynamic equilibrium. The unique NH₃ release patterns, discussed in the section “Ammonia Release and Convective Mass Transfer”, with a slight decrease and then a gradual increase after manure disturbances, could be explained with this change in pH equilibrium. A new dynamic equilibrium could have been established when NH₃ release stopped increasing (figs. 3–6). Ni et al. (2000e) studied the gradual NH₃ release increase detected under field condition and attributed this to the co-release of CO₂ from manure.

Change in pH also affects release of H₂S from liquid media. It is known that higher pH is unfavorable to H₂S release (Rafson, 1998) and vice versa. Therefore, the co-releases of CO₂ and NH₃ in this study should have affected the H₂S release. However, because of the special mechanism of bubble release that resulted in significant variation in measured H₂S release fluxes, the effect of pH on H₂S release could not be isolated and quantitatively shown (table 6).

Table 6. Summary of release mechanisms identified in this study.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Convection mass transfer</th>
<th>Bubble release</th>
<th>Interaction release</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>H₂S</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes*</td>
</tr>
<tr>
<td>CO₂</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>SO₂</td>
<td>Yes</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Theoretically. It could not be quantitatively shown in this study due to the mechanism of H₂S bubble release.
Conclusions

The following conclusions were drawn:

1. Different mechanisms were involved in the releases of NH$_3$, H$_2$S, CO$_2$ and SO$_2$ from liquid swine wastes.

2. Convection mass transfer governed the process of NH$_3$ release, which was only slightly affected by the disturbances of the manure, but largely affected by airflow rates. It also influenced H$_2$S release.

3. Bubble release was dominant in the process of H$_2$S, CO$_2$ and SO$_2$ release when manure was disturbed.

4. Burst release of H$_2$S from swine manure can be explained by the mechanism of bubble release. Unevenly distributed temporal bubble releases may be the direct cause of burst H$_2$S release.

5. The degree of involvement of convection mass transfer and bubble releases was different in H$_2$S, CO$_2$, and SO$_2$ releases probably due to different solubilities of the gases.

6. Manure might need to have a certain density of dissolved and MABs of H$_2$S before release of H$_2$S can take place. In this test, the time needed to build up H$_2$S concentration in manure after mixing was ten days.

7. Although bubble release was easily induced by manure disturbance, the rate of bubble release under normal conditions is more difficult to predict compared with the convection mass transfer release.

8. Bubble release causes temporal variation of certain gases. Localized bubble releases may also worsen spatial variation of these gases.

9. Bubble release introduces H$_2$S and other odorous chemical compounds into the headspace of manure storage. Thus, there is a possibility that odor emission from swine wastes under field conditions are also subject to burst releases.

10. There existed a dynamic pH gradient change in the surface manure under the influence of airflow over surface manure. Under steady state conditions with a high airflow rate of 7.0 L/min, the surface manure pH was raised by 1.3. This elevated pH could greatly accelerate NH$_3$ release, but was unfavorable for H$_2$S release. Changes in release fluxes of different gases caused pH gradient change and a dynamic equilibrium of pH in surface manure. Therefore, there was an interaction among gas releases.

11. Measurement of pH to characterize manure in respect of its gas release should take into account the dynamic change of the pH and its gradient inside manure.

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