Measurement Techniques and Models for Ammonia Emissions At the Farm Level

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- Properties of gases.
  - Highly soluble.
  - \( \text{NH}_3 \)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Solubility (g/100 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>89.9</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>0.66</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>0.003</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>0.003</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>0.26</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>0.34</td>
</tr>
</tbody>
</table>

* at 0°C
Properties of gases.

Highly soluble.

NH₃

Slightly soluble.

CH₄, N₂O, H₂S, N₂, etc.

Solubilities* in water

NH₃ -- 89.9 g/100 ml
H₂S -- 0.66 g/100 ml
N₂ -- 0.003 g/100 ml
CH₄ -- 0.003 g/100 ml
N₂O -- 0.26 g/100 ml
CO₂ -- 0.34 g/100 ml

*at 0°C
• Properties of gases.
  • Highly soluble.
    • NH₃
  • Slightly soluble.
    • CH₄, N₂O, H₂S, N₂, etc.
• Reactive gases.
  • NH₃, H₂S, PH₃

Solubilities* in water
NH₃ -- 89.9 g/100 ml
H₂S -- 0.66 g/100 ml
N₂ -- 0.003 g/100 ml
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*at 0°C
• Properties of gases.
  • Ammonia properties.
    • Most abundant alkaline constituent in atmosphere.
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  • Most abundant alkaline constituent in atmosphere.
  • Can neutralize acid gases.
    • Acid/base gas neutralization.
      • Ammonium sulfate.
      • Ammonium nitrate.
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• On soil, oxidizes to $\text{NO}_3$ (removes an electron acting as promoting acidification).
Properties of gases.

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Ammonium sulfate.

Ammonium nitrate.

On soil, oxidizes to $\text{NO}_3$ (removes an electron acting as promoting acidification).

Highly reactive.
Properties of gases.

Ammonia properties.

Most abundant alkaline constituent in atmosphere.
Can neutralize acid gases.

Acid/base gas neutralization.

Ammonium sulfate.
Ammonium nitrate.

On soil, oxidizes to NO$_3$ (removes an electron acting as promoting acidification).

Highly reactive.

Ubiquitous (every plant has an ammonia compensation point; >0 concentration will be maintained in the biosphere).
• Properties of gases.
• Ammonia properties.
• Properties of emissions.
  • Chemical properties:
    • $\text{NH}_4 \text{ concentration of the medium and the associated free NH}_3 \text{ in solution.}$
    • Hydrogen ion concentration (pH)

\[
p_{(\text{NH}_3)} = RT \left(10^{\frac{n_1 - n_2}{T}}\right) \left[\frac{\text{NH}_4^+}{H^+}\right]
\]
• Properties of gases.
• Ammonia properties
• Properties of emissions.
  • Chemical properties.
• Physical properties:
  • Solution temperature.

\[
p_{(NH_3)} = RT \left( 10^{\frac{n_1-n_2}{T}} \right) \frac{[NH_4^+]}{H^+}
\]

\[
D_{NH_3} = n_1 \frac{T}{\exp\left(\frac{n_2}{T} - n_3\right)}
\]

Note: There was no significant difference in average daily windspeed.

Lagoon Water Temperature vs NH3 Flux Density

Rainfall Effects

Water Temperature (deg C) vs NH3 Flux Density (kg/ha/day)
• Properties of gases.
• Ammonia properties
• Properties of emissions.
  • Chemical properties.
• Physical properties:
  • Solution temperature.
  • Turbulence.
  • Decrease boundary layer.
  • Increase gradient.

Note: Water temperature varied less than 1.2 deg C.

Note: There was no significant difference in average daily windspeed.

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Note: Water temperature varied less than 1.2 deg C.
• Measurement technologies.
  • Appropriate--non-interference.
    • Gradient techniques--Based on the concept of turbulent diffusion of gas along its mean concentration gradient.

\[ F_{FG} = -K_g \left( \frac{\partial \rho_g}{\partial z} \right) \]
Measurement technologies.
- Appropriate--non-interference.
- Gradient techniques.
  - Aerodynamic (Momentum Balance) method
    - Valid only in neutral conditions so must be corrected for atmospheric stability.
    - Must be cautiously used over rough surfaces.
    - Relative ease in field measurements.
    - With corrections, valid 24 hours per day.
    - Determines representative emissions due to non-interference of atmospheric conditions.

\[
K_m = - \frac{k^2 \Delta u \Delta z}{\ln \left( \frac{z_2 - z_d}{z_1 - z_d} \right)} \left[ \frac{z_2 - z_d}{z_1 - z_d} \right]^2 \Psi
\]
• Measurement technologies.
  • Appropriate—non-interference.
  • Gradient techniques.
    • Aerodynamic (Momentum Balance) method
    • Energy balance method
      • Physically based and no corrections necessary.
      • Requires large number of measurements.
      • Error may be large under low radiation periods.
    • Accurate and useful during daytime conditions.

\[ R_n + G + \int_{z_1}^{z_2} \beta(z) dz + \ell k_{E(z)} \frac{\partial e}{\partial z} + c_p \rho k_{H(z)} \frac{\partial T}{\partial z} + \lambda k_{C(z)} \frac{\partial c}{\partial z} + M = 0 \]
• Measurement technologies.
  • Appropriate--non-interference.
  • Gradient techniques.
    • Aerodynamic (Momentum Balance) method
    • Energy balance method

• Cautions: Not useful in or around structures; however, may be used if the structures are *uniform in space* and turbulence has sufficient *profile development*. 
• Measurement technologies.
  • Appropriate--non-interference.
  • Gradient techniques.
  • Mass-balance methods
    • Integrated horizontal flux (IHF).
      • Physically based.
      • Requires minimum fetch.
      • Instrumentation relatively simple.
  • Very useful for measuring field treatment effects.

\[ F_{IHF} = \frac{1}{x} \int_{z_0}^{z_p} (u \rho_g + u' \rho_g') \, dz \]
• Measurement technologies.
  • Appropriate--non-interference.
  • Gradient techniques.
  • Mass-balance methods
    • Integrated horizontal flux (IHF).
    • Modified IHF.
      • Same principle as MMD.
      • Useful for variable sources and has minimal interference and/or stress on turbulence, crops, or animals.
      • Must be used in a general cross-wind direction.
• Measurement technologies.
  • Appropriate--non-interference.
  • Gradient techniques.
  • Mass-balance methods
  • Backward Lagrangian stochastic analysis (bLS).
    • Can determine a given source relationship from a measured concentration.
    • Generate ‘parcel’ trajectories backward in time and space and emission is inferred from touchdown.
    • Need only windspeed, wind direction, and stability plus coordinates of source and instrumentation.
    • Instrumentation simple, remote measurement, source can be any shape or size.
• **Measurement technologies.**
  • *bLS* works well, but—no ‘silver bullet’.

• Measurement technologies.
  • *bLS* works well, but—no ‘silver bullet’.
  • Inaccurate when accuracy of the MOST-based description of the atmosphere is suspect.
  
  • $|L| = 2$ m
  • $u_* = 0.15$ m sec$^{-1}$
Measurement technologies.

- *bLS* works well, but—no ‘silver bullet’.
- Inaccurate when accuracy of the MOST-based description of the atmosphere is suspect.
- Poor touchdowns.
• **Measurement technologies.**
  • *bLS* works well, but—no ‘silver bullet’.
    • Inaccurate when accuracy of the MOST-based description of the atmosphere is suspect.
  • **Poor touchdowns.**
  • Accuracies comparable.
    • ‘Ideal conditions’, ± 15-20%
    • Large-scale and spatial source complexity, ± 20-30%.
• Measurement technologies.
  • *bLS* works well, but—no ‘silver bullet’.
    • Inaccurate when accuracy of the MOST-based description of the atmosphere is suspect.
  • Poor touchdowns.
  • Accuracies comparable.
• Easy to use:
  • Single 3-D sonic anemometer.
• Measurement technologies.
  • $bLS$ works well, but—no ‘silver bullet’.
    • Inaccurate when accuracy of the MOST-based description of the atmosphere is suspect.
  • Poor touchdowns
  • Accuracies comparable.
• Easy to use:
  • Single 3-D sonic anemometer.
  • Gas sensor.
• Measurement technologies.
  • Appropriate--non-interference.
  • Non-appropriate--interference.
    • Chambers.
      • May give higher emissions if gas-free air is supplied.
      • Destroys normal climatic characteristics.
      • Soluble and reactive gases will sorb and desorb on enclosure and tubing.
        (polyethylene<Teflon<glass<stainless steel<nylon).
      • Spatial variability high, large errors.
      • Useful only for relative and non-soluble gas comparisons.
• Measurement technologies.
  • Appropriate--non-interference.
  • Inappropriate--interference.
  • Non appropriate--other.
    • Gaussian plume/puff dispersion
      • Key parameters are standard deviation of the plume/puff spread in each direction, $s_x, s_y, s_z$.
      • Sigmas fitted empirically for each situation.
      • For most agricultural situations ($z<100m, x<1000m$), these models are unreliable.
      • In agricultural situations, Gaussian models should be used with a great deal of caution.
• Measurement technologies.
  • Appropriate—non-interference.
  • Non-appropriate—interference.
  • Non-appropriate—other.
    • Gaussian plume/puff dispersion.
  • Tracer gases.
    • A ratioing technique comparing known tracer emissions with unknown gas emissions.
    • Limitation that tracer may not simulate the emission source.
    • Limitation that vertical and horizontal distribution of tracer may be different from emission plume.
    • If tracer weight higher than unknown source (ex. SF$_6$), emission rates biased high.
• Problems with current flux data for modeling.
• Inappropriate measurement techniques.

Emissions from Similar Swine Lagoons

(Tracers*) (Micromet.**)
(kg/ha-day) (kg/ha-day)

Ammonia 5841 19
Methane 1227 42
Nitrous Oxide 201 ~0

* Eklund and LaCosse (1995), tracers.
• Problems with current flux data for modeling.
• Inappropriate measurement techniques.
• Different techniques give variable answers.

Comparison of lagoon emissions determined by different techniques on a swine production farm in North Carolina.

<table>
<thead>
<tr>
<th>Method</th>
<th>Season</th>
<th>Lagoon Emissions (kg NH$_3$-N/ha/day)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chambers</td>
<td>Summer</td>
<td>57.8</td>
<td>Aneja et al. (1999)</td>
</tr>
<tr>
<td>Flux-gradient</td>
<td>Summer</td>
<td>26.7</td>
<td>Harper et al. (2001)</td>
</tr>
<tr>
<td>Gaussian model</td>
<td>Summer</td>
<td>42.3</td>
<td>McCulloch (1999)</td>
</tr>
<tr>
<td>Tracers</td>
<td>Summer</td>
<td>96.0</td>
<td>Todd et al. (2001)</td>
</tr>
</tbody>
</table>

*Debatable as to the most nearly accurate emissions.*
**Comparison of measurement techniques**.

Note: All components independently measured.

Fig. 1. Mass-balance of individually-measured nitrogen components in a North Carolina swine farm [after Harper et al. (2003)].
Comparison of measurement techniques*.

Note:

Use of emissions by chamber technique would give 10% more N emissions than N entering the farm.

Use of the Gaussian technique would give 7% more N emissions than N entering the farm.

Use of the tracer technique would give 20% more emissions than N entering the farm.

Note: Recently-completed studies (Harper et al., 2003) of three lagoons in Utah have shown similar emission rates — 8.3 vs. 7.5% emissions from swine finisher farms.
Available models for ammonia emissions from AFOs.

Statistical.

Harper et al., 2000 (Lagoons, Georgia only, 6 seasons)

Input: $\text{NH}_4^+$ concentration, lagoon pH, $T_{\text{water}}$, windspeed.

Input range limited to GA conditions ($\text{NH}_4^+$, 230-290 mg L$^{-1}$; pH, 7.4-8.0; $T_{\text{water}}$, 10-30°C; $u$, 160-470 cm sec$^{-1}$.

Fit, $R^2 = 0.94$

Calibrated on non-interference emissions measurement.
Available models for ammonia emissions from AFOs.

Statistical.

Harper et al., 2001 (Lagoons, Georgia only, 6 seasons)

Harper et al., 2003 (Lagoons, GA and NC, 12 seasons)

Input: $\text{NH}_4^+$ concentration, lagoon pH, $T_{\text{water}}$, windspeed.

Input range limited to Southeast U.S. conditions
($\text{NH}_4^+$, 180-740 µg $\text{NH}_4^+$-N mL$^{-1}$; pH, 7.4-8.3; $T_{\text{water}}$, 6.1-29.5°C; u, 100-1000 cm sec$^{-1}$).

Fit, $R^2 = 0.78$

Calibrated on non-interference emissions measurement.
• Available models for ammonia emissions from AFOs.
  • Statistical.
    • Harper et al., 2001 (Lagoons, Georgia only, 6 seasons)
    • Harper et al., 2003 (Lagoons, GA and NC, 12 seasons)
    • Aneja et al., 2003 (Lagoons, NC, 4 seasons)
      • Input: $T_{water}$ only
      • Input range limited to measured NC conditions and only to farms measured because of lack of other influences on emissions (no effect of turbulence, pH, and chemical concentration).
      • Fit to lagoons measured with ranges $NH_4^+$, 550-750 mg L$^{-1}$ and pH, 7.5-8.5, $R^2 = 0.82$.
      • Calibrated on chamber emissions measurement.
Available models for ammonia emissions from AFOs.

- Statistical.
  - Harper et al., 2001 (Lagoons, Georgia only, 6 seasons)
  - Harper et al., 2003 (Lagoons, GA and NC, 12 seasons)
  - Aneja et al., 2003 (Lagoons, NC, 4 seasons)
  - Harper et al., 2003 (Housing, NC, 4 seasons)
- Management (3) + climatic factors (2):
  - No geographical limitation.
  - Input: animal wt., 55-200 kg an\(^{-1}\); fan operation, 650-14,400 min day\(^{-1}\); \(\text{NH}_4^+\), 0.1-14.4 µg \(\text{NH}_4^+\)-N g\(^{-1}\); feed, 1.5-2.25 kg an\(^{-1}\) day\(^{-1}\); and \(T_{\text{water}}\), 15-29 °C.
  - Fit, \(R^2 = 0.97\).
  - Based on mass-balance measurements.
Available models for ammonia emissions from AFOs.

- Statistical.
  - Harper et al., 2001 (Lagoons, Georgia only, 6 seasons)
  - Harper et al., 2003 (Lagoons, GA and NC, 12 seasons)
  - Aneja et al., 2003 (Lagoons, NC, 4 seasons)
  - Harper et al., 2003 (Housing, NC, 4 seasons)

- Management (3) + climatic factors (2):
- Management (2) + climatic factors (1):
  - No geographical limitation.
  - Input: animal wt., 55-200 kg an\(^{-1}\); NH\(_4^+\), 0.1-14.4 \(\mu\)g NH\(_4^+\)-N g\(^{-1}\); feed, 1.5-2.25 kg an\(^{-1}\) day\(^{-1}\)
  - Fit, \(R^2 = 0.64\).
  - Based on mass-balance measurements.
• Available models for ammonia emissions from AFOs.
  • Statistical.
    • Harper et al., 2001 (Lagoons, Georgia only, 6 seasons)
    • Harper et al., 2003 (Lagoons, GA and NC, 12 seasons)
    • Aneja et al., 2003 (Lagoons, NC, 4 seasons)
    • Harper et al., 2003 (Housing, NC, 4 seasons)
  • Process.
    • De Visscher et al., 2002 (Lagoons)
      • Emissions from lagoons only.
      • Input: $\text{NH}_4^+$ concentration, lagoon pH, $T_{\text{water}}$, windspeed.
      • Fit, $R^2 = 0.7$ (no limitation on input ranges)
Available models for ammonia emissions from AFOs.

Statistical.
- Harper et al., 2001 (Lagoons, Georgia only, 6 seasons)
- Harper et al., 2003 (Lagoons, GA and NC, 12 seasons)
- Aneja et al., 2003 (Lagoons, NC, 4 seasons)
- Harper et al., 2003 (Housing, NC, 4 seasons)

Process.
- De Visscher et al., 2002 (Lagoons)
- Harper et al., 2004 (Housing)
  - Based on ration input, feed consumption, $T_{\text{water}}$, animal characteristics (size, type), $T_{\text{floor}}$, $T_{\text{ambient}}$ - $T_{\text{house}}$ differential, etc.
  - Will be tested on humid East and arid West locations.
  - In preparation.
Summary--How do we assure appropriate and reliable information for model development?

• Make sure that the most appropriate measurement technology was used (for ammonia, use of non-interference techniques should be required).
• Summary--How do we get appropriate and reliable information?
  • Use of the most appropriate measurement technology (use of non-interference techniques should be preferred in principle when possible).
  • Use of proper or more-sensitive analytical equipment.
• **Summary**--How do we get appropriate and reliable information?
  • Use of the most appropriate measurement technology (use of non-interference techniques should be preferred in principle when possible).
  • Use of proper or more-sensitive analytical equipment.
  • More integrated research (i.e. Systems’ Analysis or Life Cycle Analysis).
Summary--How do we get appropriate and reliable information?

- Use of the most appropriate measurement technology (use of non-interference techniques should be preferred in principle when possible).
- Use of proper or more-sensitive analytical equipment.
- More integrated research (i.e. Systems’ Analysis or Life Cycle Analysis).
- Long-term research (at least one to two years of three seasons each).
• Conclusion--correct and accurate models for emissions prediction require appropriate technologies and equipment for reliable verification data.
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Research to protect natural resources and sustain agriculture in the Southern Piedmont and beyond.