Modelling of Ammonia Emissions

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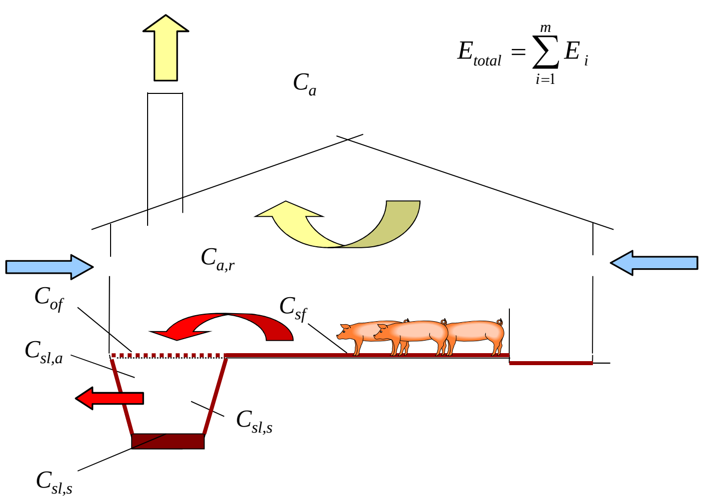
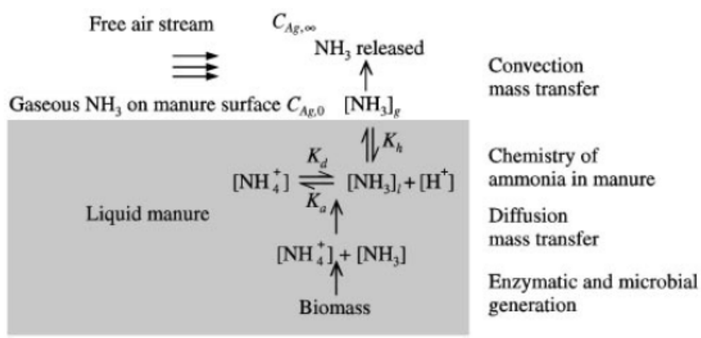
The concept model of emission from a livestock building



The mechanism of ammonia release from manure



Emission & emission coefficient

The core model is a model of convective mass transfer. Determination of the convective mass transfer coefficient is essential for modelling NH_3 release. This coefficient ranges from $1.2x10^{-4}$ to $1.3x10^{-6}$ m/s as investigated in laboratory and field experiments.

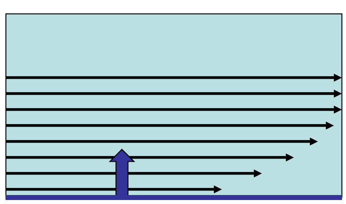
Definations of the emission coefficients: overall emission coefficient; Gas phase convective mass transfer coefficient;

Emission & emission coefficient (2)

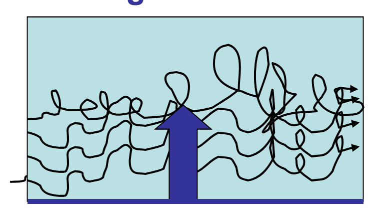
- It usually suffices to express emission coefficient as a function of air velocity at the manure surface and air or manure temperature.
- Determination of the gaseous NH_3 concentration at the manure surface is also essential. This concentration can be calculated using some *sub-models*, which may include *Henry's constant*, *dissociation constant*, *pH*, manure production by animals, NH_3 generation in manure and NH_3 diffusion in manure.
- The Henry's constant found in a reviewed reports has different definitions and units. A standard Henry's constant is needed.

Boundary layer

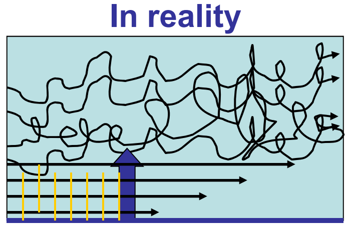
Laminar boundary layer
low emission



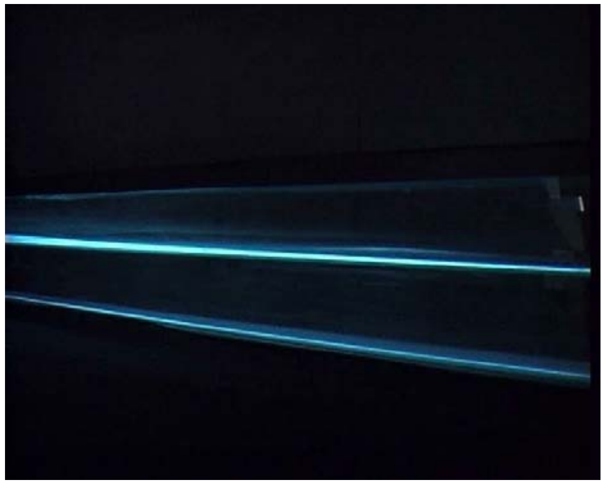
Turbulent boundary layer
high emission



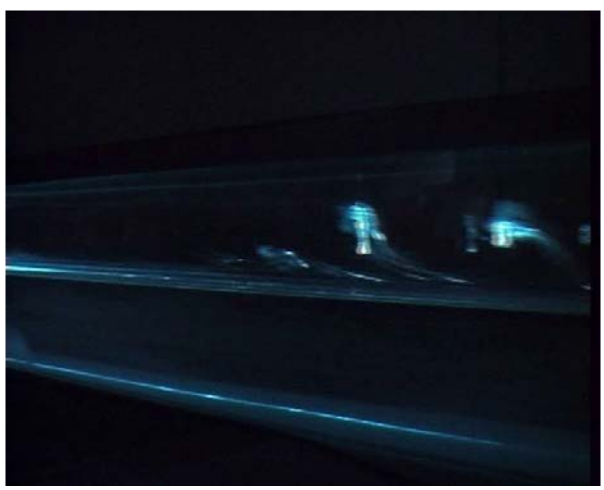
In reality



Example of laminar flow



Example of turbulent flow

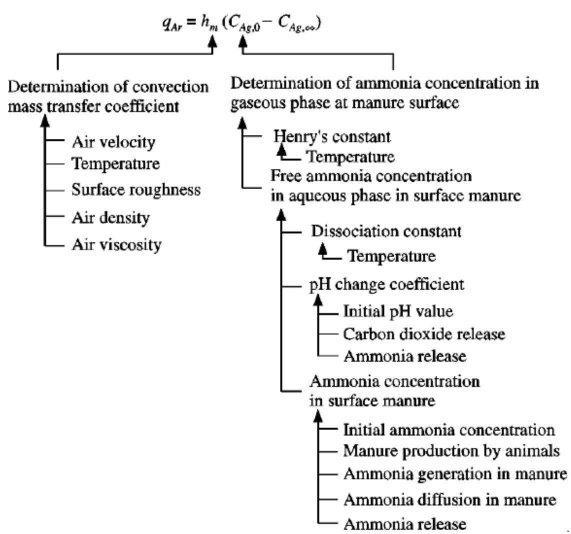


Conception model in math

- **Emission coefficient**

  = f (Re, Sc, *D*, *TI*, *TS*…)

Summarised general structure of the reported mechanistic models of ammonia release from manure (Ni, 1999)



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Ammonia Kinetics in Solusion

The form of ammonia that can be volatilized from a solution is free ammonia

$$\sum NH_3 = NH_3 + NH_4^+$$

$$NH_4^+ \Leftrightarrow NH_3 + H^+$$

where NH_3 and NH_4^+ are at equilibrium at all points in the liquid (effectively instantaneous)

The ammonia dissociation constant can be expressed as:

$$K_d = \frac{NH_3H^+}{NH_4}$$

Ammonia Kinetics in Solusion (2)

The fraction of NH_3 in manure is

$$f = \frac{[NH_3]}{[\sum NH_3]}$$

Since

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

$$f = \frac{K_d 10^{pH}}{K_d 10^{pH} + 1}$$

Estimation of K_d & K_H

Dissociation constant for ammonia in water:

$$K_d = 10^{-(0.0897+2729/T)}$$

where, T is the liquid temperature in ºK
In liquid pig manure, it was dound that the K_d is about one-fifth of the K_d in water (Zhang et al., 1994).

Henry's law constant, K_H, at air-liquid surface:

$$K_H = \frac{C_l}{C_g}$$

$$K_H = 1384 \times 1.053^{(293-T)}$$

The equilibrium ratio of ammonia in the liquid phase and ammonia in the gas phase is often expressed as a **ratio of ammonia concentration and the partial pressure of the ammonia**, which is called the Henry coefficient (Kh).

Again, by applying the ideal gas law at 10°C, this can be converted to the Henry constant. ($H_{cc} = C_l/C_g = H_{cp}RT$ *and here* $K_H = H_{cc}$; $K_h = H_{cp}$)).

The Henry coefficient, expressed in g·cm^{-3} atm^{-1}, was given by Hashimoto and Ludington (1971) as:

$$K_h = 1.013 \times (1.053)^{293-T}$$

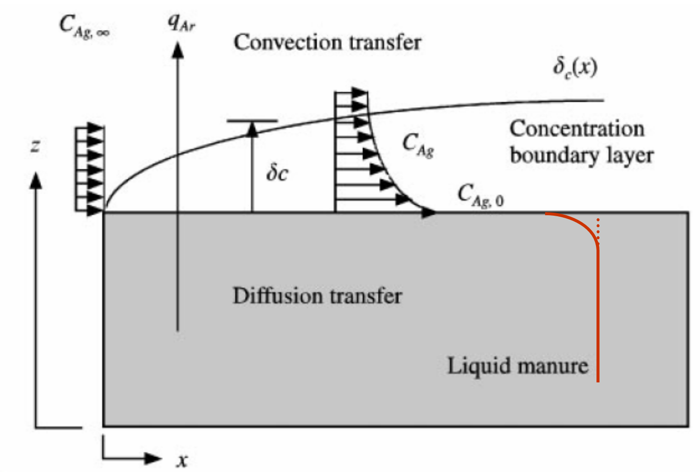
This results in the following expression for Henry's constant:

$$K_H = 1384 \times 1.053^{(293-T)}$$

(Elzing & Monteny, 1997)

Concentration boundary layer theory adopted in ammonia release models

Note: δc, thickness of concentration boundary layer; C_{Ag}, concentration of gaseous NH_3; $C_{Ag,\infty}$, concentration of gaseous NH_3 in free air stream; $C_{Ag,0}$, concentration of gaseous NH_3 at liquid surface; q_{Ar}, flux of NH_3 release; x horizontal distance; z, vertical distance.



The Overall Mass Transfer Coefficient

Emission flux N

$$N_g = k_g (C_{gb} - C_{gi})$$

$$N_l = k_l (C_{lb} - C_{li})$$

$$N_g = N_l$$

$$C_{gi} = C_{li} / K_H$$

These investigators considered mass transfer from a liquid to a gas to take place through two phases, one in the liquid and one in the gas. As with heat transfer, an overall mass transfer coefficient can be written:

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{K_H k_l}$$

where the driving force analogous to temperature gradient is the component partial pressure gradient. Henry's law coefficient, K_H, is introduced to allow concentration gradients within the liquid to be replaced by their equivalent partial pressure gradients. The k_g relates to partial pressure and k_l relates to concentration. If the bulk fluids are well mixed, then essentially all resistance to mass transfer occurs within the two boundary layers each side of the interface. Under these conditions, Halsam et al. determined experimentally that:

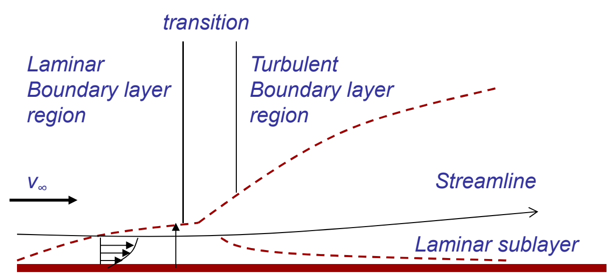
$$k_g = f(v^{0.8} T^{-1.4})$$

$$k_l = g(T^4)$$

(Anderson *et al.*, 1987)

The Boundary Layer Concept

The observation of decreasing region of influence of shear stress as the Reynolds number is increased led Ludwig Prandtl to the boundary-layer concept in 1904.



Boundary layer on a flat plate

The Boundary Layer Concept

The criterion for the type of boundary layer present is the magnitude of Reynolds number, Re_x, known as the local Reynolds number, based on the distance x from the leading edge.

$$\mathrm{Re} \equiv \frac{x v \rho}{\mu}$$

(a) $Re_x < 2x10^5$ the boundary layer is laminar

(b) $2x10^5 < Re_x < 3x10^6$ the boundary layer may be either laminar or turbulent

(c) $3x10^6 < Re_x$ the boundary layer is turbulent

μ (dynamic viscosity)=1.82 (kg/m s) x 10^{-5} (at temperature 20 ºC)

The Boundary Layer Concept

For laminar flow:

$$\frac{k_c x}{D_{AB}} = Sh_x = 0.332\,\mathrm{Re}_x^{1/2}\,Sc^{1/3}$$

For turbulent flow:

$$\frac{k_c x}{D_{AB}} = Sh_x = 0.0292\,\mathrm{Re}_x^{4/5}\,Sc^{1/3}$$

where k_c is convective transfer coefficient at location x

The Boundary Layer Concept

For laminar flow:

$$k_c = \frac{Sh_x}{x} D_{AB} = \frac{D_{AB}}{x} 0.332 \,\mathrm{Re}_x^{1/2}\, Sc^{1/3}$$

For turbulent flow:

$$k_c = \frac{Sh_x}{x} D_{AB} = \frac{D_{AB}}{x} 0.0292 \,\mathrm{Re}_x^{4/5}\, Sc^{1/3}$$

The Boundary Layer Concept

For laminar flow:

$$\overline{k_c} L = \int_0^L \frac{Sh_x}{x} D_{AB} = \int_0^L \frac{D_{AB}}{x} 0.332 \,\mathrm{Re}_x^{1/2}\, Sc^{1/3}$$
$$= 0.664 D_{AB} Sc^{1/3}\, \mathrm{Re}_L^{1/2}$$

For turbulent flow:

$$\overline{k_c} L = \int_0^L \frac{Sh_x}{x} D_{AB} = \int_0^L \frac{D_{AB}}{x} 0.0292 \,\mathrm{Re}_x^{4/5}\, Sc^{1/3}$$
$$= 0.0365 D_{AB} Sc^{1/3}\, \mathrm{Re}_L^{4/5}$$

where $\overline{k_c}$ is average convective transfer coefficient along the length L

The Boundary Layer Concept

For laminar flow:

$$\frac{\overline{k_c} L}{D_{AB}} = Sh_L = 0.664 Sc^{1/3} \mathrm{Re}_L^{1/2}$$

For turbulent flow:

$$\frac{\overline{k_c} L}{D_{AB}} = Sh_L = 0.0365 Sc^{1/3} \mathrm{Re}_L^{4/5}$$

The Boundary Layer Concept

Schmidt number, Sc, is the ratio of momentum diffusivity (viscosity) and mass diffusivity, and is used to characterize fluid flows in which there are simultaneous momentum and mass diffusion convection processes:

$$Sc = \frac{\upsilon}{D} = \frac{\mu}{\rho D} = \frac{viscous\ diffusion\ rate}{molecular(mass)\ diffusion\ rate}$$

*Roughly, considering only nitrogen and oxygen and using 80%/20% instead of 78%/21%, the average molecular weight of air is about 0.8 * 0.028 + 0.2 * 0.032 = 0.0288 kg/mol*

Molar mass of NH_3 = 17.03052 g/mol

The Boundary Layer Concept

The diffusivity (coefficient) of NH_3 in air may be calculated by an empirical relation developed by Fuller et al. (1966):

$$D_{NH_3,Air} = \frac{10^{-7}\left(273.15+T\right)^{1.75}\left(1/M_{NH_3}+1/M_a\right)^{1/2}}{p\left[(\Sigma_{NH_3} v_i)^{1/3}+(\Sigma_a v_i)^{1/3}\right]^2}$$

where diffusion volumes for molecules of air, $\Sigma_a v$, and NH_3 $\Sigma_{NH3} v$ have a value of 20.1 and 14.9 respectively (Fuller et al., 1966).

Roughly, considering only nitrogen and oxygen and using 80%/20% instead of 78%/21%, the average molecular weight of air is about 0.8x0.028 + 0.2x0.032 = 0.0288 kg/mol

Molar mass of NH_3 = 17.03052 g/mol

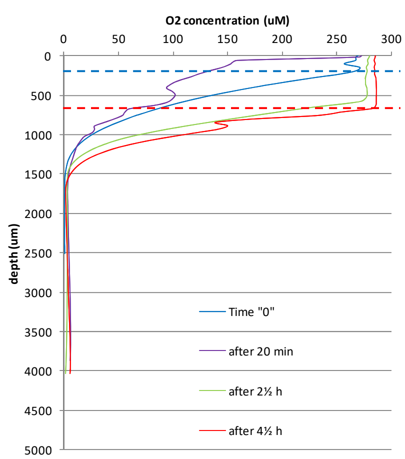
Exercise

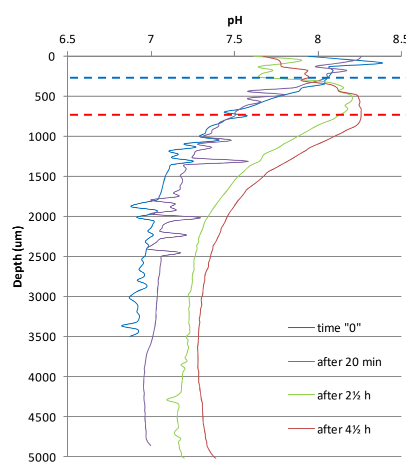
- Liquid manure at temperature of 10 ^oC, with pH of 8, TAN of 2.38 g/l, calculate the ammonia concentration at gas phase boundary layer in equilibrium condition.
- What about concentration level when manure temperature is 25 ^oC?
- Check the results when pH is varied to 7 in the case 1.

Exercise

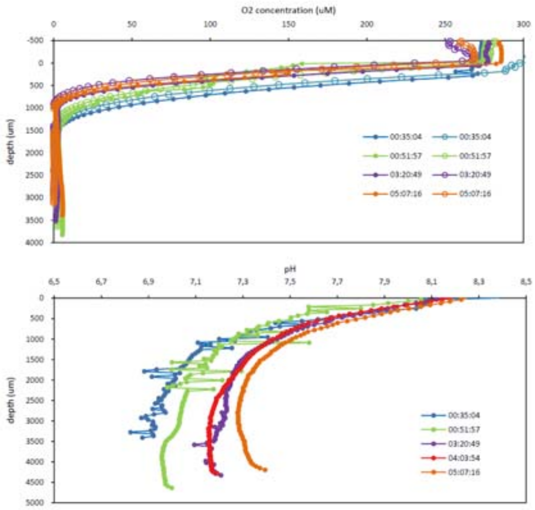
- Calculate Sh number for air in both laminar & turbulent flow at velocity of 0 - 0.5 m/s, over a emission surface length, L, of 6 m
- Calculate air phase mass transfer coefficient k_a for NH_3 at temperature of 20 ^oC at the same air velocity ranges and different flow types

O_2 and pH at boundary layer of slurry





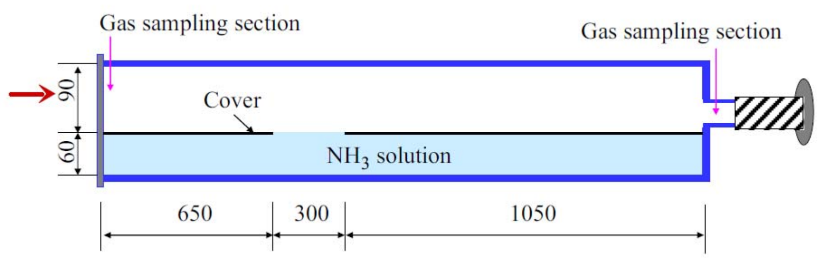
O_2 and pH at boundary layer of slurry



Boundary Layer, Inlet Air Momentum & Ventilation Rate Effects on modelling of Emission

Day 1, Part 2

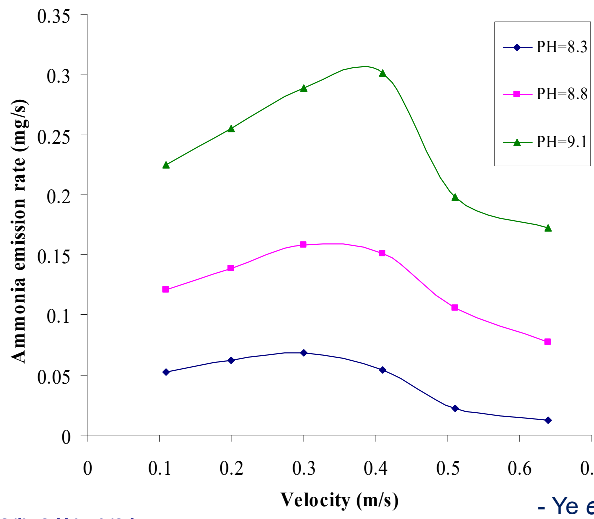
Ammonia emission measurement in a small wind tunnel



All dimension in mm

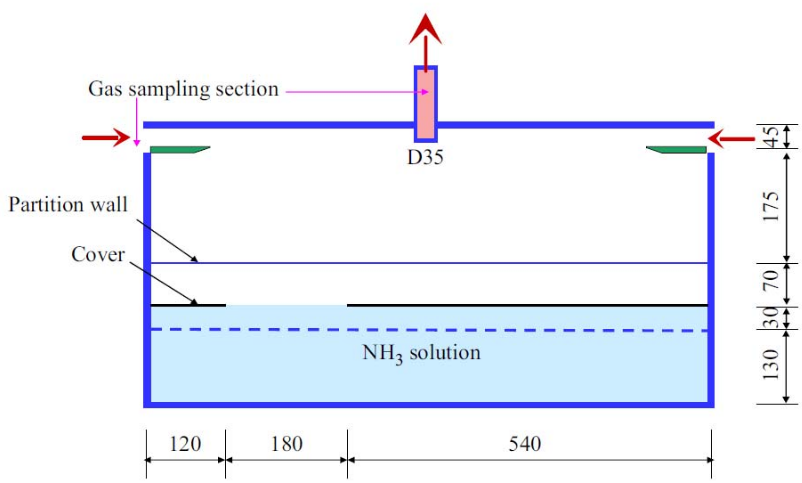
- Ye *et al.*, 2008a

Ammonia emission rate and air velocity above the emission surface in the small wind tunnel with different pH values



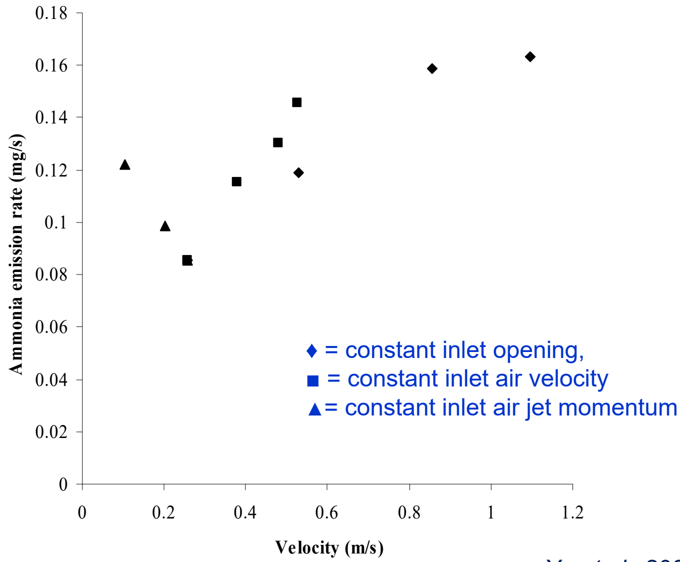
- Ye *et al.*, 2008a

A 1:12.5 scale model experiment



- Ye *et al.*, 2008a

In the scale model experiment



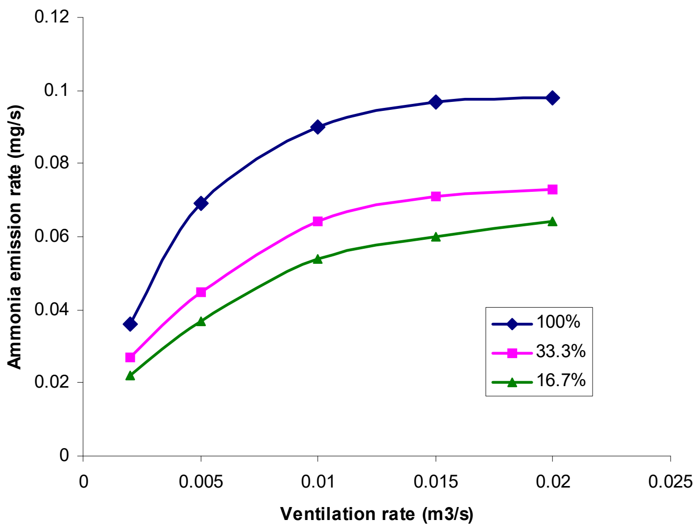
- Ye *et al.*, 2008a

NH_3 emissions affected by ventilation rates *with scale model & pig slurry*

Head space height: 0.026, 0.05 & 0.072m

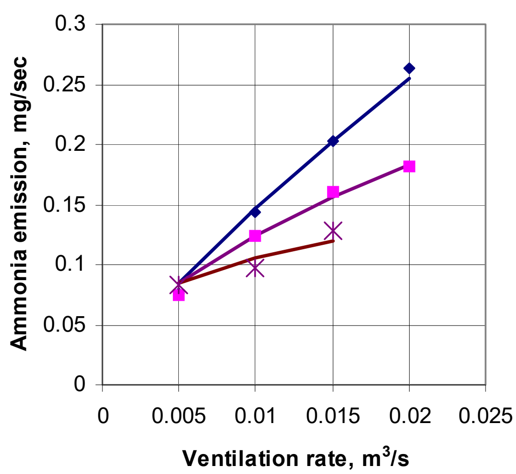
- Ye *et al.*, 2008b

1:12.5 scale model room; Pit head space height = 0.05m



- Ye *et al.*, 2008b

Effects of ventilation control strategies on emission



- Zhang *et al.*, 2008

Boundary Layer, Inlet Air Momentum & Ventilation Rate Effects on modelling of Emission

References:

Ye Z; Zhang G; Li B; Strøm JS; Tong G; Dahl PJ (2008a). Influence of airflow and liquid properties on the mass transfer coefficient of ammonia in aqueous solutions. Biosystems Engineering, 100(3): 422-434.

Ye Z; Zhang G; Li B; Strøm JS; Dahl PJ (2008b). Ammonia emissions affected by airflow in a model pig house: effects of ventilation rate, floor slat opening, and headspace height in a manure storage pit. The Transaction of the ASABE, 51(6), 2113-2122

Zhang, G., B. Bjerg, J. S. Strøm, S. Morsing, P. Kai, G. Tong, and P. Ravn. 2008. Emission effects of three different ventilation control strategies--A scale model study. Biosystems Engineering 100: 96-104

Boundary Layer, Inlet Air Momentum & Ventilation Rate Effects on modelling of Emission

Thinking:

Based on the literature we studied,

- Can we build a steady state ammonia emission model for a farm animal housing system?

- Can we build a dynamic ammonia emission model for a farm animal housing system?

Identify the potential, challenges and further research efforts, that might be needed.

A case discussion:

Read

Blanes-Vidal, V., S. G. Sommer, and E. S. Nadimi. 2009. Modelling surface pH and emissions of hydrogen sulphide, ammonia, acetic acid and carbon dioxide from a pig waste lagoon. Biosystems Engineering 104:510-521.

Describe

1. General considerations for modelling emission from a source surface;
2. Important factors that may influence the emission process across the boundary layer;
3. Approach that you may consider for emission modelling – and why.