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What happens to nitrogen when manure is added to the surface of CLM4.5

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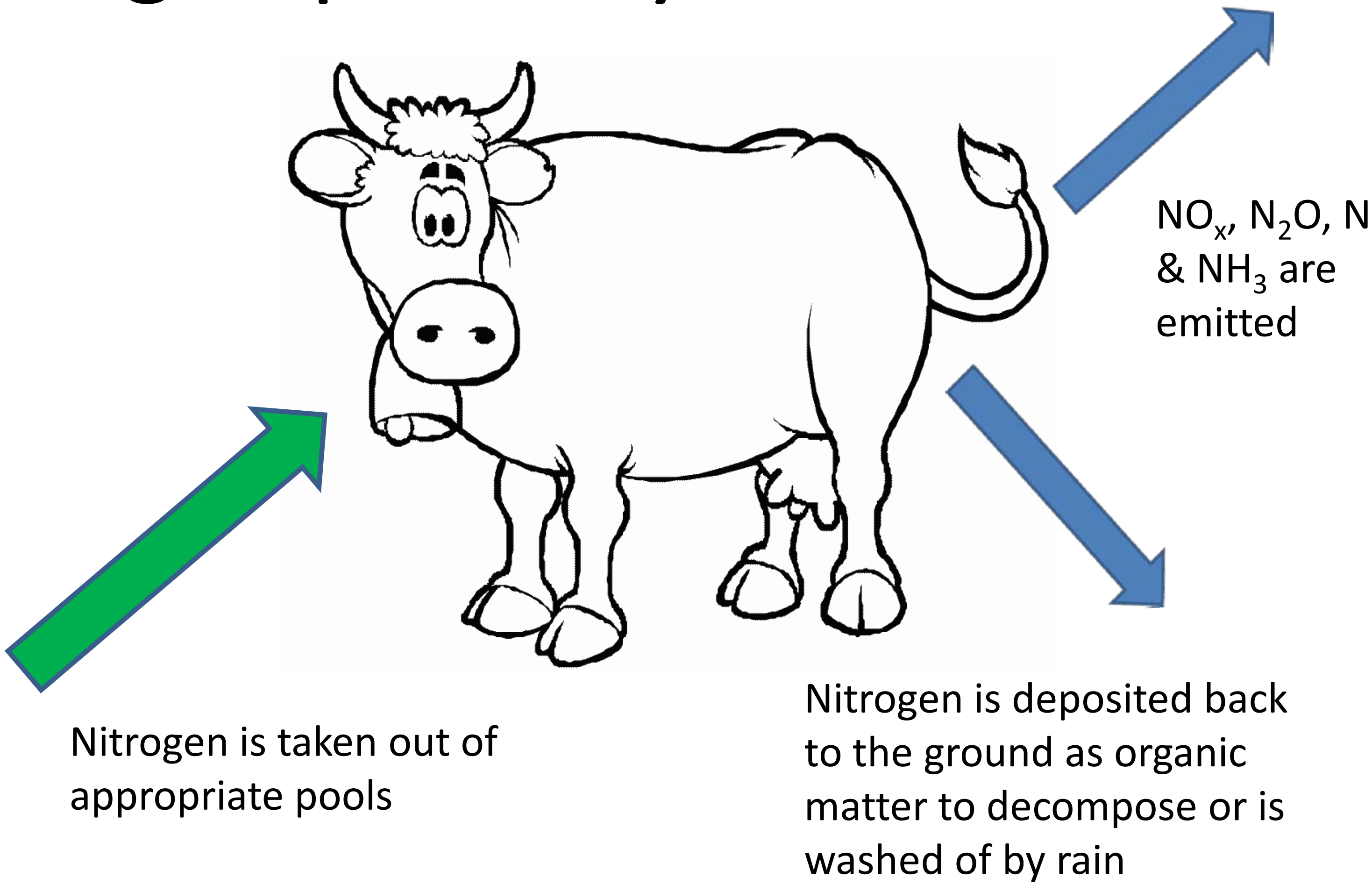
Rationale: N is added to the surface of the Earth as manure what does this do to the biogeochemistry?

Aim: To build a zeroth order model to calculate nitrogen pathways from manure

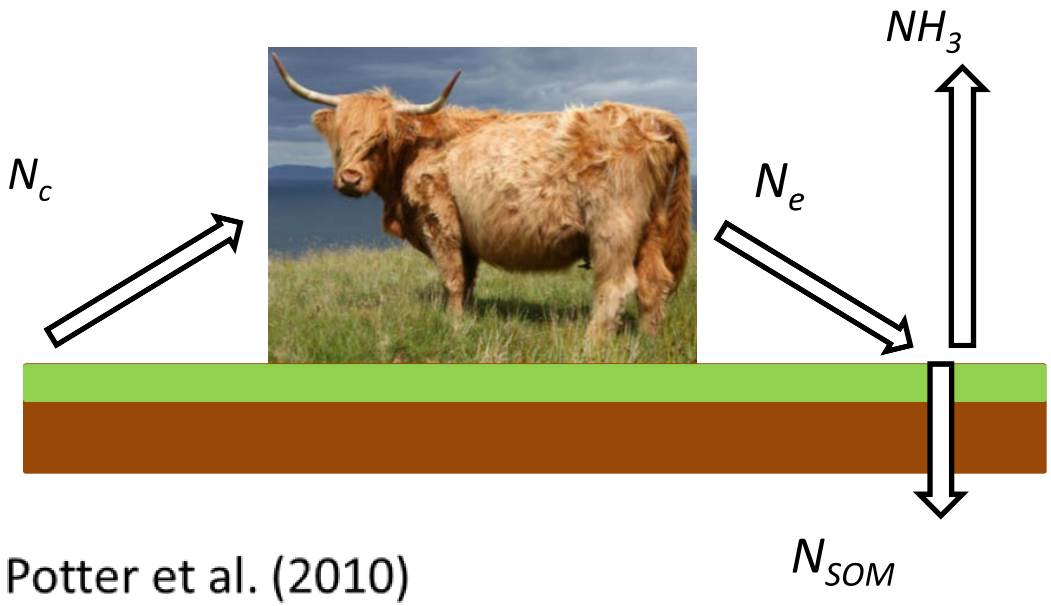
- Current Methodology
  - Emission factors
- How could this be done better?
  - Semi-empirical model
  - Validation
  - Improvements
- What next?

Nitrogen pathways from manure



Empirical Model

Emission factor



Method:

N_e is based on Potter et al. (2010)

N_c equals N_e

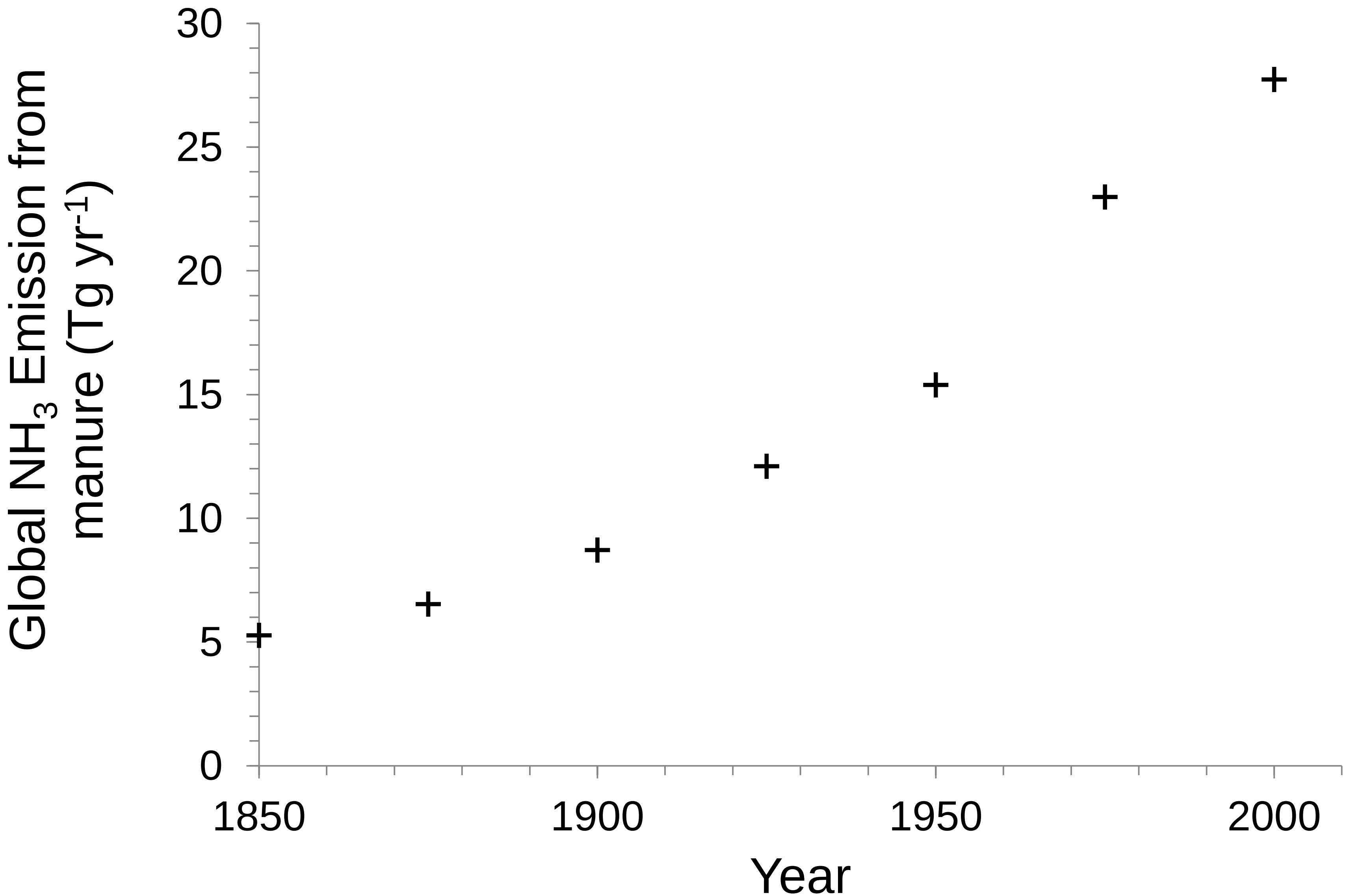
NH_3 is calculated using volatilization rates (F_{fa}) from Bouwman et al. 2002.

- 21 % of N_e volatilizes in developed countries (F_{fa} = 0.21)
- 26 % of N_e volatilizes in developing countries (F_{fa} = 0.26)

$$NH_3 = F_{fa}N_e$$

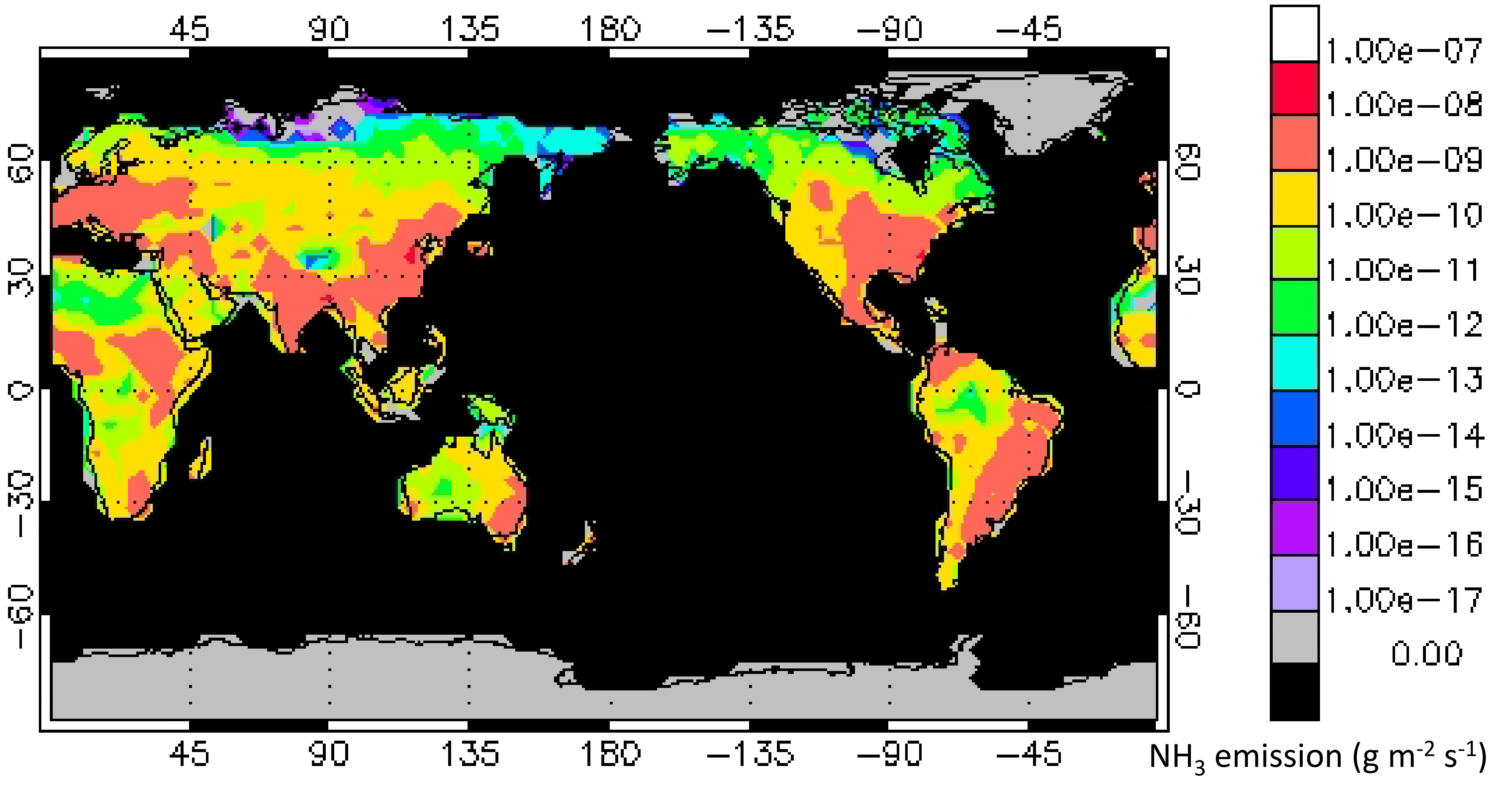
Any unvolatilized nitrogen is then returned as soil organic matter (N_{SOM})

$$N_{SOM} = N_e - NH_3$$

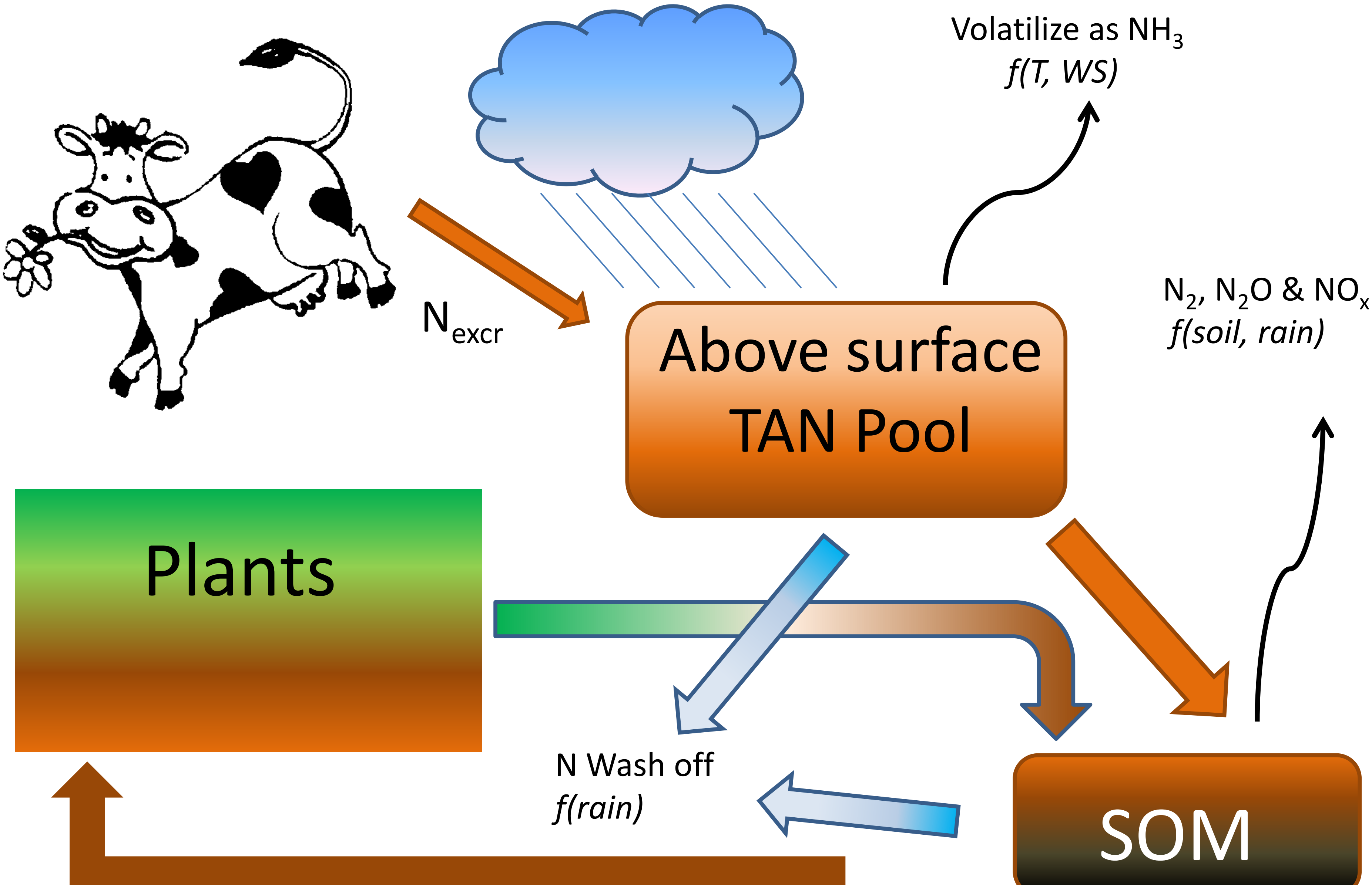


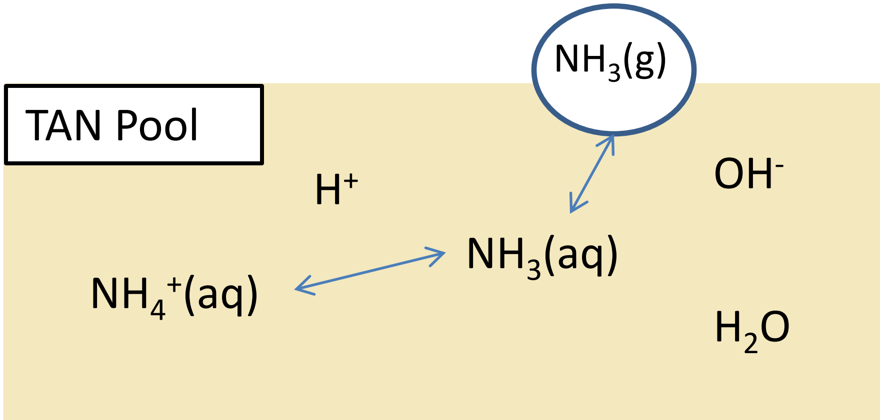
Global NH_3 Emission from manure (Tg yr^{-1})
30
25
20
15
10
5
0
1850
1900
1950
2000
Year

NH_3 emission	1850 Tg NH_3 $year^{-1}$	2000 Tg NH_3 $year^{-1}$
CLM4.5 (Emission factor)	5.3	27.7
Galloway et al. (2004)	5.9	26.3



Semi-Empirical Model


Volatilize as NH_3
$f(T, WS)$
N_{excr}
N_2, N_2O & NO_x
$f(soil, rain)$
Above surface TAN Pool
Plants
N Wash off
$f(rain)$
SOM



Volatilization of NH_3 gas from the TAN pool depends on Henry's Law and dissociation equations (Sutton et al., 1994; Nemitz et al., 2000; Loubet et al., 2009).

i) Henry's Law: The temperature dependent bi-directional flow :

$$NH_3(g) + H_2O \overset{k_{ha}}{\longleftrightarrow} NH_3(aq)$$

Where, equilibrium rate, k_{ha}, is governed by the T dependent Henry's Law constant

ii) Dissociation Equations:

Ionization of $NH_3(aq)$ in the presence of H^+ forms NH_4^+:

$$NH_3(aq) + \ H^+ \overset{k_b}{\leftrightarrow} NH_4{}^+(aq)\ ;\ K_b = \frac{[OH^-][NH_4{}^+(aq)]}{[NH_3(aq)]}$$

Acidity is defined by the bi-directional relationship of water and H^+ and OH^-:

$$H_2O \overset{k_w}{\leftrightarrow} H^+ + \ OH^-\ ;\ k_w = [H^+][OH^-]$$

iii) Combining i) Henry's Law and ii) the dissociation equations gives the NH_3 gas concentration at the surface of the TAN pool:

$$\chi_s = [NH_3(g)] = \frac{[NH_4{}^+(aq)]\, k_w}{k_{ha} k_b [H^+]}$$

Excreted N builds in a nitrogen (TAN) pool that will either:

1. **Wash off:** Impose a "wash-off" factor, 0.024 g TAN mm^{-1} (Brouder et al., 2005)

2. **Volatilize as NH_3 (Monteith and Unsworth, 1990; Nemitz et al., 2000; Loubet et al., 2009):**

$$NH_3 = \frac{\chi_s - \chi_a}{R_a + R_b + R_s}$$

Where, NH_3 is ammonia volatilized (g m^{-2} s^{-1})

X_s is the NH_3 (g) concentration at the surface (g m^{-3})

X_a is the free atmosphere NH_3 (g) concentration (g m^{-3})

R_a, R_b and R_s aerodynamic, boundary layer and surface resistances (s m^{-1})

3. **Forms SOM:** N soil organic mineral through nitrification (Stange & Neue, 2009).

$$N_{SOM} = \frac{2\, R_{max} f(T)}{3.6x10^9 P_{TAN}}$$

Where, N_{som} is the nitrification rate (g m^{-2} s^{-1})

R_{max} is the maximal nitrification rate (manure = 84 µg N kg^{-1} h^{-1})

$f(T)$ is the effect of soil temperature 0 → 1

P_{TAN} is the mass of TAN in manure (g TAN g $manure^{-1}$)

4. **Forms N_2, N_2O & NO_x through nitrification and denitrification**

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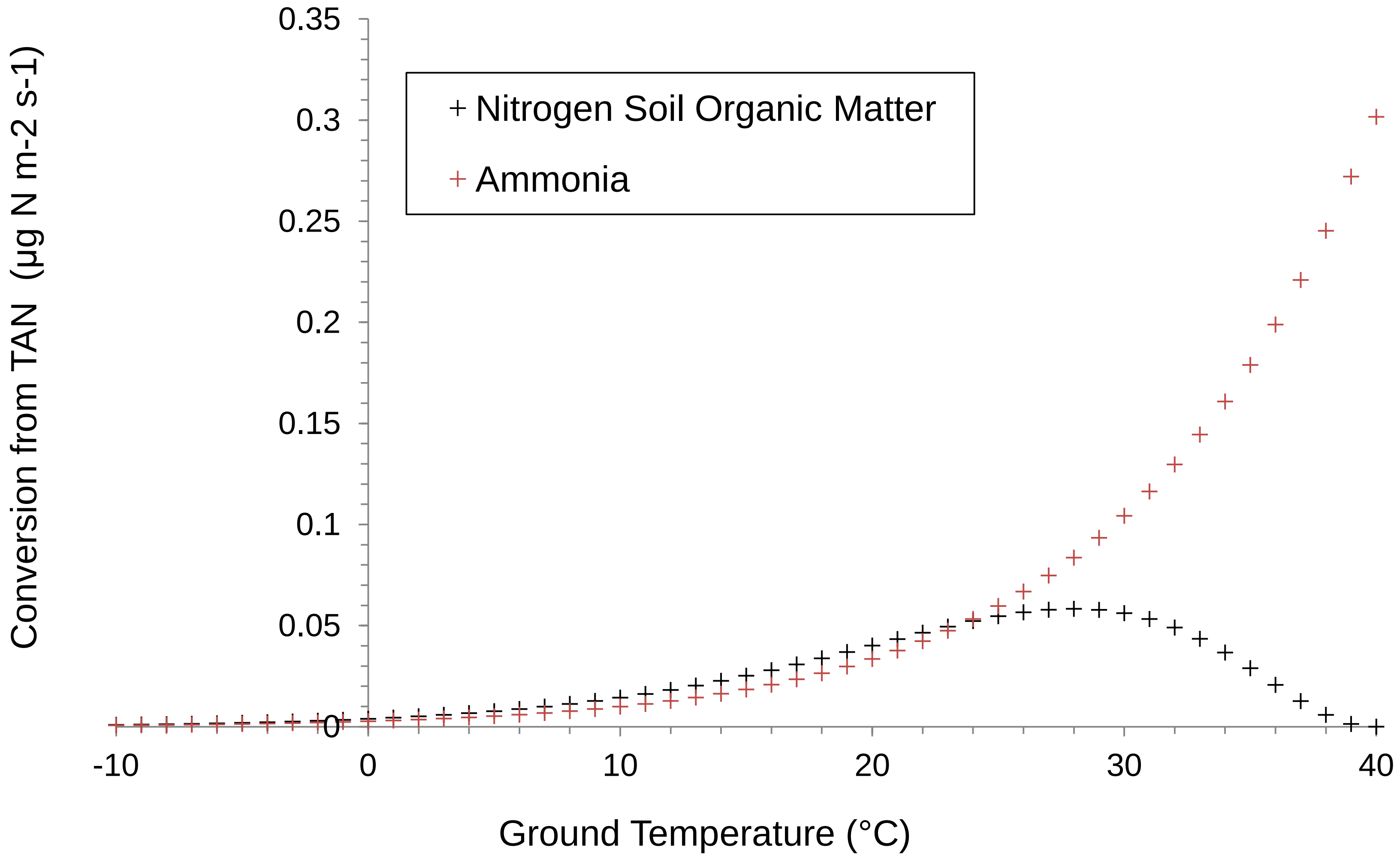
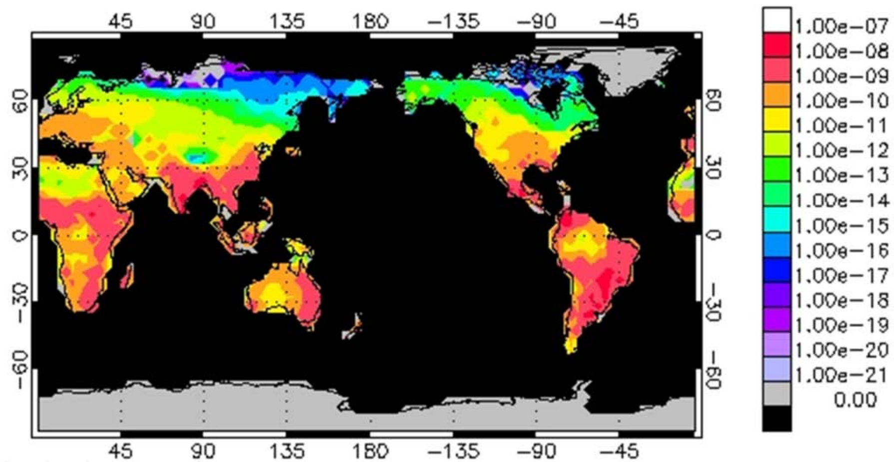
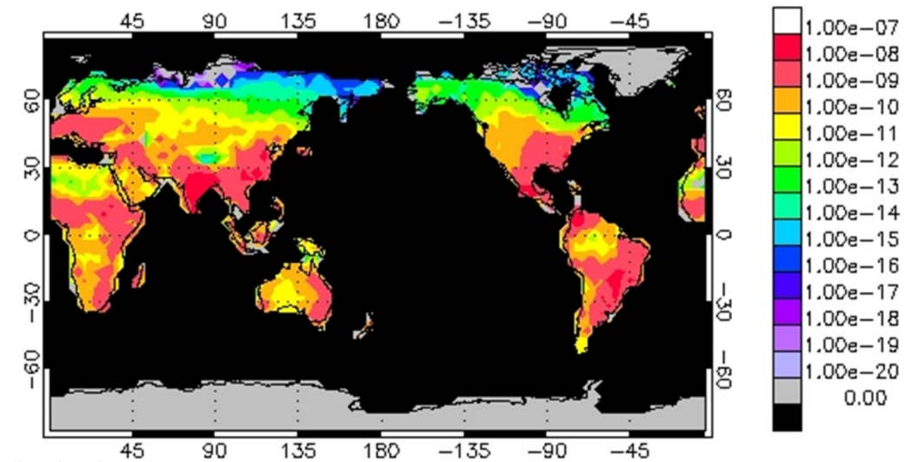
Response to ground temperature



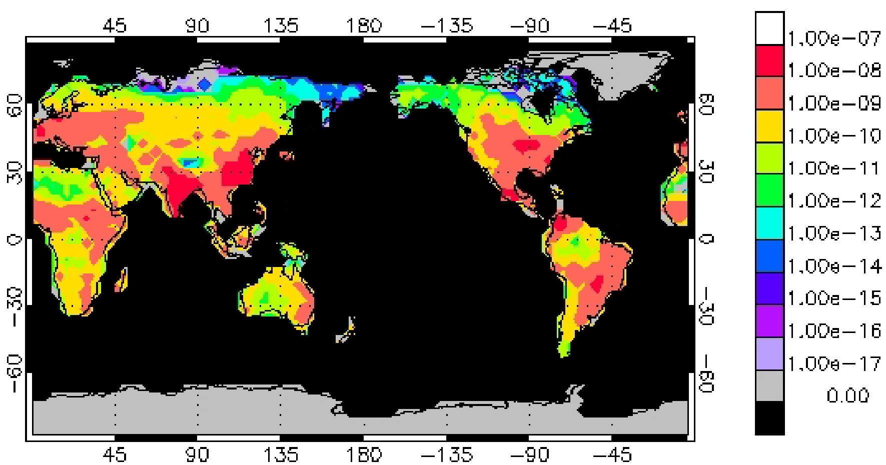
January



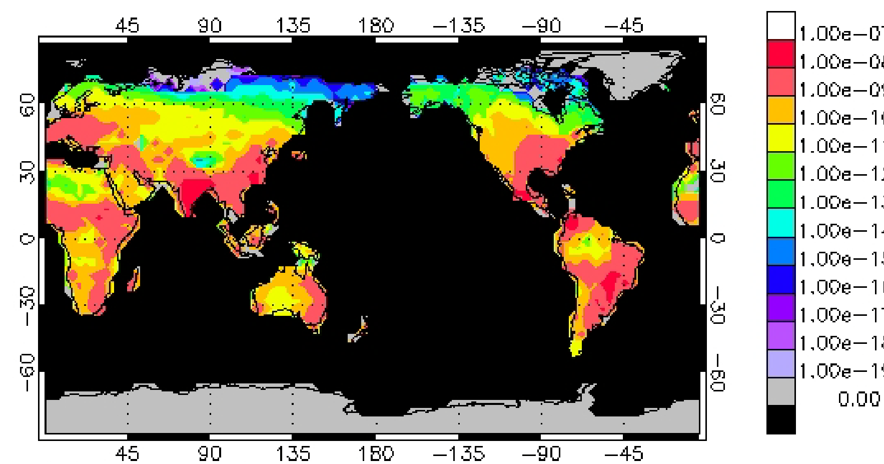
April



July



October



Seasonal changes in NH_3 emission (g m^{-2} s^{-1})

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1850 Nitrogen pathways

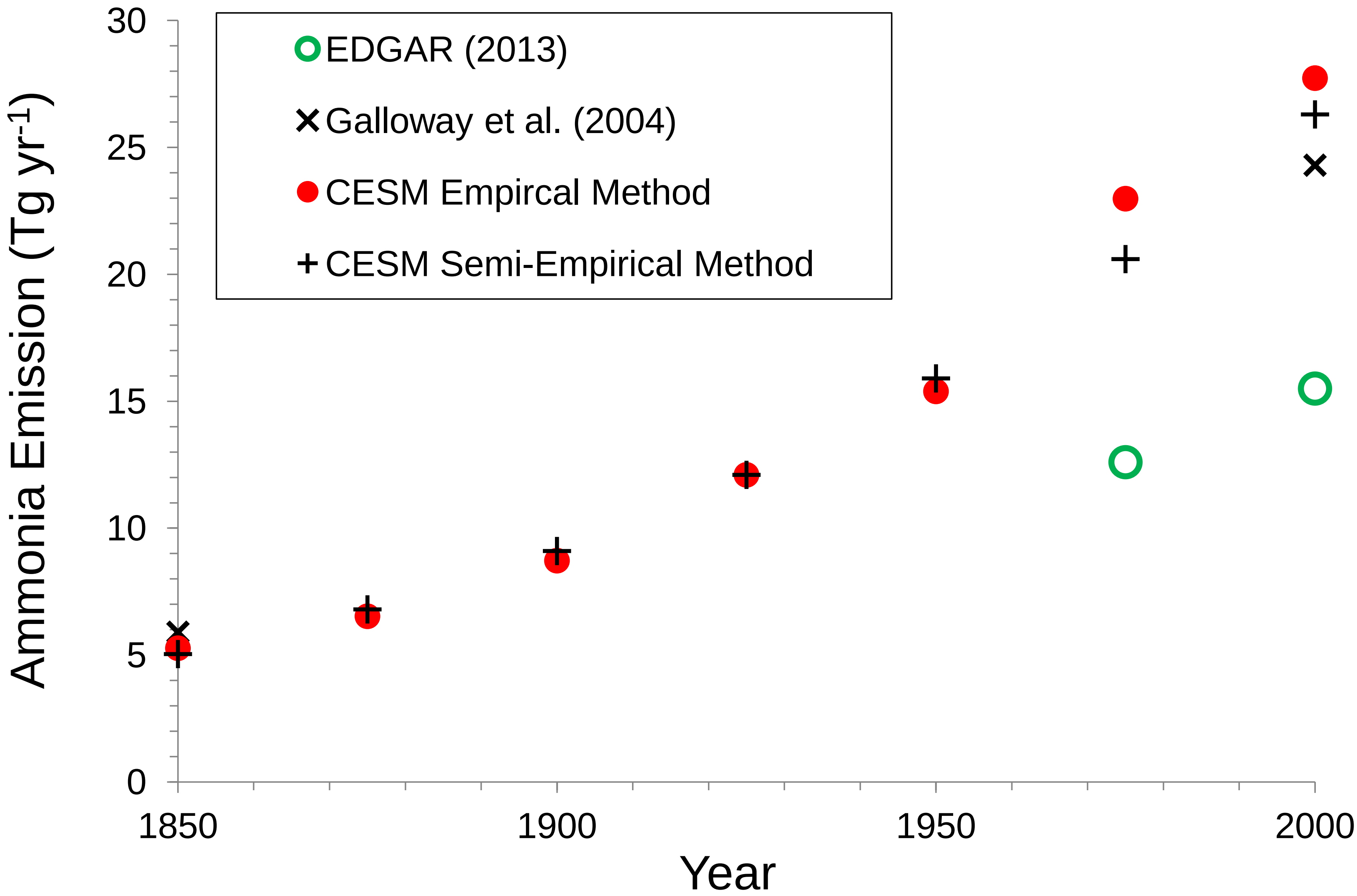
Source	N Input (Tg)	NH_3 (Tg)	N run off (Tg)	N to SOM (Tg)	N_2O (Tg)	NO_x (Tg)
CLM4.5*	25.5	5.03	8.75	5.33	0.122	0.03
Galloway (2004)		5.9				

* N_2O and NO_x have been calculated as a product of nitrification only

2000 Nitrogen pathways

Source	N Input (Tg)	NH_3 (Tg)	N run off (Tg)	N to SOM (Tg)	N_2O (Tg)	NO_x (Tg)
CLM4.5*	138.4	26.3	47.6	21.1	0.45	0.1
Galloway et al. (2004)		24.3				
EDGAR		15.5			2.08	1.06

* N_2O and NO_x have been calculated as a product of nitrification only


EDGAR (2013)
Galloway et al. (2004)
CESM Empircal Method
CESM Semi-Empirical Method
Ammonia Emission (Tg yr-1)
30
25
20
15
10
5
0
1850
1900
1950
2000
Year

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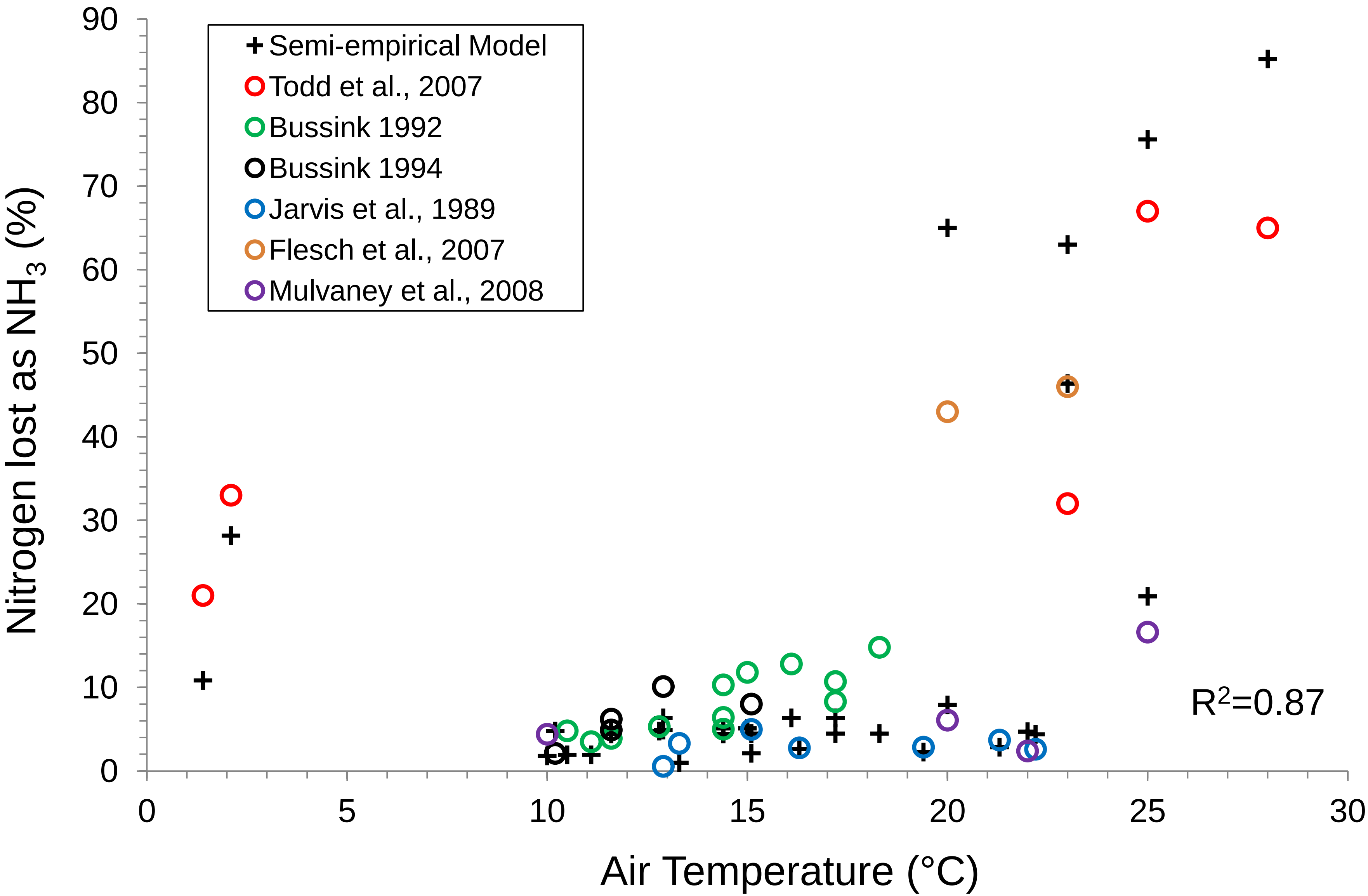
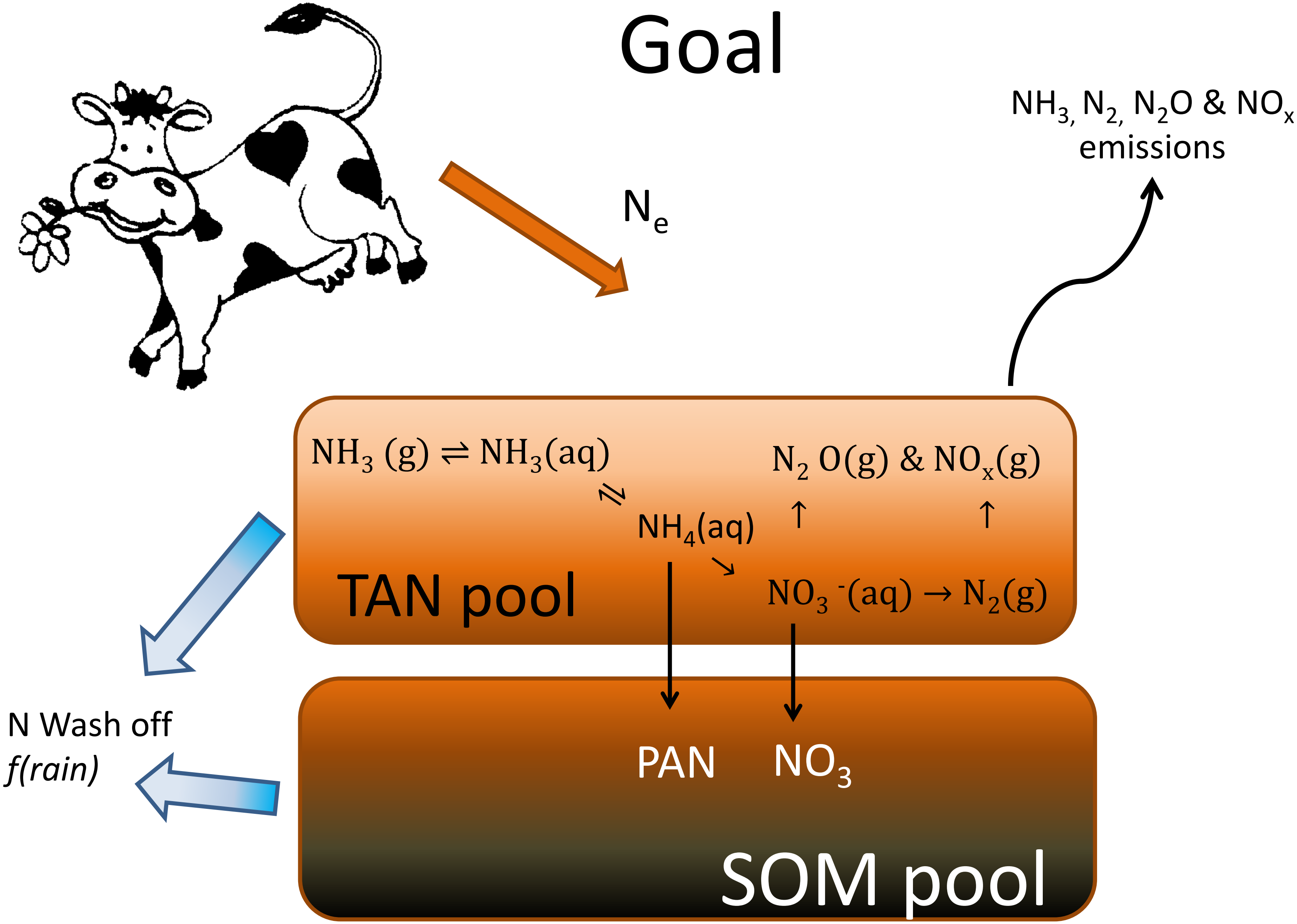


Further work

- Calculate other N emissions (NO_x, N_2O & N_2)
- Model the rate of plant-available nitrogen (PAN) formed from the TAN pool
- Validate other N emissions
- Use a similar method to estimate N pathways from artificial fertilizers

Goal



N_e
NH_3, N_2, N_2O & NO_x emissions
$NH_3 (g) \rightleftharpoons NH_3(aq)$
$N_2 O(g)$ & $NO_x(g)$
$NH_4(aq)$
$NO_3^-(aq) \rightarrow N_2(g)$
TAN pool
N Wash off
f(rain)
PAN
NO_3
SOM pool