Ficks second law of diffusion in cartesian coordinates is:

1.1

Where *C* is the concentration of oxygen in the surface layer (µmol cm-3) at time, *t* (s) at manure depth, *x* (µm). *D* is the diffusion coefficient (cm2 s-1) and *R* is the rate of oxygen consumption (µmol cm-3 s-1). Assuming respiration follows first order kinetics (references) and the system is in steady state, then we can reformulate eq 1.1.

1.2

Where *k* is the positive first order rate constant. Setting , eq 1.2 has the general solution

1.3

The concentration of oxygen must approach zero with increasing manure depths when oxygen consumption is the only process affecting the change of oxygen concentration. This condition can only be true if *A = 0*. The equation is then reduced to:

1.4

At the manure surface oxygen is equilibrium with the air phase, which provides the first of two boundary conditions:

1.5

The second boundary condition is the oxygen gradient at the manure surface, which is measurable with a microsensor:

1.6

Applying first 1.5 to 1.4 and then 1.6 to the derivative of 1.4 give the unknowns (eq. 1.7 and eq. 1.8). Resubstituting α with gives the first order rate constant in eq. 1.9.

1.7

1.8

1.9

We fitted eq. 1.4 to oxygen profiles swine and cattle manure by changing . This allowed us to calculate *k*.

The matlab code for this approach using data from manure4 at steady state (24 h):

syms k D kH Cair dc0 C x

D=2.2\*10^-5 % cm^2\*s^-1

kH = 0.0013/1000\*10^6 % umol cm^-3 ATM^-1

Cair = 0.208 % ATM

dc0 = 0.007 % umol cm^-3 um^-1 red from data

C=kH\*Cair\*exp(-sqrt((D\*dc0^2)/(kH^2\*Cair^2)/D)\*x) % umol cm^-3

fplot(C,[0 1000])

1. Dalby FR et al. (2021) A mechanistic model of methane emission from animal slurry with a focus on microbial groups. PLoS ONE 16(6): e0252881.
2. Dalby FR et al. (2021). Understanding methane emission from stored animal manure: A review to guide model development. J Environ Qual. 2021 Jul;50(4):817-835. doi: 10.1002/jeq2.20252. PMID: 34021608.
3. Dalby FR et al. (2023). Simple Management Changes Drastically Reduce Pig House Methane Emission in Combined Experimental and Modeling Study. Environmental Science & Technology 2023 57 (9), 3990-4002. DOI: 10.1021/acs.est.2c08891
4. Dalby FR et al. Pig slurry organic matter transformation and methanogenesis at ambient and low temperatures. Under review, JEQ (2023)



Solving ficks second law with numerically, we don’t need to set dC/dt =0. Instead we use method of lines to discretize the PDE into a system of ODEs. Applying method of lines to 1.1 and letting R = k\*C, the central difference approximation for the second space derivative is:

1.11

Substituting 1.11 into 1.10, we get the ODE system.

1.12

With boundary and initial conditions:

We solve this ODE system and optimize parameter k with an objective function and get:

