Process Rate Estimator

A modeling side-hustle for the ETH group sustainable agroecosystems

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1 Introduction

Denitrification is the natural process by which nitrate (NO_3^-) in the soil are converted by bacteria into nitrous oxide (N_2O) or pure nitrigen (N_2). The latter is called *total denitrification* — the full process described in Equation 1 takes place.

$$NO_3^- \xrightarrow[\text{reductase}]{\text{Nitrate}} NO_2^- \xrightarrow[\text{reductase}]{\text{Nitrite}} NO \xrightarrow[\text{reductase}]{\text{Nitrite oxide}} N_2O^- \xrightarrow[\text{reductase}]{\text{Nitrous oxide}} N_2 \tag{1}$$

Denitrification occurs in conditions where oxygen is limited, such as waterlogged soils. It is part of the nitrogen cycle, where nitrogen is circulated between the atmosphere, organisms and the earth.

2 Formal model description

2.1 Model parameters

Table 1: Overview of the parameters used in the model.

Symbol	Code	Name	Value	Unit
BD	`BD`	Bulk density (mass of the many particles of the material divided by the bulk volume)	1.686	g cm^{-3}
θ_w	`theta_w`	Soil volumetric water content		
θ_a	`theta_a`	Air-filled porosity	$1-\frac{\theta_w}{\theta_t}$	
θ_t	`theta_t`	Total soil porosity	$1-\frac{BD}{2.65}$	
T	`temperature`	Soil temperature	298	K
D_s	`D_s`	Gas diffusion coefficient	Equation 3	m^{2}s^{-1}
D_fw	`D_fw`	Diffusivity of N_2O in water	Equation 5	
D_fa	`D_fa`	Diffusivity of N_2O in air	Equation 6	
$D_\text{fa,NTP}$		Free air diffusion coefficient under standard conditions	Equation 6	
n	`n`	Empirical parameter (*1*)	1.81	
H	`H`	Dimensionless Henry's solubility constant	Equation 4	
ρ	`rho`	Gas density of N_2O	1.26×10^6	mg m$_{-3}$

The diffusion fluxes between soil increments are described by Frick's law (Equation 2).

$$F_{\mathrm{calc}} = \frac{dC}{dZ} D_{\mathrm{s}} \rho \tag{2}$$

Here, D_s is the gas diffusion coefficient, ρ is the gas density of N_2O, and $\frac{dC}{dZ}$ is the N_2O concentration gradient from lower to upper depth. The fluxes are calculated based on N_2O concentration gradients between 105-135 cm, 75-105 cm, 45-75 cm, 15-45 cm, and 0-15 cm depth layers, and ambient air above the soil surface.

θ_w is the soil volumetric water content, θ_a the air-filled porosity, and θ_T is the total soil porosity.

The gas diffusion coefficient D_{s} was calculated according Equation 3 as established by Millington and Quirk in 1961 (*2*).

$$D_{\mathrm{s}} = \left(\frac{\theta_w^{\frac{10}{3}} + D_{\mathrm{fw}}}{H} + \theta_a^{\frac{10}{3}} \times D_{\mathrm{fa}} \right) \times \theta_T^{-2} \tag{3}$$

Here, H represents a dimensionless form of Henry's solubility constant (H') for N_2O in water at a given temperature. The constant H for N_2O is calculated as follows:

$$H = \frac{8.5470 \times 10^5 \times \exp \frac{-2284}{\mathrm{T}}}{\mathrm{R} \times \mathrm{T}} \tag{4}$$

Here, R is the gas constant, and T is the temperature (T = 298 K).

D_{fw} was calculated according to Equation 5 as documented by Versteeg and Van Swaaij (1988) (*3*).

$$D_{\mathrm{fw}} = 5.07 \times 10^{-6} \times \exp \frac{-2371}{\mathrm{T}} \tag{5}$$

$$D_{\mathrm{fa}} = D_{\mathrm{fa,\ NTP}} \times \left(\frac{\mathrm{T}}{273.15} \right)^n \times \left(\frac{101'325}{\mathrm{P}} \right) \tag{6}$$

2.2 Smoothing curves

The N_2O concentration, site preference as well as $\delta^{18}O$ are estimated as a function of time for every depth and every column, separately. To achieve this function approximation, Kernel Regression as implemented in `npreg` is used (*4*).

2.3 State function set

Still to do.

3 The data

The study uses data collected from a mesocosm experiment – i.e. an outdoor experiment that examines the natural environment under controlled conditions. The experiment was set up as a randomized complete block design, with 4 varieties and 3 replicates, using 12 non-weighted lysimeters. A non-weighted lysimeter is a device to measure the amount of water that drains through soil, and to determine the types and amounts of dissolved nutrients or contaminants in the water. Each lysimeter had five sampling ports with soil moisture probes and custom-built pore gas sample, at depths of 7.5, 30, 60, 90 and 120 cm below soil surface.

$$4 \times 3 \times 5 \times 161 = 9660 \tag{7}$$

Equation 7 shows how many observations we should expect to have. In reality, some observations are missing.

Code	Name	Description
`day_column_depth`	Combination	
`date_R`	Weird date	Year + DOY
`column`	Column	
`depth`	Measurement depth	
`increment`	?	
`variety`	Wheat variety	
`moisture`	Soil moisture	
`concNO3N`	NO_3-N concentration	Nitrate nitrogen concentration ($[NO_3] = [NO_3\text{-}N] * 4.43$).
`NO3N_ha`		
`corrected.N2O`		
`corrected.CO2`		
`mgN2ONm3`		
`gN2ONha`		
`gCO2Cha`		
`CN`		
`d15Nbulk`		
`d15Nalpha`		
`d15Nbeta`		
`SP`	Site preference	
`d18O`		Ratio of stable isotopes oxygen-18 (^{18}O) and oxygen-16 (^{16}O).

References

1. Massman, W. A review of the molecular diffusivities of H2O, CO2, CH4, CO, O3, SO2, NH3, N2O, NO, and NO2 in air, O2 and N2 near STP. *Atmospheric environment* **32**, 1111–1127 (1998).
2. Millington, R. & Quirk, J. Permeability of porous solids. *Transactions of the Faraday Society* **57**, 1200–1207 (1961).
3. Versteeg, G. F. & Van Swaaij, W. P. Solubility and diffusivity of acid gases (carbon dioxide, nitrous oxide) in aqueous alkanolamine solutions. *Journal of Chemical & Engineering Data* **33**, 29–34 (1988).
4. Hayfield, T. & Racine, J. S. Nonparametric econometrics: The np package. *Journal of Statistical Software* **27**, 1–32 (2008).