

E:I Calculations

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Introduction

Here we go over the steps to calculate the evaporation to input (E:I) ratios for sub-arctic lakes based on stable isotopes of water. The steps here follow a comprehensive article on all the theory, assumptions, and much more by Gibson et al. 2016. We highly recommend this text for working with stable water isotopes and mass balances.

Other useful publications are: (list of pubs) Gibson & Edwards 2002, Yi, Y et al 2008, Renee Brooks et al 2014, Wolfe??

E:I Calculations based from ^{18}O

The Theory - Isotope Mass Balance

Assuming our lakes are at steady-state, short term or seasonal variations are minimal, we can write an isotope mass balance as:

Equation 1

$$I = Q + E$$

and with the isotopic values:

Equation 2

$$I\delta_I = Q\delta_Q + E\delta_E$$

where

I = inflow

Q = lake outflow

E = lake evaporation

δ = isotopic values of each

We also assume that our lake is well mixed so that $\delta_Q = \delta_L$, there is no long-term storage, and that $Q = I - E$. Although our lakes have no visible outflows, we assume that if there is any loss that it will be of the same signature of the lake.

We end up with the equation:

Equation 3

$$\frac{E}{I} = \frac{\delta_I - \delta_L}{\delta_E - \delta_L}$$

As proposed by Gibson et al. 2016, we estimate δ_E using the Craig and Gordon (1965) model and convention of Gonfiantini (1986) (ratio of liquid versus vapour):

Equation 4

$$\delta_E = \left(\frac{\delta_L - \varepsilon^+}{\alpha^+} - h\delta_A - \varepsilon_K \right) / (1 - h + 10^{-3}\varepsilon_K)$$

where δ_E (‰) and:

ε^+ = equilibrium isotopic separation (Horita & Wesolowski, 1994)

α^+ = equilibrium fractionation h = relative humidity normalized to water surface temperature (decimal) δ_A = atmospheric moisture ε_K = kinetic isotopic separation

The separation values can be calculated by:

Equation 5: $\varepsilon^+ = (\alpha^+ - 1) \times 1000$

Equation 6: $\varepsilon_K = \theta \times C_K(1 - h)$

where θ = transport resistance parameter

C_K = kinetic constant (14.2‰ for ^{18}O (Horita et al. 2008))

The equilibrium isotopic fractionation and separation values are temperature-dependent, and can be calculated by (Horita & Wesolowski, 1994):

Equation 7

$$\alpha^+(^{18}\text{O}) = \exp \left(\frac{-7.685}{10^3} + \frac{6.7123}{273.15 + T} - \frac{1666.4}{(273.15 + T)^2} + \frac{350410}{(273.15 + T)^3} \right)$$

where

T = temperature at water surface (C)

By substituting the Eq 4 into Eq 3, we get:

Equation 8

$$\frac{E}{I} = \frac{\delta_L - \delta_I}{m(\delta^* - \delta_L)}$$

where

m = temporal enrichment slope defined by:

Equation 9

$$m = \frac{h - 10^{-3} \times (\varepsilon_K + \varepsilon^+/\alpha^+)}{1 - h + 10^{-3} \times \varepsilon_K}$$

δ^* (‰) = limiting isotopic composition, defined by:

Equation 10

$$\delta^* = \frac{h\delta_A + \varepsilon_K + \varepsilon^+/\alpha^+}{h - 10^{-3} \times (\varepsilon_K + \varepsilon^+/\alpha^+)}$$

The last step is to calculate δ_A (‰) via evaporation flux-weighted values of δ_P :

Equation 11

$$\delta_A = \frac{\delta_P - k\varepsilon^+}{1 + 10^{-3}k\varepsilon^+}$$

where

k = seasonality (0.5 for highly seasonal; 1 for non-seasonal)

Alternatively, Gibson & Edwards 2002 estimate δ_A using flux-weighted precip via:

Equation 12

$$\delta_A^{fw} = \alpha^*(T^{fw})\delta_P^{fw} - \varepsilon^*(T^{fw})$$

and

Equation 13

$$\varepsilon_K = C_K(1 - h^{fw})$$

but we used Equation 11 for this publication.

Calculating E:I Values from $\delta^{18}\text{O}\text{-H}_2\text{O}$ (‰)

We have created a function in R to calculate E:I ratios, based on $\delta^{18}\text{O-H-2O}$, using the above equations. Environmental conditions (i.e. evaporation rate, humidity, temperatures, etc.) are set for the sub-arctic around Yellowknife, NT.

The function is based on a table with the following input parameters per sample:

- dL (‰) = -11.77, steady-state lake isotope value (measured value from field)
- dI (‰) = -20.7, source water, likely precipitation (value from Gibson 2001 and GNIP 1999)
- dP (‰) = -23, average value during evaporation season (signal of rain)
- temp (C) = 14.3, average temp. on lake (from Gibson & Reid, 2010)
- humid (dec) = 0.68, relative humidity (from Gibson & Reid, 2010)
- evap (m/yr) = 0.397, annual evap. rate of area (from Gibson & Reid 2010)
- k = 0.7, estimated for our area

```

eee2eye <- function(df, dL, dI, dP, temp, humid, evap, k){

  #Calculate isotope fractionation and separation factors:
  alpha_plus <- exp((-7.685/(10^3)) + (6.7123/(273.15 + df[[temp]]))) - (1666.4/((273.15 + df[[temp]])^2)
  e_plus_permille <- (alpha_plus - 1) * 1000

  theta <- 1
  Ck_permille <- 14.2
  ek_permille <- theta * Ck_permille * (1 - df[[humid]])

  #Calculate dA
  dA_permille <- (df[[dP]] - (df[[k]] * e_plus_permille)) / (1 + ((10^-3) * df[[k]] * e_plus_permille))

  #Calculate temporal enrichment slope (m)
  m <- (df[[humid]] - (10^-3) * (ek_permille + (e_plus_permille / alpha_plus))) / (1 - df[[humid]] + ((10^-3) * (ek_permille + (e_plus_permille / alpha_plus))))

  #Calculate limiting isotopic composition
  dstar_permille <- ((df[[humid]] * dA_permille) + ek_permille + (e_plus_permille/alpha_plus)) / (df[[humid]] + ((10^-3) * (ek_permille + (e_plus_permille / alpha_plus))))

  #Calculate our E:I based on lake sig
  df$E.I <- (df[[dL]] - df[[dI]]) / (m * (dstar_permille - df[[dL]]))

  return(df)
}

ei_input <- read.csv("F:/PostDoc/Publications/Manuscript 1 - Changes Due to Precip/SAMMS DOM and Precip")

ei_input <- eee2eye(ei_input, 'd18O_H2O_permille', 'dI_permille', 'dP_permille', 'temp_C', 'h_dec', 'evap')

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