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: Gibson & Edwards. 2002
Yi et al. 2008
Wolfe et al. 2007
MacDonald et al. 2016
Brock et al. 2007

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

$$\delta_E = \frac{\frac{\delta_L - \varepsilon^+}{\alpha^+} - h\delta_A - \varepsilon_K}{1 - h + 10^{-3}\varepsilon_K}$$

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 18O (Horita et al. 2008))

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

Equation 7

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

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).

k is a very difficult parameter to quantify in that we don't know much about it. For this reason we created a small function that you could approximate a `k` value based on the decimal latitude of your sampling site:

```
k_season <- function(x) {
  k <- (((90 - x) / 90 ) * 0.5)+0.5
  return(k)
}
```

Alternatively, Gibson & Edwards 2002 estimate δ_A using flux-weighted precipitation 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 δ^{18}O-H$_2$O (‰)

We have created a function in R to calculate E:I ratios, based on ^18O-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, represents a flux-weight precip value (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)
- k = 0.7, estimated for our area

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

  #check if using values or specific columns for each parameter
  dL_input <- if(is.numeric(dL) == TRUE) {
    dL
  } else {
    df[[dL]]
  }

  dI_input <- if(is.numeric(dI) == TRUE) {
    dI
  } else {
    df[[dI]]
  }

  dP_input <- if(is.numeric(dP) == TRUE) {
    dP
  } else {
    df[[dP]]
  }

  temp_input <- if(is.numeric(temp) == TRUE) {
    temp
  } else {
    df[[temp]]
  }

  humid_input <- if(is.numeric(humid) == TRUE) {
    humid
  } else {
```

```r
    df[[humid]]
  }

  k_input <- if(is.numeric(k) == TRUE) {
    k
  } else {
    df[[k]]
  }

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

  theta <- 1
  Ck_permille <- 14.2
  ek_permille <- theta * Ck_permille * (1 - humid_input)


  #Calculate dA
  dA_permille <- (dP_input - (k_input * e_plus_permille)) / (1 + ((10^-3) * k_input * e_plus_permille))

  #Calculate temporal enrichment slope (m)
  m <- (humid_input - (10^-3) * (ek_permille + (e_plus_permille / alpha_plus))) / (1 - humid_input + ((
  
  #Calculate limiting isotopic composition
  dstar_permille <- ((humid_input * dA_permille) + ek_permille + (e_plus_permille/alpha_plus)) / (humid_

  #Calculate our E:I based on lake sig
  df$E.I <- (dL_input - dI_input) / (m * (dstar_permille - dL_input))

  return(df)

}

ei_input <- data.frame(dL_permille = c(-11.77, -15.67, -18.23),
                       dI_permille = c(-20.7, -18.2, -20.2),
                       dP_permille = c(-23, -28, -32),
                       temp_C = c(14.3, 12.1, 8.9),
                       h_dec = c(0.68, 0.71, 0.58),
                       k = c(0.7, 0.72, 0.65))

#adding calculated E:I
ei_input <- eee2eye(ei_input, 'dL_permille', 'dI_permille', 'dP_permille', 'temp_C', 'h_dec', 'k')
```

or with numerical inputs:

```r
ei_input <- eee2eye(ei_input, 'dL_permille', -20.7, 'dP_permille', 14.3, 0.68, 0.7)
```