Open Rayleigh - Revised

PAZ

13 février 2018

Introduction

Degradation extent is calculated based on open system Rayleigh equations. The following steps have been taken:

1. The initial transect (cumulative) mass has been calculated based on the original farmer surveys (Book 05, MassDischarge_Outlet).
2. Mass has been converted to concentration (by assuming a constant soil bulk density)
3.

Data used

- **MassBalance_R.csv** (Book 07)

Packages

```
library(sm)
library(vioplot)

library(dplyr)
library(tidyr)
library(zoo)
library(reshape)
library(ggplot2)
library("ggrepel")

if (FALSE){
  library("plotly")
  library("cowplot")
  library("gridExtra")
  library("Cairo")
  library("GGally")
  library("scales")

  library("plotKML")

  # Stats
  library("vegan")
  library("cluster")

  # Saving a xlxs file
```

```
  # library(xlsx)
  }
```

Parameters & assumptions

```
source("global.R")

# Fresh tilled
rho1 = 0.98*10^6 # soil density [g/m3] Leaching experiment, "freshly tilled" soil
depth1 = 0.007 # [m] # Fresh tilled

epsilon_true = epsilon_lab
epsilon_streit = -1.9
```

Farmer plots on transects

```
farm = read.csv2("Data/FarmerPlots.csv", header = TRUE, dec = ".")
farm$Farmer = as.character(farm$Farmer)
farm$onTrans = as.character(farm$onTrans)
farm$Crop = as.character(farm$Crop)
farm$Transect = as.character(farm$Transect)
farm$Date = as.POSIXct(farm$Date, "%d/%m/%Y", tz = "EST")
# Consider only plots on transect
farm = subset(farm, onTrans == "True")
```

Technical sheets

Below are Mercantor Gold and Dual Gold dossages for Corn and Beet. Based on the technical sheets initial concentrations are too low for what was measured in the field. Inspection of the cumulative initial concentration (below) against measured concentrations suggest that Friess and Mathis may have doubled the MG dose. Both farmers also applied MG significantly earlier than all other farmers (about 2-3 weeks). Increasing dosage may have therefore been a motivation to ensure effective weed control. Doubling the dose for Friess and Mathis results in adequate minimum initial concentrations for both North and Talweg and South transects, respectively.

```
DOUBLED = TRUE
if (DOUBLED){
  double = 2
} else {
  double = 1
}

# Product Conc [g/L S-met]
# Dual Gold & Mercantor Gold
DG = 915 # g/L S-met
MG = 960 # g/L

# Dosages # L/m2
```

```
Dbeet = NA
Dcorn = 2.1 * 1/10^4 # L/Ha * 1 Ha / 10000 m2
Mbeet = 0.6 * 1/10^4 * double
Mbeet.Friess = 0.6 * 1/10^4 * double # (Likely larger dosage, early in the season)
Mbeet.Mathis = 0.6 * 1/10^4 * (double+1) # (Likely larger dosage, early in the season)
Mcorn = 2.0 * 1/10^4

# Dosage X Prod. Conc = g/m2
```

Applications - Initial survey

1. Compute the cummulative mass applied for each transect in separate tables
2. Compute D* and B* and evaluate required conditions
3. Determine whether ε or the initial mass applied needs to be revised for each transect.

```
farm1 = farm
farm1$appMass = ifelse(farm$Farmer == "Schmitt", farm$m2*Dcorn*DG,
                       ifelse(farm$Crop == "Corn", farm$m2*Mcorn*MG,
                              ifelse(farm$Farmer == "Friess", farm$m2*Mbeet.Friess*MG,
                                     ifelse(farm$Farmer == "Mathis", farm$m2*Mbeet.Mathis*MG,
                                            farm$m2*Mbeet*MG)))) # [g S-met]
```

Import measured concentrations & δC

```
soils = read.csv2("Data/WeeklySoils_Rng.csv", header = TRUE)
names(soils)
```

```
##  [1] "ID"                   "Transect"             "Wnum"
##  [4] "Date.Soil"            "Date.ti"              "Conc.mug.g.dry.soil"
##  [7] "Conc.ComSoil.SD"      "Mass.Soil.g"          "theta.prct"
## [10] "N_compsoil"           "comp.d13C"            "comp.d13C.SD"
## [13] "N_isoComp"            "prctError"            "DD13C.comp"
## [16] "comp.IMP.d13C"        "MassSoil.g"           "MassSoil.g.SD"
## [19] "Area.N"               "Area.T"               "Area.S"
```

```
soils$Date = as.POSIXct(soils$Date.Soil, "%d/%m/%Y %H:%M", tz = "EST")
soils$Transect = as.character(soils$Transect)
soils = soils[, c( "Date", "Transect" , "Conc.mug.g.dry.soil", "comp.d13C" , "DD13C.comp")]
```

Separate into transects

Initial soil concentrations based on total mass applied (Open Rayleigh requirements)

Open system Rayleigh calculations require estimation of cumulative initial concentration ($C_{Tr_0}(t)$) after any number of plot applications a taking place in a composite sample (i.e. Transect (Tr)) and given by:

$$C_{Tr_0}(t) = \frac{\sum_{a=1}^{A} M_a(t)}{A_{Tr} \cdot D \cdot \rho_b}$$

where, $M_a(t)$ is the total mass applied on transect Tr due to application a at time t, the total plot area associated to the transect (A_{Tr}) (i.e. this is proportional to sampling points along transect, and not extrapolated to areas that the transect did not cross).

North

```
# Inputs
north1 = subset(farm1, Transect == "N")
nArea = sum(north1$m2)
n = north1 %>%
  group_by(Date) %>%
  summarize(totMass = sum(appMass),
            totArea = sum(m2))
n = n[order(n$Date),]
n$cumMass = cumsum(n$totMass)
n$cumConc = ((n$cumMass/(nArea*depth1))*(1/rho1))*10^6 # ug s-met/g soil
n = n[, c("Date", "cumConc")]

# Measured & Inputs (merged)
northSoils = subset(soils, Transect == "N")
northSoils = merge(northSoils, n, by = "Date", all = T)
northSoils$cumConc = na.locf(northSoils$cumConc)
northSoils = northSoils[complete.cases(northSoils$Conc.mug.g.dry.soil),]

northSoils = northSoils[2:nrow(northSoils) , ]
```

Talweg

```
# Inputs
talweg1 = subset(farm1, Transect == "T")
nArea = sum(talweg1$m2)
t = talweg1 %>%
  group_by(Date) %>%
  summarize(totMass = sum(appMass),
            totArea = sum(m2))
t = t[order(t$Date),]
t$cumMass = cumsum(t$totMass)
t$cumConc = ((t$cumMass/(nArea*depth1))*(1/rho1))*10^6 # ug s-met/g soil
t = t[, c("Date", "cumConc")]

# Measured & Inputs (merged)
talwegSoils = subset(soils, Transect == "T")
talwegSoils = merge(talwegSoils, t, by = "Date", all = T)
talwegSoils$cumConc = na.locf(talwegSoils$cumConc)
talwegSoils = talwegSoils[complete.cases(talwegSoils$Conc.mug.g.dry.soil),]
talwegSoils = talwegSoils[2:nrow(talwegSoils) , ]
```

South

```
# Inputs
south1 = subset(farm1, Transect == "S")
nArea = sum(south1$m2)
s = south1 %>%
  group_by(Date) %>%
  summarize(totMass = sum(appMass),
            totArea = sum(m2))
s = s[order(s$Date),]
s$cumMass = cumsum(s$totMass)
s$cumConc = ((s$cumMass/(nArea*depth1))*(1/rho1))*10^6 # ug s-met/g soil
s = s[, c("Date", "cumConc")]

# Measured & Inputs (merged)
southSoils = subset(soils, Transect == "S")
southSoils = merge(southSoils, s, by = "Date", all = TRUE)
southSoils$cumConc = na.locf(southSoils$cumConc)
southSoils = southSoils[complete.cases(southSoils$Conc.mug.g.dry.soil),]
southSoils = southSoils[2:nrow(southSoils) , ]
```

Accounting for dilution

The Rayleigh equation assumes that f reflects solely reduction in concentrations due to degradation and should thus be expressed as $f_{degradation}$. Accounting for dilution processes, the remaining fraction that is measured in the field sample becomes then f_{total}, where:

$$f_{total} = f_{degradation} \cdot f_{dilution} = \frac{C_t}{C_0}$$

```
northSoils$ftot = northSoils$Conc.mug.g.dry.soil/northSoils$cumConc
talwegSoils$ftot = talwegSoils$Conc.mug.g.dry.soil/talwegSoils$cumConc
southSoils$ftot = southSoils$Conc.mug.g.dry.soil/southSoils$cumConc
```

Rearanging,

$$f_{degradation} = f_{total} \cdot F$$

The dilution factor F (i.e. the number of times the source volume has become diluted at the observation location) can be calculated if ϵ_{lab} is known such that:

$$F = e^{(\Delta/\epsilon_{lab} - ln f_{total})}$$

$$\Delta = 1000 \cdot ln\Big(\frac{10^{-3}\delta_t^{13}C + 1}{10^{-3}\delta_0^{13}C + 1}\Big)$$

```
# Streitwieser Semiclassical Limits
northSoils$Delta <- 1000*log( (10^-3*northSoils$comp.d13C +1)/(10^-3*d13Co+1) )
talwegSoils$Delta <- 1000*log( (10^-3*talwegSoils$comp.d13C +1)/(10^-3*d13Co+1) )
southSoils$Delta <- 1000*log( (10^-3*southSoils$comp.d13C +1)/(10^-3*d13Co+1) )
```

```r
northSoils$Fdil =
  exp( northSoils$Delta/epsilon_true -log(northSoils$ftot) )
talwegSoils$Fdil =
  exp(talwegSoils$Delta/epsilon_true -log(talwegSoils$ftot) )
southSoils$Fdil =
  exp(southSoils$Delta/epsilon_true -log(southSoils$ftot) )

# (B) Streitwieser Semiclassical Limits
northSoils$Fdil_mx =
  exp( northSoils$Delta/epsilon_streit -log(northSoils$ftot) )
talwegSoils$Fdil_mx =
  exp(talwegSoils$Delta/epsilon_streit -log(talwegSoils$ftot) )
southSoils$Fdil_mx =
  exp(southSoils$Delta/epsilon_streit -log(southSoils$ftot) )
```

The above allows us to calculate the breakdown (B*) and dilution factors (D*). Note that the relationships D* > 1 and B* < 1 must be met, otherwise ϵ_{true} is incorrect or iniitial concentrations are incorrect (or both).

Note that to meet the relationships D* > 1 and 0 < B* < 1 initial concentrations need to be accurate. From Van Breukelen (2007):

(i) if B* exceeds 1, the predicted concentration decrease is larger than observed (i.e. too much degradation being predicted with the chosen ε_{lab}, and thus ε_{true}should be more negative),
(ii) if B* is negative, downgradient concentrations are higher than the source concentration.

Modified to top soils, in the above cases, application of the open system Rayleigh equation [would] thereby point out that the boundary conditions [e.g. initial concentrations] must be different.

Calculating B* and D* is given by:

$$B^* = \frac{log(f_{deg})}{log(f_{tot})}$$

$$D^* = \frac{log(f_{dil})}{log(f_{tot})} = 1 - B^*$$

and their relationship $D * /B*$ which relates the extent of dilution relative to degradation.

```r
# (A) Lab epsilon
northSoils$Dstar = log(1/northSoils$Fdil)/log(northSoils$ftot)
northSoils$Bstar = 1 - northSoils$Dstar # log(northSoils$fdeg)/log(northSoils$ftot)
northSoils$DB = northSoils$Dstar/northSoils$Bstar

talwegSoils$Dstar = log(1/talwegSoils$Fdil)/log(talwegSoils$ftot)
talwegSoils$Bstar = 1 - talwegSoils$Dstar  # log(talwegSoils$fdeg)/log(talwegSoils$ftot)
talwegSoils$DB = talwegSoils$Dstar/talwegSoils$Bstar

southSoils$Dstar = log(1/southSoils$Fdil)/log(southSoils$ftot)
southSoils$Bstar = 1 - southSoils$Dstar # log(southSoils$fdeg)/log(southSoils$ftot)
southSoils$DB = southSoils$Dstar/southSoils$Bstar

# (B) Streitwieser Semiclassical Limits
northSoils$Dstar_mx = log(1/northSoils$Fdil_mx)/log(northSoils$ftot)
northSoils$Bstar_mx = 1 - northSoils$Dstar_mx # log(northSoils$fdeg)/log(northSoils$ftot)
northSoils$DB_mx = northSoils$Dstar_mx/northSoils$Bstar_mx
```

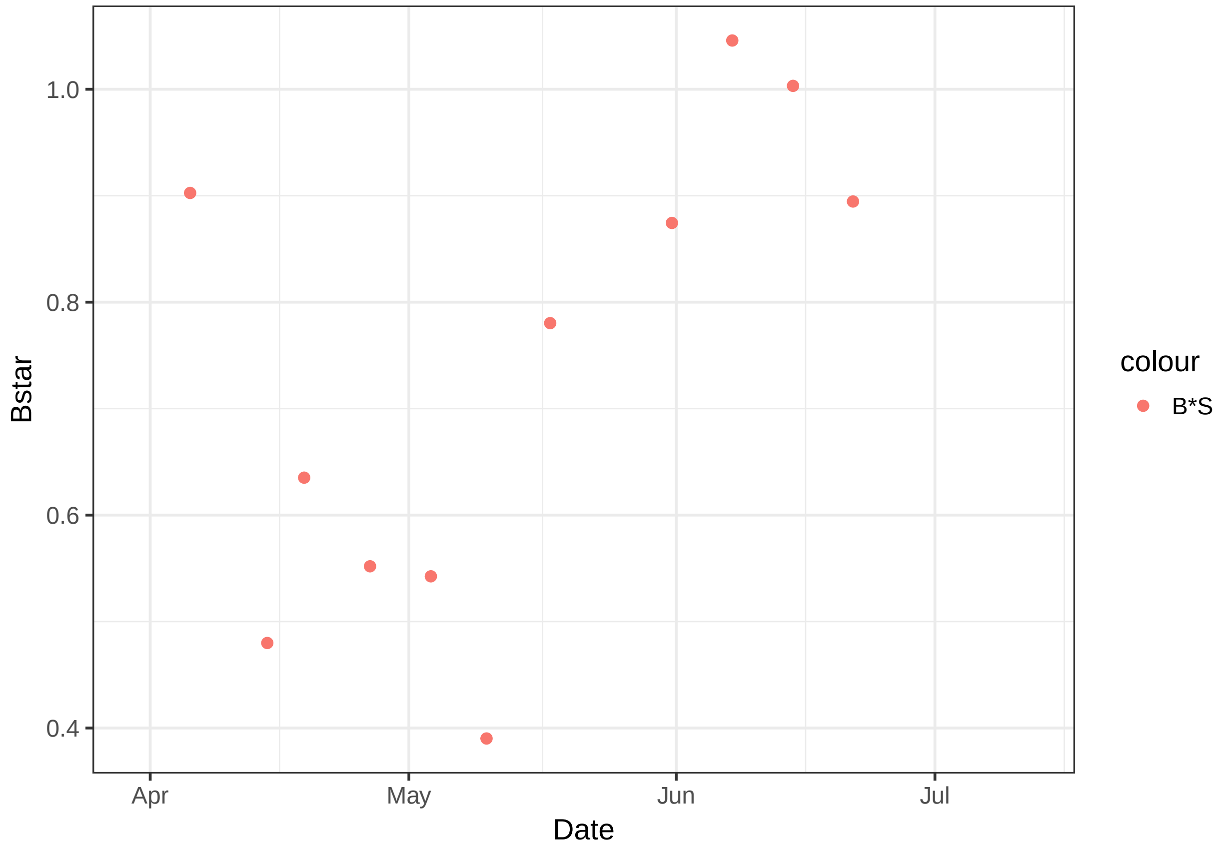
```
talwegSoils$Dstar_mx = log(1/talwegSoils$Fdil_mx)/log(talwegSoils$ftot)
talwegSoils$Bstar_mx = 1 - talwegSoils$Dstar_mx  # log(talwegSoils$fdeg)/log(talwegSoils$ftot)
talwegSoils$DB_mx = talwegSoils$Dstar/talwegSoils$Bstar

southSoils$Dstar_mx = log(1/southSoils$Fdil_mx)/log(southSoils$ftot)
southSoils$Bstar_mx = 1 - southSoils$Dstar_mx # log(southSoils$fdeg)/log(southSoils$ftot)
southSoils$DB_mx = southSoils$Dstar_mx/southSoils$Bstar_mx
```

Rayleigh (closed system, Elsner's notation)

$$ln(\frac{1000 + \delta^{13}C_0 + \Delta\delta^{13}C}{1000 + \delta^{13}C_0}) = (\alpha - 1) \cdot lnf = \frac{\epsilon}{1000} \cdot lnf$$

Plotting

```
if (FALSE){
ggplot(data = northSoils , aes(x=Date))+
  geom_point(aes(y = Dstar, colour = "D*N")) +
  theme_bw()

ggplot(data = talwegSoils , aes(x=Date))+
  geom_point(aes(y = Dstar, colour = "D*T")) +
  theme_bw()

ggplot(data = southSoils , aes(x=Date))+
  geom_point(aes(y = Dstar, colour = "D*S")) +
  theme_bw()
}

if (TRUE){
  ggplot(data = northSoils , aes(x=Date))+
  geom_point(aes(y = Bstar, colour = "B*N")) +
  theme_bw()

  ggplot(data = talwegSoils , aes(x=Date))+
    geom_point(aes(y = Bstar, colour = "B*T")) +
    theme_bw()

  ggplot(data = southSoils , aes(x=Date))+
    geom_point(aes(y = Bstar, colour = "B*S")) +
    theme_bw()
}
```



1.0
0.8
0.6
0.4
Bstar
Apr
May
Jun
Jul
Date
colour
B*S