

Rayleigh Calculations

PAZ

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Introduction

Degradation extent is calculated based on closed and open system Rayleigh equations

Packages

```
library(sm)
library(vioplot)

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

library("plotly")
library("cowplot")
library("gridExtra")
library("Cairo")
library("GGally")
library("scales")

library("plotKML")

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

# Saving a xls file
# library(xlsx)
```

Lab parameters

```
# Initial signature measured in tank
initialDelta = d13Co = -32.253

# Define initial concentration (for Raleigh plots)
#Co <- 8 # ug/g dry soil (based on Corn applications)
# Co <- 6.53 # ug/g dry soil (based on Max conc. measured in soils)
# Note: Each transect now has individual starting concentration
```

```

# rho1 = 0.99*106 # soil density [g/m3] (assume for April)
# rho2 = 2.20*106 # soil density [g/m3] (assume for May & June)
# depth = 0.01 # [m]

# Reference values
# Ehssan values:
epsilon_mean= -2.2 # ± 0.4
dE <- 0.4
epsilon_max = epsilon_mean + dE
epsilon_min = epsilon_mean - dE

epsilon_lab = epsilon_mean

# Calculated in this Book from Bulk signatures and bulk concentrations
epsilonField_max = -1.3 + 0.24
epsilonField_min = -1.3 - 0.24
epsilonField_mean = -1.3 # ± 0.24
epsilon_field = epsilonField_mean

```

Soils

```

soils = read.csv2("Data/MassBalance_R.csv", # File contains both soils & waters
                 na.strings=c('#DIV/0!', '', 'NA'), header = TRUE)
names(soils)

```

```

## [1] "ti" "WeekSubWeek"
## [3] "Event" "Duration.Hrs"
## [5] "timeSinceApp" "timeSinceApp.NoSo"
## [7] "timeSinceApp.N" "timeSinceApp.T"
## [9] "timeSinceApp.S" "diss.d13C"
## [11] "SD.d13C" "CumOutDiss.g"
## [13] "CumOutFilt.g" "TotSMout.g"
## [15] "TotSMout.g.SD" "MELsm.g"
## [17] "MELsm.g.SD" "Appl.Mass.g"
## [19] "Appl.Mass.g.OT" "CumAppMass.g"
## [21] "CumAppMass.g.N" "CumAppMass.g.T"
## [23] "CumAppMass.g.S" "CumAppMass.g.OT"
## [25] "CumAppMass.g.N.OT" "CumAppMass.g.T.OT"
## [27] "CumAppMass.g.S.OT" "iniCo.ug.g.N"
## [29] "iniCo.ug.g.T" "iniCo.ug.g.S"
## [31] "CumOutSmeto.g" "CumOutMELsm.g"
## [33] "MassSoil.g.North" "MassSoil.g.SD.North"
## [35] "Conc.mug.g.dry.soil.N" "comp.d13C.North"
## [37] "comp.d13C.SD.North" "ID.N"
## [39] "Area.N" "Area.T"
## [41] "Area.S" "MassSoil.g.Talweg"
## [43] "MassSoil.g.SD.Talweg" "Conc.mug.g.dry.soil.T"
## [45] "comp.d13C.Talweg" "comp.d13C.SD.Talweg"
## [47] "ID.T" "MassSoil.g.South"
## [49] "MassSoil.g.SD.South" "Conc.mug.g.dry.soil.S"

```

```
## [51] "comp.d13C.South"      "comp.d13C.SD.South"
## [53] "ID.S"                 "DD13C.North"
## [55] "DD13C.Talweg"         "DD13C.South"
## [57] "CatchMassSoil.g"      "CatchMassSoil.g.SD"
## [59] "BulkCatch.d13"        "BulkCatch.d13.SD"
## [61] "DD13.Bulk"            "Area.Catchment"
## [63] "BulkCatch.Conc"       "iniCo.Bulk"

soils$ti <- as.POSIXct(strptime(soils$ti, "%Y-%m-%d %H:%M", tz="EST"))
colnames(soils)[colnames(soils) == "ti"] <- "Date.ti"

keepSoils <- c(
  "Date.ti", "WeekSubWeek", "ID.N",
  "Area.N", "Area.T", "Area.S",
  "iniCo.ug.g.N", "iniCo.ug.g.T", "iniCo.ug.g.S",
  # Applied
  "CumAppMass.g.N", "CumAppMass.g.T", "CumAppMass.g.S",
  "CumAppMass.g" ,
  "CumAppMass.g.OT", "CumAppMass.g.N.OT", "CumAppMass.g.T.OT" , "CumAppMass.g.S.OT",
  # Concentrations
  "BulkCatch.Conc", "iniCo.Bulk",
  "Conc.mug.g.dry.soil.N", "Conc.mug.g.dry.soil.T", "Conc.mug.g.dry.soil.S",
  # Masses
  "CatchMassSoil.g", "CatchMassSoil.g.SD",
  "MassSoil.g.North", "MassSoil.g.Talweg", "MassSoil.g.South" ,
  "MassSoil.g.SD.North" , "MassSoil.g.SD.Talweg", "MassSoil.g.SD.South",
  # Isotopes
  "diss.d13C", "SD.d13C",
  "comp.d13C.North" , "comp.d13C.SD.North",
  "comp.d13C.Talweg", "comp.d13C.SD.Talweg",
  "comp.d13C.South" , "comp.d13C.SD.South",
  "BulkCatch.d13", "BulkCatch.d13.SD")

# Test
sum(is.na(soils$Date.ti)) == 0

## [1] TRUE

soils <- soils[, colnames(soils) %in% keepSoils]
```

Rayleigh (closed system, Elsner's notation)

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

were,

$$f = \frac{C_t}{C_0}$$

Accounting for dilution

The Rayleigh equation above 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:

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

Following Van Breukelen (2007),

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

where 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:

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

were,

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

Dilution factor (F)

```
soils$ftot.N <- soils$Conc.mug.g.dry.soil.N/soils$iniCo.ug.g.N
soils$ftot.T <- soils$Conc.mug.g.dry.soil.T/soils$iniCo.ug.g.T
soils$ftot.S <- soils$Conc.mug.g.dry.soil.S/soils$iniCo.ug.g.S

soils$ftot.Bulk <- soils$BulkCatch.Conc/soils$iniCo.Bulk

# Van Breukelen notation
soils$Delta.N <- 1000*log( (10^-3*soils$comp.d13C.North +1)/(10^-3*d13Co+1) )
soils$Delta.T <- 1000*log( (10^-3*soils$comp.d13C.Talweg +1)/(10^-3*d13Co+1) )
soils$Delta.S <- 1000*log( (10^-3*soils$comp.d13C.South +1)/(10^-3*d13Co+1) )
soils$Delta.Bulk <- 1000*log( (10^-3*soils$BulkCatch.d13 +1)/(10^-3*d13Co+1) )

soils$Fdil.N =
  exp( soils$Delta.N/epsilon_lab -log(soils$ftot.N) )
soils$Fdil.T =
  exp( soils$Delta.T/epsilon_lab -log(soils$ftot.T) )
soils$Fdil.S =
  exp( soils$Delta.S/epsilon_lab -log(soils$ftot.S) )

soils$Fdil.Bulk =
  exp( soils$Delta.Bulk/epsilon_lab -log(soils$ftot.Bulk) )
median(soils$Fdil.N, na.rm = T)

## [1] 3.345962
median(soils$Fdil.T, na.rm = T)

## [1] 1.997551
median(soils$Fdil.S, na.rm = T)

## [1] 2.129
```

```
median(soils$Fdil.Bulk, na.rm = T)
```

```
## [1] 2.370776
```

```
# soils$Fdil <- ifelse(soils$Fdil < 1, NA, soils$Fdil)
```

We can now obtain $f_{dilution}$ and $f_{degradation}$:

```
soils$fdil.N <- 1/soils$Fdil.N
```

```
soils$fdeg.N <- soils$ftot.N * soils$Fdil.N
```

```
soils$Dprct.N <- (1- soils$fdil.N)*100
```

```
soils$Bprct.N <- (1-soils$fdeg.N)*100
```

```
soils$Tprct.N <- (1- (1 - soils$Bprct.N/100) * (1 - soils$Dprct.N/100) )*100
```

```
# Talweg
```

```
soils$fdil.T <- 1/soils$Fdil.T
```

```
soils$fdeg.T <- soils$ftot.T * soils$Fdil.T
```

```
soils$Dprct.T <- (1- soils$fdil.T)*100
```

```
soils$Bprct.T <- (1-soils$fdeg.T)*100
```

```
soils$Tprct.T <- (1-soils$ftot.T)*100
```

```
#South
```

```
soils$fdil.S <- 1/soils$Fdil.S
```

```
soils$fdeg.S <- soils$ftot.S * soils$Fdil.S
```

```
soils$Dprct.S <- (1- soils$fdil.S)*100
```

```
soils$Bprct.S <- (1-soils$fdeg.S)*100
```

```
soils$Tprct.S <- (1-soils$ftot.S)*100
```

```
# Bulk
```

```
soils$fdil.Bulk <- 1/soils$Fdil.Bulk
```

```
soils$fdeg.Bulk <- soils$ftot.Bulk * soils$Fdil.Bulk
```

```
soils$Dprct.Bulk <- (1- soils$fdil.Bulk)*100
```

```
soils$Bprct.Bulk <- (1-soils$fdeg.Bulk)*100
```

```
soils$Tprct.Bulk <- (1-soils$ftot.Bulk)*100
```

Calculating degradation and respective statistical variation errors in B, according to (???):

$$|\Delta B| = \frac{1}{|\epsilon|} \cdot (100 - B[\%]) \cdot \sqrt{(\ln(1 - B[\%]/100))^2 \cdot (\Delta\epsilon)^2 + (\Delta\delta_x)^2 + (\Delta\delta_0)^2}$$

```
# Deg effective
```

```
soils$DD.N <- soils$comp.d13C.North - d13Co
```

```
soils$DD.T <- soils$comp.d13C.Talweg - d13Co
```

```
soils$DD.S <- soils$comp.d13C.South - d13Co
```

```
soils$DD.Bulk <- soils$BulkCatch.d13 - d13Co
```

```
soils$Belsner.N <- (1- ((1000 + d13Co + soils$DD.N)/(1000+ d13Co))^(1000/epsilon_lab) )*100
```

```
soils$Berr.Stat.N <- (1/-epsilon_lab)*
```

```
(100-soils$Belsner.N)*( (log(1-soils$Belsner.N/100))^2 * dE^2 + (soils$comp.d13C.SD.North)^2 + (.5)^2
```

```
soils$Belsner.T <- (1- ((1000 + d13Co + soils$DD.T)/(1000+ d13Co))^(1000/epsilon_lab) )*100
```

```

soils$Berr.Stat.T <- (1/-epsilon_lab)*
  (100-soils$Belsner.T)*( (log(1-soils$Belsner.T/100))^2 * dE^2 + (soils$comp.d13C.SD.Talweg)^2 + (.5)^2 )

soils$Belsner.S <- (1- ((1000 + d13Co + soils$DD.S)/(1000+ d13Co))^(1000/epsilon_lab) )*100
soils$Berr.Stat.S <- (1/-epsilon_lab)*
  (100-soils$Belsner.S)*( (log(1-soils$Belsner.S/100))^2 * dE^2 + (soils$comp.d13C.SD.South)^2 + (.5)^2 )

soils$Belsner.Bulk <- (1- ((1000 + d13Co + soils$DD.Bulk)/(1000+ d13Co))^(1000/epsilon_lab) )*100

```

Calculating errors from systematic variation in input parameters, in this case ϵ_{lab} :

```

soils$Belsner.BulkField <- (1- ((1000 + d13Co + soils$DD.Bulk)/(1000+ d13Co))^(1000/epsilon_field) )*100
soils$Bdiff.LabField <- soils$Belsner.BulkField - soils$Belsner.Bulk

```

```

soils$Berr.Stat.Bulk <- (1/-epsilon_lab)*
  (100-soils$Belsner.Bulk)*( (log(1-soils$Belsner.Bulk/100))^2 * dE^2 + (0.5)^2 + (.5)^2 )^(1/2)

soils$Berr.Stat.Field <- (1/-epsilon_field)*
  (100-soils$Belsner.BulkField)*( (log(1-soils$Belsner.BulkField/100))^2 * dE^2 + (0.5)^2 + (.5)^2 )^(1/2)

```

As well as the breakdown (B^*), dilution factors (D^*):

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

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

```

soils$Dstar.N = log(soils$fdil.N)/log(soils$ftot.N)
soils$Bstar.N = log(soils$fdeg.N)/log(soils$ftot.N)
soils$DB.N = soils$Dstar.N/soils$Bstar.N

soils$Dstar.T = log(soils$fdil.T)/log(soils$ftot.T)
soils$Bstar.T = log(soils$fdeg.T)/log(soils$ftot.T)
soils$DB.T = soils$Dstar.T/soils$Bstar.T

soils$Dstar.S = log(soils$fdil.S)/log(soils$ftot.S)
soils$Bstar.S = log(soils$fdeg.S)/log(soils$ftot.S)
soils$DB.S = soils$Dstar.S/soils$Bstar.S

soils$Dstar.Bulk = log(soils$fdil.Bulk)/log(soils$ftot.Bulk)
soils$Bstar.Bulk = log(soils$fdeg.Bulk)/log(soils$ftot.Bulk)
soils$DB.Bulk = soils$Dstar.Bulk/soils$Bstar.Bulk

median(soils$DB.N, na.rm = T)

## [1] 1.191514

median(soils$DB.T, na.rm = T)

## [1] 0.6768974

median(soils$DB.S, na.rm = T)

## [1] 0.569117

mean(soils$DB.N, na.rm = T)

## [1] 1.943195

```

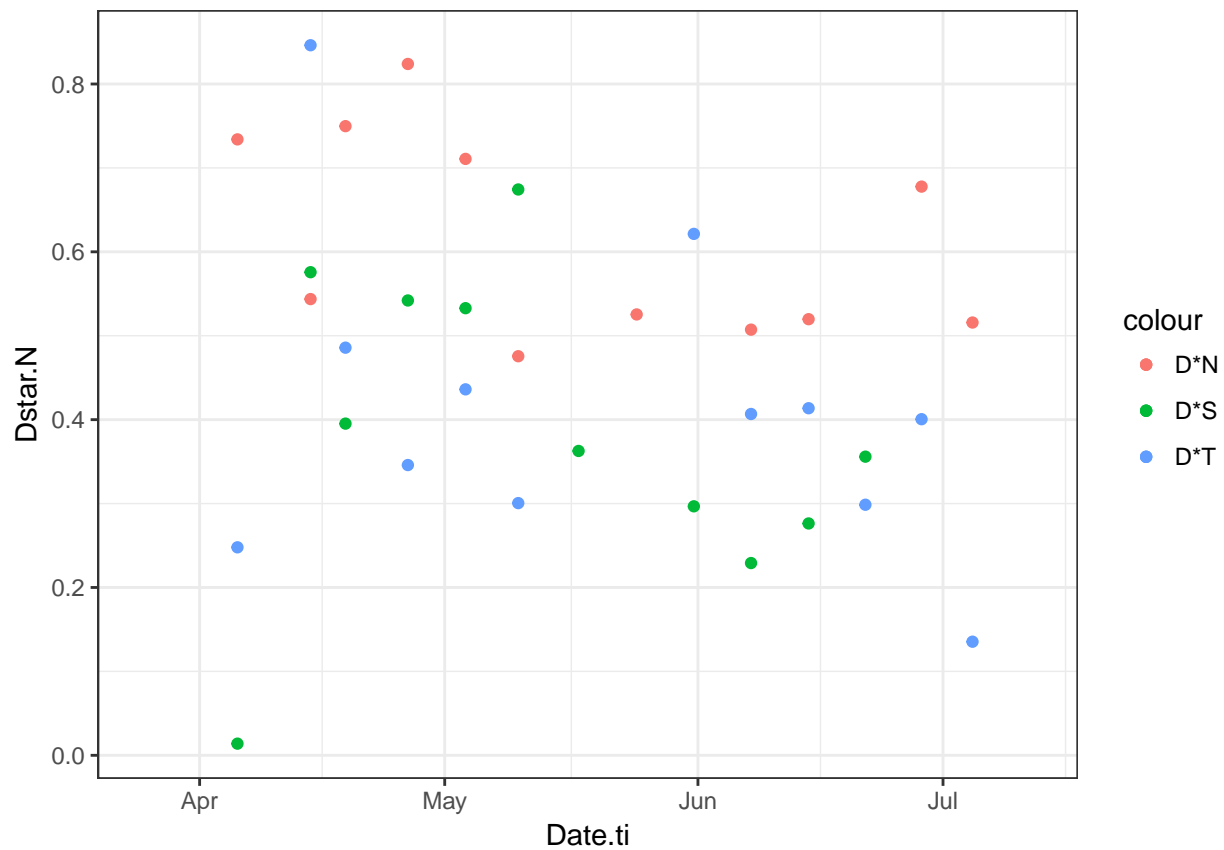
```
mean(soils$DB.T, na.rm = T)
```

```
## [1] 1.065808
```

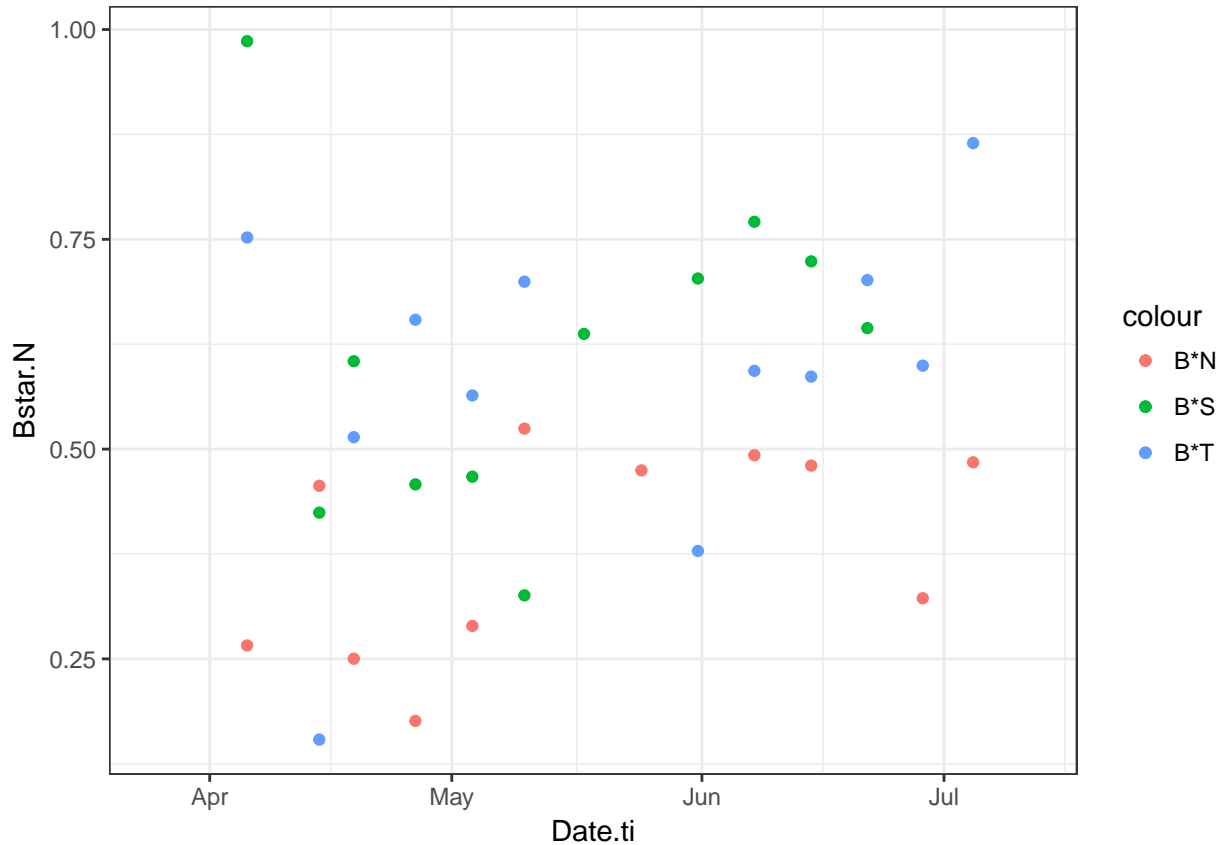
```
mean(soils$DB.S, na.rm = T)
```

```
## [1] 0.7856066
```

```
ggplot(data = soils , aes(x=Date.ti))+  
  geom_point(aes(y = Dstar.N, colour = "D*N")) +  
  geom_point(aes(y = Dstar.T, colour = "D*T")) +  
  geom_point(aes(y = Dstar.S, colour = "D*S")) +  
  theme_bw()
```



```
ggplot(data = soils , aes(x=Date.ti))+  
  geom_point(aes(y = Bstar.N, colour = "B*N")) +  
  geom_point(aes(y = Bstar.T, colour = "B*T")) +  
  geom_point(aes(y = Bstar.S, colour = "B*S")) +  
  theme_bw()
```



Calculating the cumulative mass that was degraded and transpoted off-site can be done by converting the change in concentration to the change in mass, with the following conversion:

$$\Delta M_t = M_t - M_0$$

don't think this is correct! Should be B% instead of B*...

$$M_{deg(t)} = \Delta M \cdot B^*$$

(thinking about dilution in the wrong way? -> Dilution factor can only be applied to concentrations, not masses)

because,

$$B^* = 1 - D^*$$

$$M_t [\mu g] = C_t [\mu g/g \text{ soil}] * \rho [g \text{ soil}/m^3] * A_T [m^2] * D [m]$$

Note here that A_T refers to the representative catchment area (subcatchment) of the given transect, and depth is 0.01 m.

```
soils$Mdeg.g.N <- soils$CumAppMass.g.N.OT*soils$Belsner.N/100
soils$Mdeg.g.T <- soils$CumAppMass.g.T.OT*soils$Belsner.T/100
soils$Mdeg.g.S <- soils$CumAppMass.g.S.OT*soils$Belsner.S/100
soils$SumDeg.g <- soils$Mdeg.g.N + soils$Mdeg.g.T + soils$Mdeg.g.S
soils$Mdeg.g <- soils$CumAppMass.g.OT*soils$Belsner.Bulk/100
```



```

#soils$Mdeg.g.N.eff <- soils$Mdeg.g.N/soils$Area.N
#soils$Mdeg.g.T.eff <- soils$Mdeg.g.T/soils$Area.T
#soils$Mdeg.g.S.eff <- soils$Mdeg.g.S/soils$Area.S

# Mass remaining needs to be calculated based on
# increasing bulk density between early and late season
# otherwise, mass balances don't add up.

colnames(soils)[colnames(soils) == "CatchMassSoil.g"] <- "Mrem.g" # Sum of N, T & S
colnames(soils)[colnames(soils) == "MassSoil.g.North"] <- "Mrem.g.N"
colnames(soils)[colnames(soils) == "MassSoil.g.Talweg"] <- "Mrem.g.T"
colnames(soils)[colnames(soils) == "MassSoil.g.South"] <- "Mrem.g.S"

soils$Mloss.g.N <- soils$CumAppMass.g.N.OT - (soils$Mdeg.g.N + soils$Mrem.g.N)
soils$Mloss.g.T <- soils$CumAppMass.g.T.OT - (soils$Mdeg.g.T + soils$Mrem.g.T)
soils$Mloss.g.S <- soils$CumAppMass.g.S.OT - (soils$Mdeg.g.S + soils$Mrem.g.S)
soils$Mloss.g <- soils$CumAppMass.g.OT - (soils$Mdeg.g + soils$Mrem.g)

length(soils)

## [1] 104

names(soils)

##      [1] "Date.ti"           "WeekSubWeek"
##      [3] "diss.d13C"         "SD.d13C"
##      [5] "CumAppMass.g.OT"   "CumAppMass.g.N.OT"
##      [7] "CumAppMass.g.T.OT" "CumAppMass.g.S.OT"
##      [9] "iniCo.ug.g.N"      "iniCo.ug.g.T"
##     [11] "iniCo.ug.g.S"      "Mrem.g.N"
##     [13] "MassSoil.g.SD.North" "Conc.mug.g.dry.soil.N"
##     [15] "comp.d13C.North"   "comp.d13C.SD.North"
##     [17] "ID.N"              "Area.N"
##     [19] "Area.T"            "Area.S"
##     [21] "Mrem.g.T"          "MassSoil.g.SD.Talweg"
##     [23] "Conc.mug.g.dry.soil.T" "comp.d13C.Talweg"
##     [25] "comp.d13C.SD.Talweg" "Mrem.g.S"
##     [27] "MassSoil.g.SD.South" "Conc.mug.g.dry.soil.S"
##     [29] "comp.d13C.South"   "comp.d13C.SD.South"
##     [31] "Mrem.g"            "CatchMassSoil.g.SD"
##     [33] "BulkCatch.d13"     "BulkCatch.d13.SD"
##     [35] "BulkCatch.Conc"    "iniCo.Bulk"
##     [37] "ftot.N"            "ftot.T"
##     [39] "ftot.S"            "ftot.Bulk"
##     [41] "Delta.N"           "Delta.T"
##     [43] "Delta.S"           "Delta.Bulk"
##     [45] "Fdil.N"            "Fdil.T"
##     [47] "Fdil.S"            "Fdil.Bulk"
##     [49] "fdil.N"            "fdeg.N"
##     [51] "Dprct.N"           "Bprct.N"
##     [53] "Tprct.N"           "fdil.T"
##     [55] "fdeg.T"            "Dprct.T"
##     [57] "Bprct.T"           "Tprct.T"
##     [59] "fdil.S"            "fdeg.S"

```

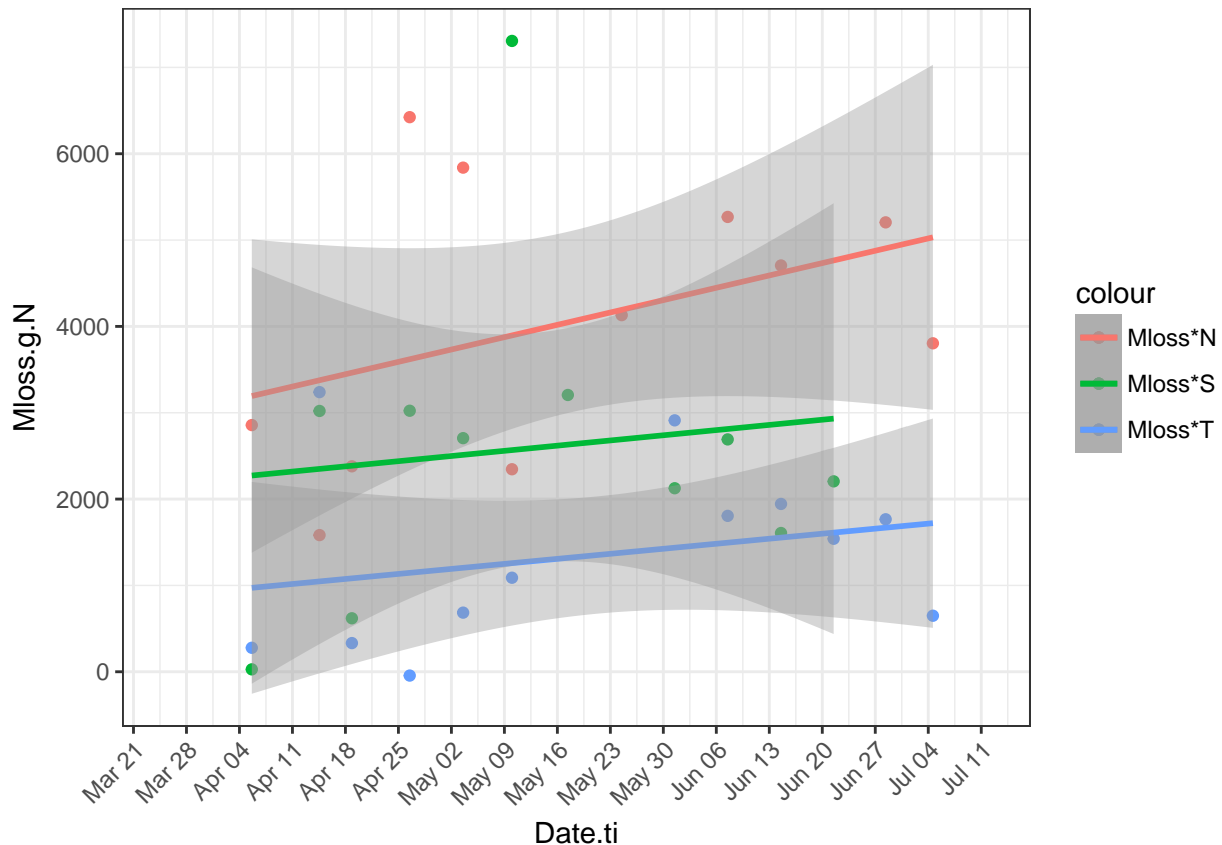
```
## [61] "Dprct.S"          "Bprct.S"
## [63] "Tprct.S"          "fdil.Bulk"
## [65] "fdeg.Bulk"        "Dprct.Bulk"
## [67] "Bprct.Bulk"       "Tprct.Bulk"
## [69] "DD.N"             "DD.T"
## [71] "DD.S"             "DD.Bulk"
## [73] "Belsner.N"        "Berr.Stat.N"
## [75] "Belsner.T"        "Berr.Stat.T"
## [77] "Belsner.S"        "Berr.Stat.S"
## [79] "Belsner.Bulk"     "Belsner.BulkField"
## [81] "Bdiff.LabField"   "Berr.Stat.Bulk"
## [83] "Berr.Stat.Field"  "Dstar.N"
## [85] "Bstar.N"          "DB.N"
## [87] "Dstar.T"          "Bstar.T"
## [89] "DB.T"             "Dstar.S"
## [91] "Bstar.S"          "DB.S"
## [93] "Dstar.Bulk"       "Bstar.Bulk"
## [95] "DB.Bulk"          "Mdeg.g.N"
## [97] "Mdeg.g.T"         "Mdeg.g.S"
## [99] "SumDeg.g"         "Mdeg.g"
## [101] "Mloss.g.N"        "Mloss.g.T"
## [103] "Mloss.g.S"        "Mloss.g"
```

```
#View(soils[, c(1, 17:20, 5:8, 12,21,26,31, 15,24,29, 96:ncol(soils)) ])
```

```
library(reshape2)
s <- soils[, c(1, 12,21,26, 96:ncol(soils)) ]
moltenSoil <- melt(s, id = "Date.ti")
```

```
# Mass Losses
```

```
ggplot(data = s , aes(x=Date.ti))+
  geom_point(aes(y = Mloss.g.N, colour = "Mloss*N")) +
  geom_point(aes(y = Mloss.g.T, colour = "Mloss*T")) +
  geom_point(aes(y = Mloss.g.S, colour = "Mloss*S")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mloss.g.N, colour = "Mloss*N")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mloss.g.T, colour = "Mloss*T")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mloss.g.S, colour = "Mloss*S")) +
  theme_bw() +
  theme(# legend.position = "top",
        axis.text.x=element_text(angle = 45, hjust = 1)) +
  scale_x_datetime(breaks = date_breaks("1 weeks"), labels = date_format("%b %d"))
```



```
# cor.test(soils$Mloss.g.N, soils$Mloss.g.T)
```

Summary absolute percent mass loss

```
soilsApril <- subset(soils, (Date.ti >= as.POSIXct("2016-04-18 20:30:00", tz = "EST")
  & Date.ti < as.POSIXct("2016-05-01 00:00:00", tz = "EST")))
# & Date.ti <= as.POSIXct("2016-05-03 13:11:00", tz = "EST"))

#soils.April <- soils.April[complete.cases(soils.April[, "ID.N"]), ]

soilsJune <- subset(soils, (Date.ti >= as.POSIXct("2016-06-01 00:56:00", tz = "EST")
  & Date.ti <= as.POSIXct("2016-06-28 14:52:00", tz = "EST")))

library(dplyr)
sa <- soilsApril %>%
  summarise_each(funs(mean(. , na.rm=T) ))

sj <- soilsJune %>%
  summarise_each(funs(mean(. , na.rm=T) ))

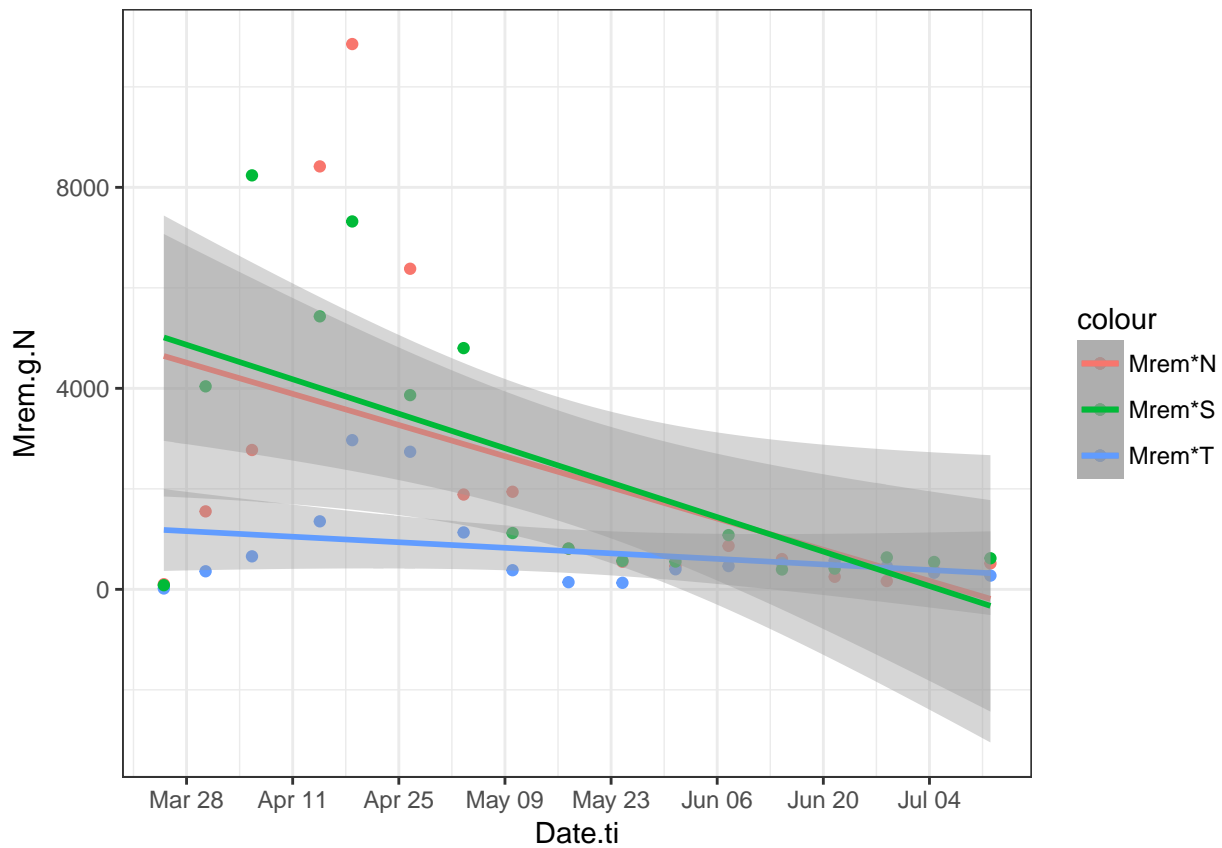
saj <- rbind(sa,sj)
saj$PrctAbsLoss <- (saj$Mloss.g/soils$CumAppMass.g.OT[nrow(soils)-1])*100

saj$PrctAbsLoss[1]/saj$PrctAbsLoss[2]*100

## [1] 70.51725
```

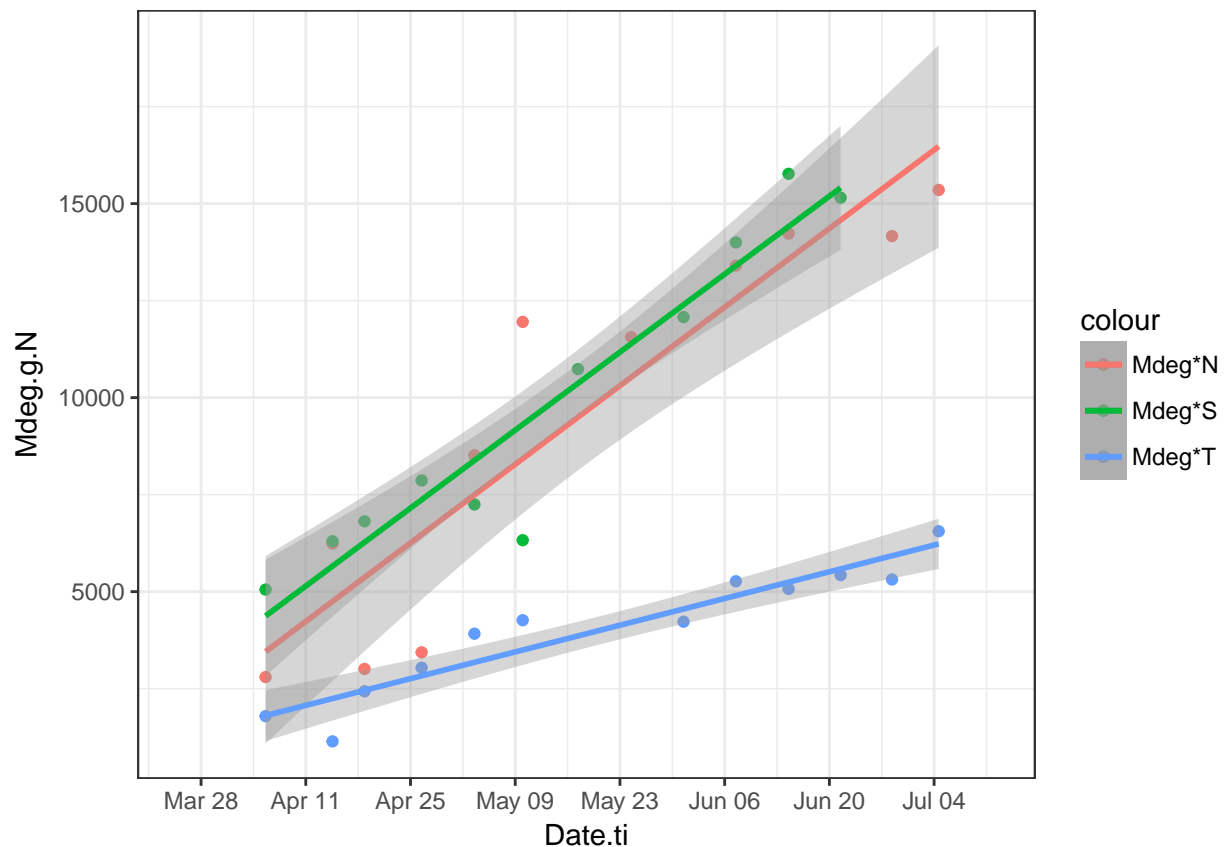
Mass remaining

```
ggplot(data = s , aes(x=Date.ti))+
  geom_point(aes(y = Mrem.g.N, colour = "Mrem*N")) +
  geom_point(aes(y = Mrem.g.T, colour = "Mrem*T")) +
  geom_point(aes(y = Mrem.g.S, colour = "Mrem*S")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mrem.g.N, colour = "Mrem*N")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mrem.g.T, colour = "Mrem*T")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mrem.g.S, colour = "Mrem*S")) +
  scale_x_datetime(breaks = date_breaks("2 weeks"), labels = date_format("%b %d")) +
  theme_bw()
```



Degradation

```
ggplot(data = s , aes(x=Date.ti))+
  geom_point(aes(y = Mdeg.g.N, colour = "Mdeg*N")) +
  geom_point(aes(y = Mdeg.g.T, colour = "Mdeg*T")) +
  geom_point(aes(y = Mdeg.g.S, colour = "Mdeg*S")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mdeg.g.N, colour = "Mdeg*N")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mdeg.g.T, colour = "Mdeg*T")) +
  stat_smooth(method = "lm", formula = y ~ x, aes(y = Mdeg.g.S, colour = "Mdeg*S")) +
  scale_x_datetime(breaks = date_breaks("2 weeks"), labels = date_format("%b %d")) +
  theme_bw()
```



Percentages

```

soils$PrctRem.N <- (soils$Mrem.g.N/soils$CumAppMass.g.N.OT)*100
soils$PrctRem.T <- (soils$Mrem.g.T/soils$CumAppMass.g.T.OT)*100
soils$PrctRem.S <- (soils$Mrem.g.S/(soils$CumAppMass.g.S.OT))*100

soils$PrctDeg <- (soils$SumDeg.g/soils$CumAppMass.g.OT)*100 # Sum of transect degradations relative to
soils$PrctDeg.N <- (soils$Mdeg.g.N/soils$CumAppMass.g.N.OT)*100
soils$PrctDeg.T <- (soils$Mdeg.g.T/soils$CumAppMass.g.T.OT)*100
soils$PrctDeg.S <- (soils$Mdeg.g.S/(soils$CumAppMass.g.S.OT))*100

soils$PrctRem <- (soils$Mrem.g/soils$CumAppMass.g.OT)*100
soils$PrctLoss <- 100 - (soils$PrctRem + soils$PrctDeg)
soils$PrctLoss.N <- 100 - (soils$PrctRem.N + soils$PrctDeg.N)
soils$PrctLoss.T <- 100 - (soils$PrctRem.T + soils$PrctDeg.T)
soils$PrctLoss.S <- 100 - (soils$PrctRem.S + soils$PrctDeg.S)

# soils$RemPlusDeg <- soils$PrctRem + soils$PrctDeg

names(soils)

## [1] "Date.ti" "WeekSubWeek"
## [3] "diss.d13C" "SD.d13C"
## [5] "CumAppMass.g.OT" "CumAppMass.g.N.OT"
## [7] "CumAppMass.g.T.OT" "CumAppMass.g.S.OT"

```

##	[9]	"iniCo.ug.g.N"	"iniCo.ug.g.T"
##	[11]	"iniCo.ug.g.S"	"Mrem.g.N"
##	[13]	"MassSoil.g.SD.North"	"Conc.mug.g.dry.soil.N"
##	[15]	"comp.d13C.North"	"comp.d13C.SD.North"
##	[17]	"ID.N"	"Area.N"
##	[19]	"Area.T"	"Area.S"
##	[21]	"Mrem.g.T"	"MassSoil.g.SD.Talweg"
##	[23]	"Conc.mug.g.dry.soil.T"	"comp.d13C.Talweg"
##	[25]	"comp.d13C.SD.Talweg"	"Mrem.g.S"
##	[27]	"MassSoil.g.SD.South"	"Conc.mug.g.dry.soil.S"
##	[29]	"comp.d13C.South"	"comp.d13C.SD.South"
##	[31]	"Mrem.g"	"CatchMassSoil.g.SD"
##	[33]	"BulkCatch.d13"	"BulkCatch.d13.SD"
##	[35]	"BulkCatch.Conc"	"iniCo.Bulk"
##	[37]	"ftot.N"	"ftot.T"
##	[39]	"ftot.S"	"ftot.Bulk"
##	[41]	"Delta.N"	"Delta.T"
##	[43]	"Delta.S"	"Delta.Bulk"
##	[45]	"Fdil.N"	"Fdil.T"
##	[47]	"Fdil.S"	"Fdil.Bulk"
##	[49]	"fdil.N"	"fdeg.N"
##	[51]	"Dprct.N"	"Bprct.N"
##	[53]	"Tprct.N"	"fdil.T"
##	[55]	"fdeg.T"	"Dprct.T"
##	[57]	"Bprct.T"	"Tprct.T"
##	[59]	"fdil.S"	"fdeg.S"
##	[61]	"Dprct.S"	"Bprct.S"
##	[63]	"Tprct.S"	"fdil.Bulk"
##	[65]	"fdeg.Bulk"	"Dprct.Bulk"
##	[67]	"Bprct.Bulk"	"Tprct.Bulk"
##	[69]	"DD.N"	"DD.T"
##	[71]	"DD.S"	"DD.Bulk"
##	[73]	"Belsner.N"	"Berr.Stat.N"
##	[75]	"Belsner.T"	"Berr.Stat.T"
##	[77]	"Belsner.S"	"Berr.Stat.S"
##	[79]	"Belsner.Bulk"	"Belsner.BulkField"
##	[81]	"Bdiff.LabField"	"Berr.Stat.Bulk"
##	[83]	"Berr.Stat.Field"	"Dstar.N"
##	[85]	"Bstar.N"	"DB.N"
##	[87]	"Dstar.T"	"Bstar.T"
##	[89]	"DB.T"	"Dstar.S"
##	[91]	"Bstar.S"	"DB.S"
##	[93]	"Dstar.Bulk"	"Bstar.Bulk"
##	[95]	"DB.Bulk"	"Mdeg.g.N"
##	[97]	"Mdeg.g.T"	"Mdeg.g.S"
##	[99]	"SumDeg.g"	"Mdeg.g"
##	[101]	"Mloss.g.N"	"Mloss.g.T"
##	[103]	"Mloss.g.S"	"Mloss.g"
##	[105]	"PrctRem.N"	"PrctRem.T"
##	[107]	"PrctRem.S"	"PrctDeg"
##	[109]	"PrctDeg.N"	"PrctDeg.T"
##	[111]	"PrctDeg.S"	"PrctRem"
##	[113]	"PrctLoss"	"PrctLoss.N"
##	[115]	"PrctLoss.T"	"PrctLoss.S"

```

dropS <- c("Area.Catch", "Area.N", "Area.T", "Area.S",
  "WeekSubWeek",
  # Isotopes Soils
  "comp.d13C.North", "comp.d13C.SD.North",
  "comp.d13C.Talweg", "comp.d13C.SD.Talweg" ,
  "comp.d13C.South", "comp.d13C.SD.South",
  "BulkCatch.d13", "BulkCatch.d13.SD",
  "DD.N", "DD.T", "DD.S", "DD.Bulk",
  # ISotopes Water
  # "diss.d13C", "SD.d13C",
  # Concentrations
  "BulkCatch.Conc" ,
  "Conc.mug.g.dry.soil.N", "Conc.mug.g.dry.soil.T", "Conc.mug.g.dry.soil.S",

  "iniCo.Bulk", "iniCo.ug.g.N" , "iniCo.ug.g.T", "iniCo.ug.g.S",

  # Mass
  "CatchMassSoil.g", "CatchMassSoil.g.SD",

  # VanBreukelen
  "Fdil.N", "Fdil.T", "Fdil.S", "Fdil.Bulk",
  "ftot.N", "ftot.T", "ftot.S", "ftot.Bulk",
  "fdil.N", "fdil.T", "fdil.S", "fdil.Bulk",
  "fdeg.N", "fdeg.T", "fdeg.S", "fdeg.Bulk",
  "Bstar.N", "Bstar.T", "Bstar.S", "Bstar.Bulk",
  "Dstar.N", "Dstar.T", "Dstar.S", "Dstar.Bulk",
  "dM.g.N", "dM.g.T", "dM.g.S"# ,
  # "Mdeg.g.N", "Mdeg.g.T", "Mdeg.g.S"
)

soilsRay <- soils[ , !colnames(soils) %in% dropS]
soilsRay <- soilsRay[complete.cases(soilsRay[ , "ID.N"]), ]
soilsRay$ID.N.x <- soilsRay$ID.N
names(soilsRay)

```

## [1] "Date.ti"	"diss.d13C"	"SD.d13C"
## [4] "CumAppMass.g.OT"	"CumAppMass.g.N.OT"	"CumAppMass.g.T.OT"
## [7] "CumAppMass.g.S.OT"	"Mrem.g.N"	"MassSoil.g.SD.North"
## [10] "ID.N"	"Mrem.g.T"	"MassSoil.g.SD.Talweg"
## [13] "Mrem.g.S"	"MassSoil.g.SD.South"	"Mrem.g"
## [16] "Delta.N"	"Delta.T"	"Delta.S"
## [19] "Delta.Bulk"	"Dprct.N"	"Bprct.N"
## [22] "Tprct.N"	"Dprct.T"	"Bprct.T"
## [25] "Tprct.T"	"Dprct.S"	"Bprct.S"
## [28] "Tprct.S"	"Dprct.Bulk"	"Bprct.Bulk"
## [31] "Tprct.Bulk"	"Belsner.N"	"Berr.Stat.N"
## [34] "Belsner.T"	"Berr.Stat.T"	"Belsner.S"
## [37] "Berr.Stat.S"	"Belsner.Bulk"	"Belsner.BulkField"
## [40] "Bdiff.LabField"	"Berr.Stat.Bulk"	"Berr.Stat.Field"
## [43] "DB.N"	"DB.T"	"DB.S"
## [46] "DB.Bulk"	"Mdeg.g.N"	"Mdeg.g.T"
## [49] "Mdeg.g.S"	"SumDeg.g"	"Mdeg.g"
## [52] "Mloss.g.N"	"Mloss.g.T"	"Mloss.g.S"
## [55] "Mloss.g"	"PrctRem.N"	"PrctRem.T"

```
## [58] "PrctRem.S"          "PrctDeg"          "PrctDeg.N"
## [61] "PrctDeg.T"          "PrctDeg.S"        "PrctRem"
## [64] "PrctLoss"           "PrctLoss.N"       "PrctLoss.T"
## [67] "PrctLoss.S"         "ID.N.x"

mean(soilsRay$Bdiff.LabField[3:8])

## [1] 17.69726

mean(soilsRay$Bdiff.LabField[12:13])

## [1] 15.25163

mean(soilsRay$Berr.Stat.Bulk[3:8])

## [1] 18.71977

mean(soilsRay$Berr.Stat.Bulk[12:13])

## [1] 10.08155

mean(soils$Berr.Stat.Field, na.rm = T)

## [1] 19.494

names(soilsRay)

## [1] "Date.ti"          "diss.d13C"        "SD.d13C"
## [4] "CumAppMass.g.OT"  "CumAppMass.g.N.OT" "CumAppMass.g.T.OT"
## [7] "CumAppMass.g.S.OT" "Mrem.g.N"         "MassSoil.g.SD.North"
## [10] "ID.N"             "Mrem.g.T"         "MassSoil.g.SD.Talweg"
## [13] "Mrem.g.S"         "MassSoil.g.SD.South" "Mrem.g"
## [16] "Delta.N"          "Delta.T"          "Delta.S"
## [19] "Delta.Bulk"       "Dprct.N"          "Bprct.N"
## [22] "Tprct.N"          "Dprct.T"          "Bprct.T"
## [25] "Tprct.T"          "Dprct.S"          "Bprct.S"
## [28] "Tprct.S"          "Dprct.Bulk"       "Bprct.Bulk"
## [31] "Tprct.Bulk"       "Belsner.N"        "Berr.Stat.N"
## [34] "Belsner.T"        "Berr.Stat.T"      "Belsner.S"
## [37] "Berr.Stat.S"      "Belsner.Bulk"     "Belsner.BulkField"
## [40] "Bdiff.LabField"   "Berr.Stat.Bulk"   "Berr.Stat.Field"
## [43] "DB.N"             "DB.T"             "DB.S"
## [46] "DB.Bulk"          "Mdeg.g.N"         "Mdeg.g.T"
## [49] "Mdeg.g.S"         "SumDeg.g"         "Mdeg.g"
## [52] "Mloss.g.N"        "Mloss.g.T"        "Mloss.g.S"
## [55] "Mloss.g"          "PrctRem.N"        "PrctRem.T"
## [58] "PrctRem.S"        "PrctDeg"          "PrctDeg.N"
## [61] "PrctDeg.T"        "PrctDeg.S"        "PrctRem"
## [64] "PrctLoss"         "PrctLoss.N"       "PrctLoss.T"
## [67] "PrctLoss.S"       "ID.N.x"
```

Calculating a field enrichment after correcting for via breakdown factor (B^*),

$$\epsilon_{field} = B^* \cdot \epsilon_{lab} = \frac{\Delta}{\ln f_{total}}$$

```
soils$Efield.N <- soils$Bstar.N * epsilon_lab
soils$Efield.T <- soils$Bstar.T * epsilon_lab
soils$Efield.S <- soils$Bstar.S * epsilon_lab
```



```
soils$Efield.Bulk <- soils$Bstar.Bulk * epsilon_lab
# soils$EfieldAdj <- soils$BstarAdj * epsilon_lab
```

```
Efield.Bulk <- mean(soils$Efield.Bulk, na.rm = T)
Efield.Bulk
```

```
## [1] -1.065417
```

```
sd(soils$Efield, na.rm = T)
```

```
## [1] NA
```

```
# median(soils$EfieldAdj)
```

Save soils and water for Bar Plots

```
# Check correct:
soils$Etrue = soils$Efield.Bulk/soils$Bstar.Bulk
median(soils$Etrue, na.rm = T) # Should be close to -2.2, YES.
```

```
## [1] -2.2
```

```
soils$Etrue <- NULL
#write.csv2(soils,
#           'Data/Rayleigh_Soils.csv', row.names = F)
```

```
write.csv2(soilsRay,
           'Data/Rayleigh_Soils.csv', row.names = F)
```

In Van Breuklen, the degraded and diluted fractions are plotted against each other. They find that in the fringe of the plume, where more dilution occurs, also more degradation occurs, likely associated to oxidant availability and lower toxicity levels.

```
if (FALSE){
  # Van Breuklen plot this
  soils$degY = -log(soils$fdeg)
  soils$dilX = -log(soils$fdil)

  DBmodel<-lm( degY ~ dilX , data= soils, subset=(!is.na(Etrue) ))
  cof_DB <- as.numeric(coef(DBmodel)[2])
  # se_DB <- summary(DBmodel)$coef[[4]]*1000
  summary(DBmodel)

  ggplot(data = subset(soils, ( !is.na(fdil) & dilX>0 )), aes(x=dilX, y=degY)) +
    geom_point()
}
```

In contrast, in top soils, a slightly negative but not significant relationship between extent of dilution and degradation was found. This is to be expected as concentration in top soils are lower than in aquifer systems for legacy contaminants. At lower concentrations, lack of sufficient substrate may be associated to lower bacterial communities capable of degradation.

Waters

Conversion of initial concentration in soils to pore water, assuming all S-met mass is available, may lead to an F_{dil_w} .

For waters, no dilution factor can be applied. The degraded fraction of off-site transport must be equivalent to catchment soils, as degradation is negligible within an event. However, it may be of interest to obtain the degradation extent that would be computed if only outlet observations were conducted, without knowledge of dilution extent in catchment soils. As such, the fraction degraded in outlet waters will be obtained via ϵ_{lab} and with the closed system Rayleigh equation, without making use of concentration data.

```
waters = read.csv2("Data/WeeklyHydroContam_R.csv")
waters$ti <- as.POSIXct(strptime(waters$ti, "%Y-%m-%d %H:%M", tz="EST"))
colnames(waters)[colnames(waters) == "ti"] <- "Date.ti"
waters$Events <- factor(waters$Events, levels = unique(waters$Events))
waters$Event <- factor(waters$Event, levels = unique(waters$Event))

names(waters)
```

```
##      [1] "Date.ti"                "WeekSubWeek"
##      [3] "tf"                    "iflux"
##      [5] "fflux"                 "changeflux"
##      [7] "maxQ"                  "minQ"
##      [9] "dryHrs"                "Duration.Hrs"
##     [11] "chExtreme"            "Peak"
##     [13] "Markers"              "TimeDiff"
##     [15] "AveDischarge.m3.h"    "Volume.m3"
##     [17] "Sampled.Hrs"          "Sampled"
##     [19] "Conc.mug.L"           "Conc.SD"
##     [21] "OXA_mean"             "OXA_SD"
##     [23] "ESA_mean"             "ESA_SD"
##     [25] "N.x"                  "diss.d13C"
##     [27] "SD.d13C"              "N_d13C.diss"
##     [29] "MES.mg.L"             "MES.sd"
##     [31] "MO.mg.L"              "Conc.Solids.mug.gMES"
##     [33] "Conc.Solids.ug.gMES.SD" "N.y"
##     [35] "filt.d13C"            "filt.SD.d13C"
##     [37] "DD13C.diss"           "DD13C.filt"
##     [39] "NH4.mM"               "TIC.ppm.filt"
##     [41] "Cl.mM"                "NO3...mM"
##     [43] "PO4..mM"              "NPOC.ppm"
##     [45] "TIC.ppm.unfilt"       "TOC.ppm.unfilt"
##     [47] "ExpMES.Kg"            "Appl.Mass.g"
##     [49] "Appl.Mass.g.OT"       "Appl.Mass.g.N"
##     [51] "Appl.Mass.g.T"        "Appl.Mass.g.S"
##     [53] "Appl.Mass.g.N.OT"     "Appl.Mass.g.T.OT"
##     [55] "Appl.Mass.g.S.OT"     "iniCo.ug.g.N"
##     [57] "iniCo.ug.g.T"         "iniCo.ug.g.S"
##     [59] "timeSinceApp"         "timeSinceApp.N"
##     [61] "timeSinceApp.T"       "timeSinceApp.S"
##     [63] "Appl.Mass.g.NoSo"     "timeSinceApp.NoSo"
##     [65] "CumAppMass.g"         "CumAppMass.g.OT"
##     [67] "CumAppMass.g.N"       "CumAppMass.g.T"
##     [69] "CumAppMass.g.S"       "CumAppMass.g.N.OT"
##     [71] "CumAppMass.g.T.OT"    "CumAppMass.g.S.OT"
```

```
## [73] "DissSmeto.mg"          "DissSmeto.mg.SD"
## [75] "DissSmeto.g"           "DissSmeto.g.SD"
## [77] "DissOXA.mg"            "DissOXA.mg.SD"
## [79] "DissOXA.g"             "DissOXA.g.SD"
## [81] "DissESA.mg"            "DissESA.mg.SD"
## [83] "DissESA.g"             "DissESA.g.SD"
## [85] "FiltSmeto.mg"          "FiltSmeto.mg.SD"
## [87] "FiltSmeto.g"           "FiltSmeto.g.SD"
## [89] "TotSMout.mg"           "TotSMout.mg.SD"
## [91] "TotSMout.g"            "TotSMout.g.SD"
## [93] "FracDiss"              "FracFilt"
## [95] "MELsm.g"               "MELsm.g.SD"
## [97] "CumOutDiss.g"          "CumOutFilt.g"
## [99] "CumOutSmeto.g"         "CumOutMELsm.g"
## [101] "BalMassDisch.g"        "prctMassOut"
## [103] "FracDeltaOut"          "Events"
## [105] "Weeks"                 "Event"
```

```
keepWater <- c(
  "Date.ti", "WeekSubWeek", "Sampled" , "Volume.m3", "AveDischarge.m3.h",
  "Markers" , "TimeDiff", "Duration.Hrs",
  "Conc.mug.L", "Conc.SD" ,
  "OXA_mean", "OXA_SD",
  "ESA_mean", "ESA_SD",
  "diss.d13C", "SD.d13C",
  "filt.d13C", "filt.SD.d13C",
  "DD13C.diss", "DD13C.filt",
  "Appl.Mass.g", "CumAppMass.g",
  "DissSmeto.g", "DissSmeto.g.SD",
  "DissOXA.g", "DissOXA.g.SD",
  "DissESA.g", "DissESA.g.SD",
  "FiltSmeto.g", "FiltSmeto.g.SD",
  "TotSMout.g", "TotSMout.g.SD",
  "MELsm.g", "MELsm.g.SD",
  "CumOutDiss.g", "CumOutFilt.g",
  "CumOutSmeto.g", "CumOutMELsm.g",
  "Events"
)
waters <- waters[ , colnames(waters) %in% keepWater]
```

Field Assumptions

Converting soil to volumetric concentrations in soils,

$$C_{soil} [\mu g/L_{soil}] = C_{soil} [\frac{\mu g}{g_{soil}}] \cdot \rho_{soil} [\frac{g_{soil}}{m^3}] \cdot \frac{1m^3}{10^3 L_{soil}}$$

$$C_{soil} [\mu g/L_{H_2O}] = \frac{C_{soil}}{\theta_{sat} + \rho_{soil} \cdot K_d}$$

```
# S-metolachlor Mass [g]
# Conc. [ug/g dry soil] * [g/10-6 ug] * density [g/m3] * depth [m]* A [m2]
# Soil bulk density: 2200 or 0.99? -> Leaching experiments: 0.98 [g/cm3]
```

```

#rho = 0.98*10-6 # soil density [g/m3]
#depth = 0.01 # [m]
theta = 0.4
# Kd = 2.397/10-6 # m3/g (aged)
Kd = 3.99/10-6 #m3/g (fresh)

# Cosed vs. Open system Rayleigh
OPEN = T

if (OPEN) {
  waters$f.diss <-
    ((10-3*waters$diss.d13C + 1)/(10-3*d13Co + 1))(1000/(epsilon_lab))

  waters$f.diss.min <-
    ((10-3*waters$diss.d13C + 1)/(10-3*d13Co + 1))(1000/(epsilon_max))

  waters$f.diss.max <-
    ((10-3*waters$diss.d13C + 1)/(10-3*d13Co + 1))(1000/(epsilon_min))

  waters$B.diss <- (1-waters$f.diss)*100
  waters$B.diss.max <- (1-waters$f.diss.min)*100
  waters$B.diss.min <- (1-waters$f.diss.max)*100
} else if (!VERTICAL){
  ws <- merge(waters, soils, by = "Date.ti", all = T )

  # Assume Bulk soils conc. doesn't evolve close to event
  ws$BulkCatch.Conc <- na.locf(ws$BulkCatch.Conc)

  # Convert concentrations from mass to vol H2O, assuming linear sorption
  ws$poolCo_w <- (ws$BulkCatch.Conc*rho/103)/(theta + rho*Kd)
  ws$iniCo_w <- (iniCo*rho/103)/(theta + rho*Kd)

  # f_tot
  # Problem here is initial Co is not applied but, available at time of discharge
  ws$ftot_w <- ws$Conc.mug.L/ws$poolCo_w

  # Van Breukelen notation
  #####
  #####
  # Do we need to change d13Co to initial at event or initial product ??
  ws$Delta_w <- 1000*log( (10-3*ws$diss.d13C.x + 1)/(10-3*d13Co+1) )

  ws$Fdil_w =
    exp( ws$Delta_w/epsilon_lab -log(ws$ftot_w) )
  median(ws$Fdil_w, na.rm = T)

  # Fdil < 1, otherwise this
  ws$Fdil_w <- ifelse(ws$Fdil_w < 1, NA, ws$Fdil_w)

  ws$fdil_w <- 1/ws$Fdil_w
  ws$fdeg_w <- ws$ftot_w * ws$Fdil_w

  ws$Dprct_w <- (1- ws$fdil_w)*100
  #ws$DprctAdj <- (1- ws$fdilAdj)*100

```

```

ws$Bprct_w <- (1-ws$fdeg_w)*100
#ws$BprctAdj <- (1-ws$fdegAdj)*100

ws$Tprct_w <- (1-ws$ftot_w)*100

ws$Dstar_w = log(ws$fdil_w)/log(ws$ftot_w)
ws$Bstar_w = log(ws$fdeg_w)/log(ws$ftot_w)

ws$Dstar_w <- ifelse(ws$Dstar_w< 0, NA, ws$Dstar_w)
ws$Bstar_w <- ifelse(ws$Bstar_w> 1, NA, ws$Bstar_w)

ws$DB_w = ws$Dstar_w/ws$Bstar_w
}

```

Save Waters for Bar Plots

```

write.csv2(waters,
           'Data/Rayleigh_Waters.csv', row.names = F)

```

Van Breukelen, Boris M. 2007. “Quantifying the degradation and dilution contribution to natural attenuation of contaminants by means of an open system Rayleigh equation.” *Environ. Sci. Technol.* 41 (14): 4980–5.