Mass Soils - Composite Weeks Alteck 2016

PAZ

November 2016

Purpose

This file merges weekly composite concentrations and isotope data.

Imports:

- **SoilCompConc_W1toW15.csv**
- **SoilCompIsotopes_W1toW15.csv** (old, not used)
- **SoilCompIsotopes_W1toW15ng.csv**

Generates:

- **WeeklySoils_Rng.csv**

Required R-packages:

```
library("plyr")
library("dplyr")
```

Working directory

```
# setwd("D:/Documents/these_pablo/Alteckendorf2016/R")
# setwd("/Users/DayTightChunks/Documents/PhD/Routput/Alteck/R")
# setwd("D:/Documents/these_pablo/Alteckendorf2016/00_TransparencyFolder")
getwd()
```

```
## [1] "D:/Documents/these_pablo/Alteckendorf2016/HydrologicalMonitoring"
```

Lab Parameters

```
# Pure and cuve isotope average
d13Co = -32.253

# Lab enrichment: Alteck
epsilon_max = -1.5 # +/- 0.3 (@ 20C, 20% vwc)
epsilon_min = -2.0 # +/- 0.2 (@ 20C, 40% vwc)

epsilon_mean = mean(c(epsilon_max, epsilon_min))
epsilon_mean
```

```
## [1] -1.75
```

```
sd(c(epsilon_max, epsilon_min))
```

```
## [1] 0.3535534
```

Filed Assumptions

```
# 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: 0.99 [g/cm3]
rho = 0.99*10^6 # soil density [g/m3]
depth = 0.005 # [m]

# Transect Areas pre-corn applications
Area_Na = 13.92663*10^4 # [m2]

# Corrections (old values):
#Area_Ta = 6.55813*10^4  # [m2] # South Burger's as Talweg
#Area_Sa = 11.05376*10^4 # [m2] # South Burger's as Talweg
Area_Ta = 4.37134*10^4  # [m2]
Area_Sa = 13.3175*10^4 # [m2] # South Burger's as South

# Transect Areas post Corn applications (not on transect)
Area_Nb = 14.9949*10^4 # [m2]

# Corrections (old values):
#Area_Tb = 6.55813*10^4  # [m2] # South Burger's as Talweg
#Area_Sb = 11.65202*10^4 # [m2] # South Burger's as Talweg
Area_Tb = 4.37134*10^4  # [m2]
Area_Sb = 13.91767*10^4 # [m2] # South Burger's as South
```

Composite Concentrations & Isotope Data - Alteckendorf 2016

Isotopes selected where cleaned according to the following rules:

   a) The isotope shift was not largely beyond (2x) Streitwieser theoretical limits (i.e. > 10)
   b) Isotope shift was non-negative
   c) Nanograms of carbon > 5.0.

1. Import CSV files

```
#weeklySoilConc = read.csv2("Data/SoilCompConc_W1toW15.csv", header = TRUE)
# Date format stopped working in CSV
# Convert in CSV via  "=TEXT(CELL.ID, "dd/mm/yyyy hh:mm")" based on xls-file date

weeklySoilConc = read.csv2("Data/SoilCompConc_W1toW15.csv", header = TRUE, dec = ".")
if (length(weeklySoilConc) == 1){
  weeklySoilConc = read.csv("Data/SoilCompConc_W1toW15.csv", header = TRUE)
}
head(weeklySoilConc)
```

```
##    Filename ID Transect Wnum Sample.Date       Date.Soil
## 1  AW-N-0x AW        N   -1  30/03/2016 25/03/2016 00:04
## 2  AW-T-0x AW        T   -1  30/03/2016 25/03/2016 00:04
## 3  AW-S-0x AW        S   -1  30/03/2016 25/03/2016 00:04
## 4   AW-N-0 AW        N    0  30/03/2016 30/03/2016 12:18
## 5   AW-T-0 AW        T    0  30/03/2016 30/03/2016 12:18
## 6   AW-S-0 AW        S    0  30/03/2016 30/03/2016 12:18
##    Conc.mug.g.dry.soil Conc.ComSoil.SD
```

```
## 1          0.0180000              NA
## 2          0.0200000              NA
## 3          0.0290000              NA
## 4          0.8893358       0.1334004
## 5          0.8007680       0.1201152
## 6          3.2039808       0.4805971
```

```r
weeklySoilConc$Date.ti <- as.POSIXct(strptime(weeklySoilConc$Date.Soil, "%d/%m/%Y %H:%M", tz="EST"))
sum(is.na(weeklySoilConc$Date.ti))
```

```
## [1] 0
```

```r
# View(weeklySoilConc)
weeklySoilConc <- weeklySoilConc[,c("Filename",
                                    "Transect",
                                    "Wnum",
                                    "Date.Soil",
                                    "Date.ti",
                                    "Conc.mug.g.dry.soil",
                                    "Conc.ComSoil.SD")]

colnames(weeklySoilConc)[colnames(weeklySoilConc) == "Filename"] <- "ID"
print("Soil Composites- Concentrations")
```

```
## [1] "Soil Composites- Concentrations"
```

```r
str(weeklySoilConc)
```

```
## 'data.frame':    51 obs. of  7 variables:
##  $ ID                 : Factor w/ 51 levels "AW-N-0","AW-N-0x",..: 2 36 19 1 35 18 3 10 11 12 ...
##  $ Transect           : Factor w/ 3 levels "N","S","T": 1 3 2 1 3 2 1 1 1 1 ...
##  $ Wnum               : int  -1 -1 -1 0 0 0 1 2 3 4 ...
##  $ Date.Soil          : Factor w/ 17 levels "03/05/2016 13:10",..: 13 13 13 16 16 16 3 7 10 14 ...
##  $ Date.ti            : POSIXct, format: "2016-03-25 00:04:00" "2016-03-25 00:04:00" ...
##  $ Conc.mug.g.dry.soil: num  0.018 0.02 0.029 0.889 0.801 ...
##  $ Conc.ComSoil.SD    : num  NA NA NA 0.133 0.12 ...
```

```r
# JESIUM data (before nangoram revision)
# weeklySoilIso = read.csv2("Data/SoilCompIsotopes_W1toW15.csv", header = TRUE)

# After nanogram revision
weeklySoilIso  = read.csv2("Data/SoilCompIsotopes_W1toW15ng.csv", header = TRUE, dec = ".")
if (length(weeklySoilIso) == 1){
  weeklySoilIso = read.csv("Data/SoilCompIsotopes_W1toW15ng.csv", header = T)
}
head(weeklySoilIso)
```

```
##    Filename ID Week Num Repl d.13C.12C DD13.32.253. Ave...STDEV
## 1   AW-N-1 AW    N   1    1   -32.890       -0.636
## 2   AW-N-1 AW    N   1    2   -32.170        0.087
## 3   AW-N-1 AW    N   1    3   -29.546        1.664
## 4  AW-N-10 AW    N  10    1   -29.360        2.898
## 5  AW-N-10 AW    N  10    3   -28.470        3.782
## 6  AW-N-10 AW    N  10    2        NA           NA
##       Deleted.d13 Deleted.DD    Rt Ampl..44 Std.Ampl.   ng..C.
## 1                             2648.2      120       904 3.982301
## 2                             2648.0      115       904 3.816372
```

```
## 3                                2648.0      109     904 3.617257
## 4                                2655.6      155     658 7.066869
## 5                                2656.4      183     658 8.343465
## 6 Injection problem                  NA       NA      NA       NA
```

```r
colnames(weeklySoilIso)
```

```
##  [1] "Filename"      "ID"          "Week"         "Num"
##  [5] "Repl"          "d.13C.12C"   "DD13.32.253." "Ave...STDEV"
##  [9] "Deleted.d13"   "Deleted.DD"  "Rt"           "Ampl..44"
## [13] "Std.Ampl."     "ng..C."
```

```r
weeklySoilIso <- weeklySoilIso[complete.cases(weeklySoilIso[, "d.13C.12C"]), ]

colnames(weeklySoilIso)[colnames(weeklySoilIso) == "DD13.32.253."] <- "DD13"
colnames(weeklySoilIso)[colnames(weeklySoilIso) == "ng..C."] <- "ngC"
colnames(weeklySoilIso)[colnames(weeklySoilIso) == "Filename"] <- "ID"

weeklySoilIso <- weeklySoilIso[, c("ID",
                                   # "Repl",
                                   "d.13C.12C",
                                   "DD13",
                                   "ngC")]

# weeklySoilIso <- subset(weeklySoilIso, DD13 < 10) # & ngC > 5)



isoCompSummary = ddply(weeklySoilIso, c("ID"), summarise,
                       N_compsoil    = length(d.13C.12C),
                       comp.d13C = mean(d.13C.12C),
                       comp.d13C.SD = sd(d.13C.12C),
                       # comp.d13C.SE = comp.d13C.SD / sqrt(N_compsoil),
                       N_ngC = length(ngC),
                       ngC.mean = mean(ngC),
                       ngC.SD = sd(ngC) #,
                       # ngC.SE = ngC.SD/sqrt(N_ngC)
                     )

isoCompSummary$prctError <- (isoCompSummary$comp.d13C.SD/isoCompSummary$comp.d13C)*-100
mean(!is.na(isoCompSummary$prctError))
```

```
## [1] 0.9705882
```

```r
sum(isoCompSummary$N_ngC == 2)/(sum(isoCompSummary$N_ngC == 2) + sum(isoCompSummary$N_ngC > 2))
```

```
## [1] 0.3939394
```

```r
print("Soil Composites - Isotopes All")
```

```
## [1] "Soil Composites - Isotopes All"
```

```r
str(weeklySoilIso)
```

```
## 'data.frame':    87 obs. of  4 variables:
##  $ ID       : Factor w/ 41 levels "AW-N-1","AW-N-10",..: 1 1 1 2 2 3 3 4 6 6 ...
##  $ d.13C.12C: num  -32.9 -32.2 -29.5 -29.4 -28.5 ...
##  $ DD13     : num  -0.636 0.087 1.664 2.898 3.782 ...
##  $ ngC      : num  3.98 3.82 3.62 7.07 8.34 ...
```

```r
print("Soil Composites - Isotopes Ave and St.Dev.")
```

```
## [1] "Soil Composites - Isotopes Ave and St.Dev."
```

```r
str(isoCompSummary)
```

```
## 'data.frame':    34 obs. of  8 variables:
##  $ ID         : Factor w/ 41 levels "AW-N-1","AW-N-10",..: 1 2 3 4 5 6 7 8 9 10 ...
##  $ N_compsoil : int  3 2 2 1 2 3 3 2 2 3 ...
##  $ comp.d13C  : num  -31.5 -28.9 -29.5 -29.5 -29 ...
##  $ comp.d13C.SD: num  1.76 0.6293 0.0636 NaN 0.4031 ...
##  $ N_ngC      : int  3 2 2 1 2 3 3 2 2 3 ...
##  $ ngC.mean   : num  3.81 7.71 8.64 1.57 5.12 ...
##  $ ngC.SD     : num  0.183 0.903 0.806 NaN 0.503 ...
##  $ prctError  : num  5.581 2.176 0.216 NaN 1.392 ...
```

2. Merge lab concentrations and isotopes

```r
comp.CoIs = merge(weeklySoilConc, isoCompSummary, by = "ID", all = T)
comp.CoIs$Wnum = as.numeric(comp.CoIs$Wnum)
comp.CoIs <- comp.CoIs[order(comp.CoIs$Wnum),]

comp.CoIs$comp.IMP.d13C <- comp.CoIs$comp.d13C
comp.CoIs$comp.IMP.d13C[is.na(comp.CoIs$comp.d13C)] <- ave(comp.CoIs$comp.d13C,
                                                           comp.CoIs$Wnum,
                                                           FUN= function(x) mean(x, na.rm = T))[is.na(c

comp.CoIs$comp.d13C <- ifelse(is.na(comp.CoIs$comp.d13C), comp.CoIs$comp.IMP.d13C, comp.CoIs$comp.d13C)

print("Merged Soil Concentrations and Isotopes")
```

```
## [1] "Merged Soil Concentrations and Isotopes"
```

```r
str(comp.CoIs)
```

```
## 'data.frame':    51 obs. of  15 variables:
##  $ ID              : Factor w/ 51 levels "AW-N-0","AW-N-0x",..: 2 19 36 1 18 35 3 20 37 10 ...
##  $ Transect        : Factor w/ 3 levels "N","S","T": 1 2 3 1 2 3 1 2 3 1 ...
##  $ Wnum            : num  -1 -1 -1 0 0 0 1 1 1 2 ...
##  $ Date.Soil       : Factor w/ 17 levels "03/05/2016 13:10",..: 13 13 13 16 16 16 3 3 3 7 ...
##  $ Date.ti         : POSIXct, format: "2016-03-25 00:04:00" "2016-03-25 00:04:00" ...
##  $ Conc.mug.g.dry.soil: num  0.018 0.029 0.02 0.889 3.204 ...
##  $ Conc.ComSoil.SD : num  NA NA NA 0.133 0.481 ...
##  $ N_compsoil      : int  NA NA NA NA NA NA 3 3 3 3 ...
##  $ comp.d13C       : num  NaN NaN NaN NaN NaN ...
##  $ comp.d13C.SD    : num  NA NA NA NA NA ...
##  $ N_ngC           : int  NA NA NA NA NA NA 3 3 3 3 ...
##  $ ngC.mean        : num  NA NA NA NA NA ...
##  $ ngC.SD          : num  NA NA NA NA NA ...
##  $ prctError       : num  NA NA NA NA NA ...
##  $ comp.IMP.d13C   : num  NaN NaN NaN NaN NaN ...
```

3. Compute Degradation Extent and Delta-delta

```r
# Pure and cuve isotope average
d13Co
```

```
## [1] -32.253
```
```r
# Lab enrichment: Alteck
epsilon_max # +/- 0.3 (@ 20C, 20% vwc)
```
```
## [1] -1.5
```
```r
epsilon_min # +/- 0.2 (@ 20C, 40% vwc)
```
```
## [1] -2
```
```r
epsilon_mean
```
```
## [1] -1.75
```
```r
sd(c(epsilon_max, epsilon_min))
```
```
## [1] 0.3535534
```
```r
# Vine
# (@ 20C, 20% vwc) -0.8 +/- 0.1
# (@ 30C, 20% vwc) -1.4 +/- 0.2
# (@ 20C, 40% vwc) -1.7 +/- 0.2
# Average

# Remaining fraction
comp.CoIs$DD13C.comp <- (comp.CoIs$comp.d13C - (d13Co))

# Max epsilon (20C, 20%)
comp.CoIs$f.max.comp <-
  ((10^(-3)*comp.CoIs$comp.d13C + 1)/(10^(-3)*d13Co + 1))^(1000/(epsilon_max))

comp.CoIs$B.max.comp <-
  (1 - comp.CoIs$f.max.comp)*100

# Min epsilon (20C, 40%)
comp.CoIs$f.min.comp <-
  ((10^(-3)*comp.CoIs$comp.d13C + 1)/(10^(-3)*d13Co + 1))^(1000/(epsilon_min))

comp.CoIs$B.min.comp <-
  (1 - comp.CoIs$f.min.comp)*100

# Mean epsilon (# Alteck)
comp.CoIs$f.mean.comp <-
  ((10^(-3)*comp.CoIs$comp.d13C + 1)/(10^(-3)*d13Co + 1))^(1000/(epsilon_mean))

comp.CoIs$B.mean.comp <-
  (1 - comp.CoIs$f.mean.comp)*100
```

3. Compute Soil S-metolachlor Mass at time t across space

For non-measured plots, the soil concentration and isotope measured at the neareast transect is assumed. The total area for each transect at the end of the season is shown below. Corn fields in the catchment were known to have received S-metolachlor applications only during the last week of May, 2017. Given that two of these plots were not included within the transects, their area were not accounted for but until after the known application dates for corn plots.

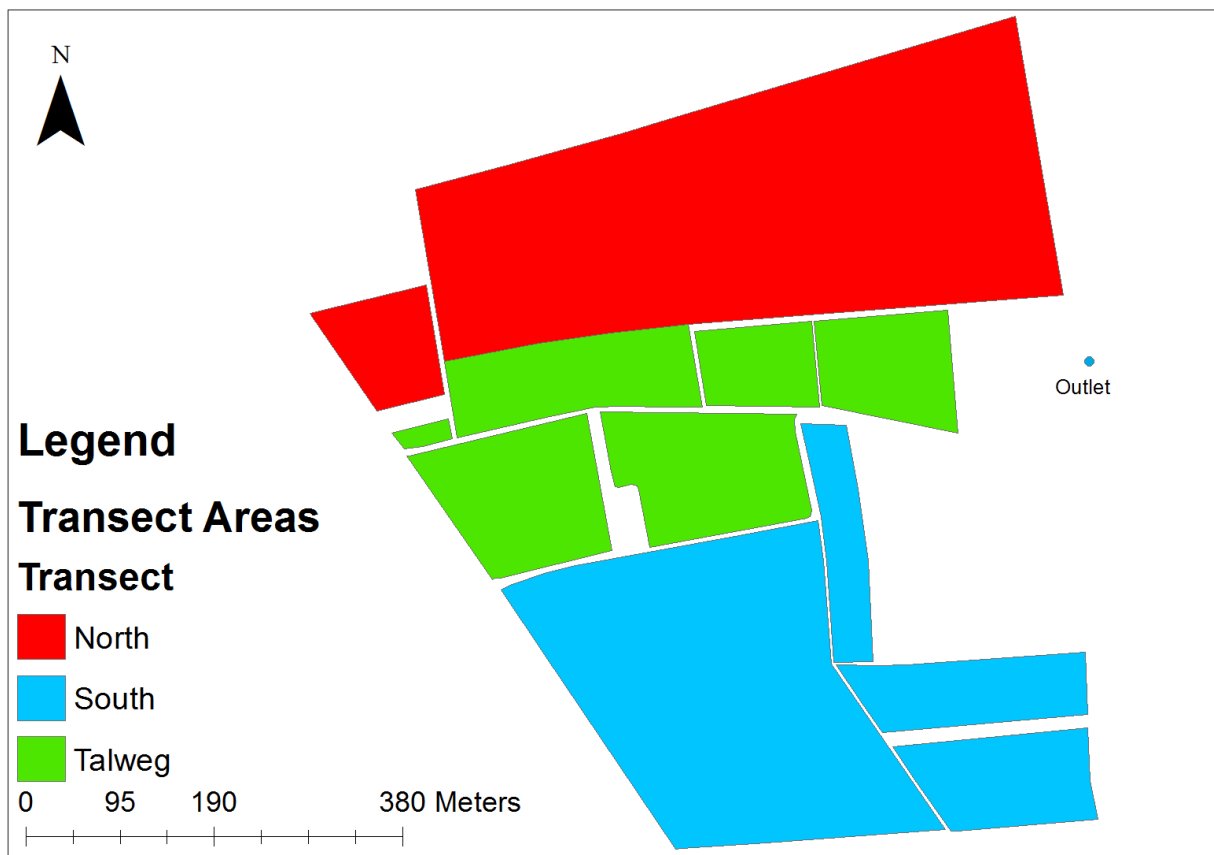The total pesticide mass for each transect at time t is then given by:

Figure 1: Transect Areas [Ha] (North: 14.995; Talweg: 8.774; South: 12.668)

$$M(t)_{Ta} = C(t)_T \cdot \rho \cdot A_T \cdot D \cdot$$

```r
# 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: 0.99 [g/cm3]
rho # soil density [g/m3]
```

```
## [1] 990000
```

```r
depth # [m]
```

```
## [1] 0.005
```

```r
# Transect Areas pre-corn applications
Area_Na # [m2]
```

```
## [1] 139266.3
```

```r
Area_Ta  # [m2]
```

```
## [1] 43713.4
```

```r
Area_Sa # [m2]
```

```
## [1] 133175
```

```r
# Transect Areas post Corn applications (not on transect)
Area_Nb # [m2]
```

```
## [1] 149949
```

```r
Area_Tb # [m2]
```

```
## [1] 43713.4
```

```r
Area_Sb # [m2]
```

```
## [1] 139176.7
```

```r
# Assign new column for S-metolachlor mass in grams
comp.CoIs$MassSoil.g <- NA

# Areas with S-metolachlor before week 9
comp.CoIs$MassSoil.g <-
  ifelse((comp.CoIs$Transect == "N" & comp.CoIs$Wnum < 6),
         comp.CoIs$Conc.mug.g.dry.soil*10^-6*rho*depth*Area_Na,
  ifelse((comp.CoIs$Transect == "T" & comp.CoIs$Wnum < 6),
         comp.CoIs$Conc.mug.g.dry.soil*10^-6*rho*depth*Area_Ta,
  ifelse((comp.CoIs$Transect == "S" & comp.CoIs$Wnum < 6),
         comp.CoIs$Conc.mug.g.dry.soil*10^-6*rho*depth*Area_Sa, comp.CoIs$MassSoil.g)))

# Areas with S-metolachlor after week 9
comp.CoIs$MassSoil.g <-
  ifelse((comp.CoIs$Transect == "N" & comp.CoIs$Wnum >= 6),
         comp.CoIs$Conc.mug.g.dry.soil*10^-6*rho*depth*Area_Nb,
  ifelse((comp.CoIs$Transect == "T" & comp.CoIs$Wnum >= 6),
         comp.CoIs$Conc.mug.g.dry.soil*10^-6*rho*depth*Area_Tb,
  ifelse((comp.CoIs$Transect == "S" & comp.CoIs$Wnum >= 6),
         comp.CoIs$Conc.mug.g.dry.soil*10^-6*rho*depth*Area_Sb, comp.CoIs$MassSoil.g)))
```

```r
# Areas as variables (for later computation of bulk catchment mass)
comp.CoIs$Area.N <-
  ifelse((comp.CoIs$Wnum < 6), Area_Na, Area_Nb)

comp.CoIs$Area.T <-
  ifelse((comp.CoIs$Wnum < 6), Area_Ta, Area_Tb)

comp.CoIs$Area.S <-
  ifelse((comp.CoIs$Wnum < 6), Area_Sa, Area_Sb)


print("S-meto mass per transect at time-t")
```

```
## [1] "S-meto mass per transect at time-t"
```

```r
str(comp.CoIs)
```

```
## 'data.frame':    51 obs. of  26 variables:
##  $ ID               : Factor w/ 51 levels "AW-N-0","AW-N-0x",..: 2 19 36 1 18 35 3 20 37 10 ...
##  $ Transect         : Factor w/ 3 levels "N","S","T": 1 2 3 1 2 3 1 2 3 1 ...
##  $ Wnum             : num  -1 -1 -1 0 0 0 1 1 1 2 ...
##  $ Date.Soil        : Factor w/ 17 levels "03/05/2016 13:10",..: 13 13 13 16 16 16 3 3 3 7 ...
##  $ Date.ti          : POSIXct, format: "2016-03-25 00:04:00" "2016-03-25 00:04:00" ...
##  $ Conc.mug.g.dry.soil: num  0.018 0.029 0.02 0.889 3.204 ...
##  $ Conc.ComSoil.SD  : num  NA NA NA 0.133 0.481 ...
##  $ N_compsoil       : int  NA NA NA NA NA NA 3 3 3 3 ...
##  $ comp.d13C        : num  NaN NaN NaN NaN NaN ...
##  $ comp.d13C.SD     : num  NA NA NA NA NA ...
##  $ N_ngC            : int  NA NA NA NA NA NA 3 3 3 3 ...
##  $ ngC.mean         : num  NA NA NA NA NA ...
##  $ ngC.SD           : num  NA NA NA NA NA ...
##  $ prctError        : num  NA NA NA NA NA ...
##  $ comp.IMP.d13C    : num  NaN NaN NaN NaN NaN ...
##  $ DD13C.comp       : num  NaN NaN NaN NaN NaN ...
##  $ f.max.comp       : num  NaN NaN NaN NaN NaN ...
##  $ B.max.comp       : num  NaN NaN NaN NaN NaN ...
##  $ f.min.comp       : num  NaN NaN NaN NaN NaN ...
##  $ B.min.comp       : num  NaN NaN NaN NaN NaN ...
##  $ f.mean.comp      : num  NaN NaN NaN NaN NaN ...
##  $ B.mean.comp      : num  NaN NaN NaN NaN NaN ...
##  $ MassSoil.g       : num  12.41 19.12 4.33 613.08 2112.12 ...
##  $ Area.N           : num  139266 139266 139266 139266 139266 ...
##  $ Area.T           : num  43713 43713 43713 43713 43713 ...
##  $ Area.S           : num  133175 133175 133175 133175 133175 ...
```

```r
tail(comp.CoIs)
```

```
##       ID Transect Wnum       Date.Soil          Date.ti
## 8  AW-N-14        N   14 04/07/2016 14:42 2016-07-04 14:42:00
## 25 AW-S-14        S   14 04/07/2016 14:42 2016-07-04 14:42:00
## 42 AW-T-14        T   14 04/07/2016 14:42 2016-07-04 14:42:00
## 9  AW-N-15        N   15 12/07/2016 01:00 2016-07-12 01:00:00
## 26 AW-S-15        S   15 12/07/2016 01:00 2016-07-12 01:00:00
## 43 AW-T-15        T   15 12/07/2016 01:00 2016-07-12 01:00:00
##    Conc.mug.g.dry.soil Conc.ComSoil.SD N_compsoil comp.d13C comp.d13C.SD
```

```
## 8                1.3336411           0.2000462              2 -28.9650        0.4030509
## 25               1.0220275           0.1533041             NA -28.4325              NA
## 42               1.5868495           0.2380274              2 -27.9000        0.1414214
## 9                0.9564201           0.1434630             NA      NaN              NA
## 26               1.1610022           0.1741503             NA      NaN              NA
## 43               1.3119054           0.1967858             NA      NaN              NA
##    N_ngC ngC.mean    ngC.SD prctError comp.IMP.d13C DD13C.comp f.max.comp
## 8      2 5.118483 0.5026825 1.3915100      -28.9650     3.2880 0.10422371
## 25    NA       NA        NA        NA      -28.4325     3.8205 0.07231637
## 42     2 5.699301 0.9395125 0.5068866      -27.9000     4.3530 0.05018729
## 9     NA       NA        NA        NA           NaN        NaN        NaN
## 26    NA       NA        NA        NA           NaN        NaN        NaN
## 43    NA       NA        NA        NA           NaN        NaN        NaN
##    B.max.comp f.min.comp B.min.comp f.mean.comp B.mean.comp MassSoil.g
## 8    89.57763  0.1834319   81.65681  0.14396503    85.60350   989.8919
## 25   92.76836  0.1394529   86.05471  0.10524533    89.47547   704.0999
## 42   94.98127  0.1060340   89.39660  0.07695258    92.30474   343.3646
## 9         NaN        NaN        NaN         NaN         NaN   709.9004
## 26        NaN        NaN        NaN         NaN         NaN   799.8430
## 43        NaN        NaN        NaN         NaN         NaN   283.8718
##     Area.N  Area.T   Area.S
## 8  149949 43713.4 139176.7
## 25 149949 43713.4 139176.7
## 42 149949 43713.4 139176.7
## 9  149949 43713.4 139176.7
## 26 149949 43713.4 139176.7
## 43 149949 43713.4 139176.7
```

```r
write.csv2(comp.CoIs, 'Data/WeeklySoils_Rng.csv', row.names = F)
```