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] "/Users/DayTightChunks/Documents/PhD/HydrologicalMonitoring"
```

Lab Parameters

```
# Pure and cuve isotope average
d13Co = -31.2144

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

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

```
# 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  0.0183 0.0205 0.0285 0.8893 0.8008 ...
##  $ Conc.ComSoil.SD    : num  NA NA NA 1.46 1.83 ...
```

```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 Wnum Repl d.13C.12C DD13...31.21. Ave...STDEV     Rt
## 1   AW-N-1 AW    N    1    1   -31.846        -0.636          NA 2648.2
## 2   AW-N-1 AW    N    1    2   -31.123         0.087          NA 2648.0
## 3   AW-N-1 AW    N    1    3   -29.546         1.664          NA 2648.0
## 4  AW-N-10 AW    N   10    1   -28.312         2.898          NA 2655.6
## 5  AW-N-10 AW    N   10    3   -27.428         3.782          NA 2656.4
## 6  AW-N-11 AW    N   11    1   -27.828         3.382          NA 2656.0
##   Ampl..44 Std.Ampl.   ng..C.
## 1      120       904 3.982301
## 2      115       904 3.816372
## 3      109       904 3.617257
## 4      155       658 7.066869
## 5      183       658 8.343465
## 6      202       658 9.209726
```

```r
colnames(weeklySoilIso)[colnames(weeklySoilIso) == "DD13...31.21."] <- "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 > 0 & 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))


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

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

```
str(weeklySoilIso)
```

```
## 'data.frame':    84 obs. of  5 variables:
##  $ ID       : Factor w/ 41 levels "AW-N-1","AW-N-10",..: 2 2 3 3 6 6 6 7 7 7 ...
##  $ Repl     : int  1 3 1 3 1 2 3 1 2 3 ...
##  $ d.13C.12C: num  -28.3 -27.4 -27.8 -28.1 -30.2 ...
##  $ DD13     : num  2.9 3.78 3.38 3.09 1.04 ...
##  $ ngC      : num  7.07 8.34 9.21 8.07 18.74 ...
```

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

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

```
str(isoCompSummary)
```

```
## 'data.frame':    33 obs. of  9 variables:
##  $ ID          : Factor w/ 41 levels "AW-N-1","AW-N-10",..: 2 3 5 6 7 8 11 12 13 14 ...
##  $ N_compsoil  : int  2 2 2 3 3 2 1 3 2 2 ...
##  $ comp.d13C   : num  -27.9 -28 -26.9 -30.2 -30.2 ...
##  $ comp.d13C.SD: num  0.625 0.206 1.802 0.105 0.4 ...
##  $ comp.d13C.SE: num  0.442 0.1455 1.274 0.0609 0.2307 ...
##  $ N_ngC       : int  2 2 2 3 3 2 1 3 2 2 ...
##  $ ngC.mean    : num  7.71 8.64 5.53 18.37 12.18 ...
##  $ ngC.SD      : num  0.9027 0.806 0.0754 0.476 0.3134 ...
##  $ ngC.SE      : num  0.6383 0.5699 0.0533 0.2748 0.1809 ...
```

2. Merge lab concentrations and isotopes

```
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"
```

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

```
## 'data.frame':    51 obs. of  16 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  0.0183 0.0285 0.0205 0.8893 3.204 ...
##  $ Conc.ComSoil.SD    : num  NA NA NA 1.46 2.77 ...
##  $ N_compsoil         : int  NA NA NA NA NA NA NA 2 NA 3 ...
##  $ comp.d13C          : num  NaN NaN NaN NaN NaN ...
##  $ comp.d13C.SD       : num  NA NA NA NA NA ...
##  $ comp.d13C.SE       : num  NA NA NA NA NA ...
##  $ N_ngC              : int  NA NA NA NA NA NA NA 2 NA 3 ...
##  $ ngC.mean           : num  NA NA NA NA NA ...
##  $ ngC.SD             : num  NA NA NA NA NA ...
##  $ ngC.SE             : num  NA NA NA NA NA ...
##  $ comp.IMP.d13C      : num  NaN NaN NaN NaN NaN ...
```

3. Compute Degradation Extent and Delta-delta

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

```
## [1] -31.2144
```

```
# Lab enrichment: Alteck
epsilon_max # +/- 0.3 (@ 20C, 20% vwc)
```

```
## [1] -1.5
```

```
epsilon_min # +/- 0.2 (@ 20C, 40% vwc)
```

```
## [1] -2
```

```
epsilon_mean
```

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

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

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

```
# 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.

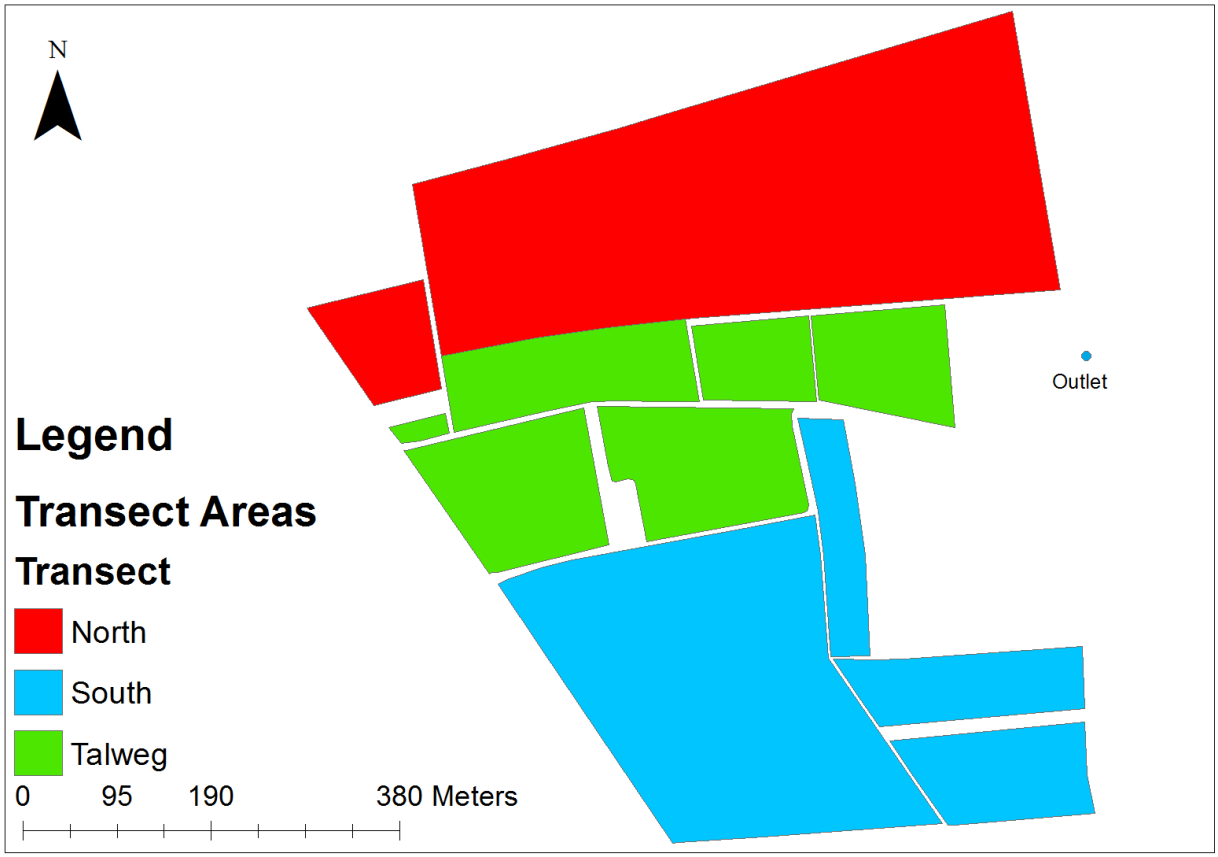

Figure 1: Transect Areas $[Ha]$ (North: 14.995; Talweg: 8.774; South: 12.668)

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

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

```
# 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
```

```
depth # [m]
```

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

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

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

```
Area_Ta  # [m2]
```

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

```
Area_Sa # [m2]
```

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

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

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

```
Area_Tb # [m2]
```

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

```
Area_Sb # [m2]
```

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

```
# 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)))

# 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"
```

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

```
## 'data.frame':    51 obs. of  27 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  0.0183 0.0285 0.0205 0.8893 3.204 ...
##  $ Conc.ComSoil.SD    : num  NA NA NA 1.46 2.77 ...
##  $ N_compsoil         : int  NA NA NA NA NA NA NA 2 NA 3 ...
##  $ comp.d13C          : num  NaN NaN NaN NaN NaN ...
##  $ comp.d13C.SD       : num  NA NA NA NA NA ...
##  $ comp.d13C.SE       : num  NA NA NA NA NA ...
##  $ N_ngC              : int  NA NA NA NA NA NA NA 2 NA 3 ...
##  $ ngC.mean           : num  NA NA NA NA NA ...
##  $ ngC.SD             : num  NA NA NA NA NA ...
##  $ ngC.SE             : 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  12.61 18.8 4.44 613.08 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 ...
```

```
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      0.09490089          2 -26.92900    1.8017081
```

```
## 25           1.0220275      0.09490089          3 -27.83867    0.9586315
## 42           1.5868495      0.09490089          3 -26.08233    1.3480372
## 9            0.9564201      0.09490089         NA       NaN           NA
## 26           1.1610022      0.09490089         NA       NaN           NA
## 43           1.3119054      0.09490089         NA       NaN           NA
##    comp.d13C.SE N_ngC ngC.mean     ngC.SD     ngC.SE comp.IMP.d13C
## 8     1.2740000     2 5.527251 0.07540238 0.05331754     -26.92900
## 25    0.5534661     3 5.734266 0.51506713 0.29737415     -27.83867
## 42    0.7782896     3 5.489510 0.75721706 0.43717947     -26.08233
## 9            NA    NA       NA         NA         NA           NaN
## 26           NA    NA       NA         NA         NA           NaN
## 43           NA    NA       NA         NA         NA           NaN
##    DD13C.comp f.max.comp B.max.comp f.min.comp B.min.comp f.mean.comp
## 8    4.285400 0.05273474   94.72653 0.11004558   88.99544  0.08028869
## 25   3.375733 0.09837564   90.16244 0.17565709   82.43429  0.13701268
## 42   5.132067 0.02953162   97.04684 0.07123861   92.87614  0.04884473
## 9         NaN        NaN        NaN        NaN        NaN         NaN
## 26        NaN        NaN        NaN        NaN        NaN         NaN
## 43        NaN        NaN        NaN        NaN        NaN         NaN
##    B.mean.comp MassSoil.g Area.N  Area.T   Area.S
## 8     91.97113   989.8919 149949 43713.4 139176.7
## 25    86.29873   704.0999 149949 43713.4 139176.7
## 42    95.11553   343.3646 149949 43713.4 139176.7
## 9          NaN   709.9004 149949 43713.4 139176.7
## 26         NaN   799.8430 149949 43713.4 139176.7
## 43         NaN   283.8718 149949 43713.4 139176.7
```

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