

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 Used

```
# 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/106 ug] * density [g/m3] * depth [m] * A [m2]
# Soil bulk density: 2200 or 0.99? -> Leaching experiments: 0.99 [g/cm3]
rho = 0.99*106 # soil density [g/m3]
depth = 0.005 # [m]

# Transect Areas pre-corn applications
Area_Na = 13.92663*104 # [m2]

# Corrections (old values):
#Area_Ta = 6.55813*104 # [m2] # South Burger's as Talweg
#Area_Sa = 11.05376*104 # [m2] # South Burger's as Talweg
Area_Ta = 4.37134*104 # [m2]
Area_Sa = 13.3175*104 # [m2] # South Burger's as South

# Transect Areas post Corn applications (not on transect)
Area_Nb = 14.9949*104 # [m2]

# Corrections (old values):
#Area_Tb = 6.55813*104 # [m2] # South Burger's as Talweg
#Area_Sb = 11.65202*104 # [m2] # South Burger's as Talweg
Area_Tb = 4.37134*104 # [m2]
Area_Sb = 13.91767*104 # [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"
```

```

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 1.46 1.83 ...

# JESIUM data (before nangoram revision)
# weeklySoilIso = read.csv2("Data/SoilCompIsotopes_WitoW15.csv", header = TRUE)

# After nanogram revision
weeklySoilIso = read.csv2("Data/SoilCompIsotopes_WitoW15ng.csv", header = TRUE, dec = ".")
if (length(weeklySoilIso) == 1){
  weeklySoilIso = read.csv("Data/SoilCompIsotopes_WitoW15ng.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

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': 114 obs. of 5 variables:
## $ ID : Factor w/ 41 levels "AW-N-1","AW-N-10",...: 1 1 2 2 3 3 4 6 6 6 ...
## $ Repl : int 2 3 1 3 1 3 3 1 2 3 ...
## $ d.13C.12C: num -31.1 -29.5 -28.3 -27.4 -27.8 ...
## $ DD13 : num 0.087 1.664 2.898 3.782 3.382 ...
## $ ngC : num 3.82 3.62 7.07 8.34 9.21 ...

```

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

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

```

str(isoCompSummary)

## 'data.frame': 41 obs. of 9 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 2 2 2 1 3 3 3 2 3 3 ...
## $ comp.d13C : num -30.3 -27.9 -28 -28.5 -27.2 ...
## $ comp.d13C.SD: num 1.115 0.625 0.206 NA 1.338 ...
## $ comp.d13C.SE: num 0.789 0.442 0.146 NA 0.773 ...
## $ N_ngC : int 2 2 2 1 3 3 3 2 3 3 ...
## $ ngC.mean : num 3.72 7.71 8.64 1.57 5.27 ...
## $ ngC.SD : num 0.141 0.903 0.806 NA 0.444 ...
## $ ngC.SE : num 0.0996 0.6383 0.5699 NA 0.2566 ...

```

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(comp.CoIs$comp.d13C)]

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 2 2 3 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 2 2 3 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 nearest 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.

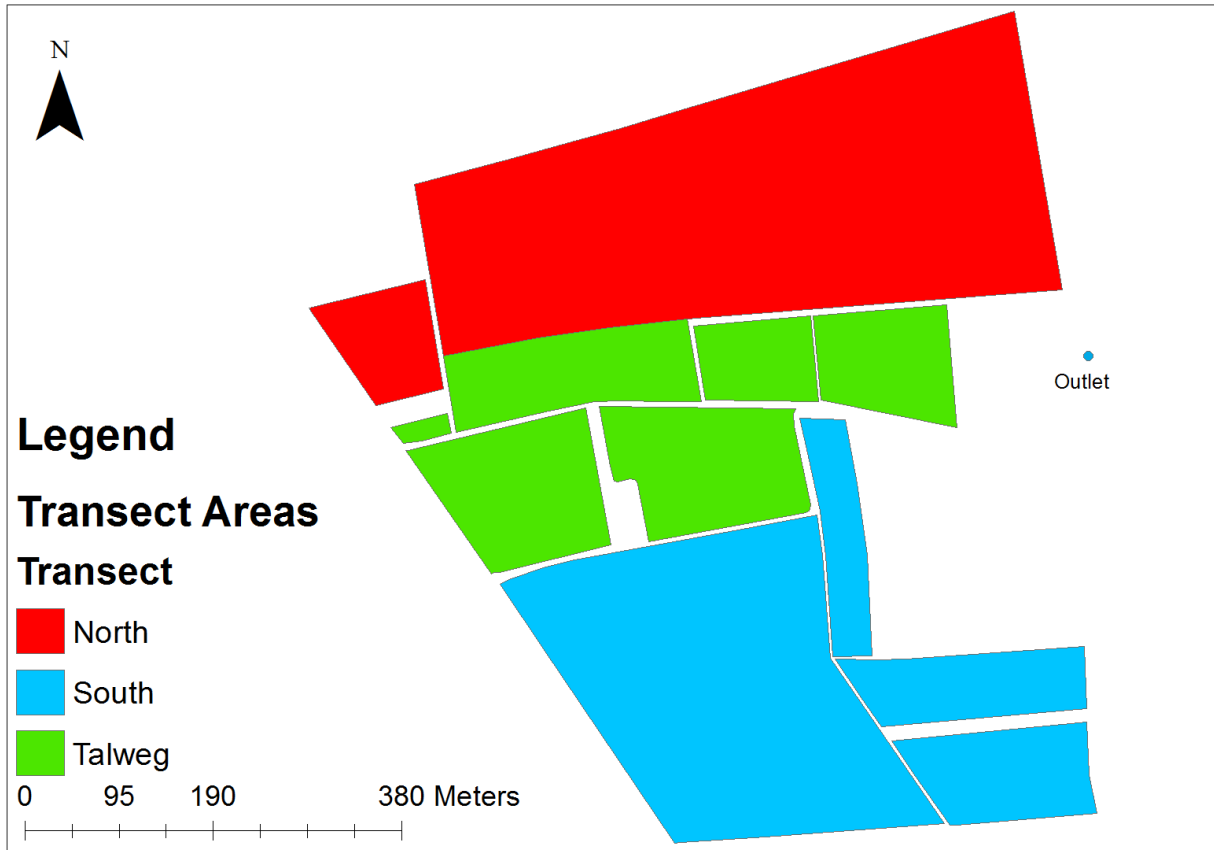


Figure 1: Transect Areas [Ha] (North: 14.995; Talweg: 8.774; South: 12.668)

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

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

```

# S-metolachlor Mass [g]
# Conc. [ug/g dry soil] * [g/106 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 2 2 3 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 2 2 3 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          3 -27.16533    1.3381466

```



```

## 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      0.7725793      3 5.272512 0.4444313 0.2565925 -27.16533
## 25      0.5534661      3 5.734266 0.5150671 0.2973741 -27.83867
## 42      0.7782896      3 5.489510 0.7572171 0.4371795 -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      4.049067 0.06200468 93.79953 0.12425628 87.57437 0.09224339
## 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      90.77566 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)
```