Mass Discharge - Outlet Alteck. 2016

PAZ

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Purpose

This file computes the discharged mass observed at the outlet. To do that it imports the weekly discharge summary and lab results for isotopes (^{13}C) and s-metolachlor concentrations.

Imports:

- **WeeklyHydro_R.csv** (R generated)
- **fluxAlteck2016_R.csv** (R generated)
- **OutletConc_W0toW17.csv**
- **MESAlteckWater.csv** (Concentration in filters)
- **Outlet_Isotopes_W0toW17.csv**
- **MESAlteck_FilterIsotopes.csv** (Isotopes in filters)
- **Outlet_ESAOXA_W0toW17.csv**
- **AO-Hydrochem.csv**

Generates:

- **WeeklyHydroContam_R.csv**

Required R-packages:

```
library("stringr")
library("plyr")
library("dplyr")
library("zoo")
library("ggplot2")
library("plotly")
```

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"
```

Outlet Data - Alteckendorf 2016

1. Hydrological data on a subweekly basis

```
weeklyhydro = read.csv2("Data/WeeklyHydro_R.csv", header = TRUE)
colnames(weeklyhydro)[colnames(weeklyhydro) == "ID"] <- "WeekSubWeek"
head(weeklyhydro)
```

```
##   WeekSubWeek AveDischarge.m3.h Volume.m3 Sampled.Hrs     Sampled
## 1       W0-0x          1.204775  14.41714    11.96667 Not Sampled
## 2        W0-1          1.213511 100.15508    82.53333     Sampled
## 3       W0-2x          1.284719  48.34827    37.63333 Not Sampled
## 4        W1-1         14.316647 390.36726    27.26667     Sampled
## 5        W1-2         15.529299 359.24445    23.13333     Sampled
## 6       W1-3x          9.107720 877.37700    96.33333 Not Sampled
```

```
weeklyflux = read.csv2("Data/fluxAlteck2016_R.csv", header = TRUE)
head(weeklyflux)
```

```
##   WeekSubWeek                  ti                  tf     iflux     fflux
## 1       W0-0x 2016-03-25 00:04:00 2016-03-25 12:02:00  1.248600  1.129227
## 2        W0-1 2016-03-25 12:04:00 2016-03-28 22:36:00  1.124382  1.313125
## 3       W0-2x 2016-03-28 22:38:00 2016-03-30 12:16:00  1.308100  1.456349
## 4        W1-1 2016-03-30 12:18:00 2016-03-31 15:34:00  1.456080 16.445436
## 5        W1-2 2016-03-31 15:36:00 2016-04-01 14:44:00 16.334349 15.184536
## 6       W1-3x 2016-04-01 14:46:00 2016-04-05 15:06:00 15.203629  5.856380
##   changeflux      maxQ      minQ Duration.Hrs  chExtreme Event  Markers
## 1 -0.1193728  1.248600  1.118296     11.96667 -0.1303036    NA       NA
## 2  0.1887431  1.380388  1.082199     82.53333  0.2560062    NA       NA
## 3  0.1482496  1.637782  0.929055     37.63333  0.3296817    NA       NA
## 4 14.9893566 38.399790  1.448977     27.26667 36.9437102     1 16.88972
## 5 -1.1498131 18.668972 13.201113     23.13333 -3.1332355    NA       NA
## 6 -9.3472489 15.895640  5.471042     96.33333 -9.7325862    NA       NA
##   TimeDiff
## 1     <NA>
## 2     <NA>
## 3     <NA>
## 4       24
## 5     <NA>
## 6     <NA>
```

2. Concentration data (dissolved and suspended solids) on a subweekly basis

```
outletConc = read.csv2("Data/OutletConc_W0toW17.csv", header = T)
outletConc$ID4 <- as.character(outletConc$ID4)
outletConc <- outletConc[outletConc$ID4 != "J+7", ]
outletConc <- outletConc[,c("WeekSubWeek", "Conc.mug.L", "Conc.SD")]
head(outletConc)
```

```
##   WeekSubWeek Conc.mug.L Conc.SD
## 1        W0-1  0.2456594 0.01931
## 2        W1-1  6.7882463 0.28942
## 3        W1-2  6.5609982 0.19064
## 4        W2-1  9.4443019 0.33354
## 5        W2-2  1.0421883 0.03904
## 6        W3-1  8.8357358 0.47086
```

```
filters = read.csv2("Data/MESAlteckWater.csv")
filters$MO.mg.L = ifelse(filters$MO.mg.L < 0, 0.0001, filters$MO.mg.L)
head(filters)
```

```
##   WeekSubWeek  MES.mg.L MES.sd MO.mg.L Conc.Solids.mug.gMES
## 1        W0-1  53.44444     NA  0.0000           0.64472899
## 2        W1-1  62.50000     NA  0.0010           0.12588974
## 3        W1-2  22.50000     NA  0.0001           0.43578716
## 4        W2-1  22.50000     NA  0.0001           0.07935267
## 5        W2-2   5.00000     NA  0.0001           0.05075270
## 6        W3-1 197.50000     NA  0.0058           0.08177487
##   Conc.Solids.ug.gMES.SD
## 1            0.023237548
## 2            0.027063685
## 3            0.123237064
## 4            0.004683719
## 5            0.001027205
## 6            0.001343089
```

```
# MESA/MOXA data cleaning
outletESAOXA = read.csv2("Data/Outlet_ESAOXA_W0toW17.csv", header = T)
outletESAOXA$ID <- as.character(outletESAOXA$ID)
split <- strsplit(outletESAOXA$ID, "-", fixed = TRUE)
outletESAOXA$ESAOXA_SD <- sapply(split, "[", 4)
split_vor <- strsplit(outletESAOXA$ID, "-SD", fixed = TRUE)
outletESAOXA$ESAOXA_Mean <- sapply(split_vor, "[", 1)

means_temp <- subset(outletESAOXA, is.na(outletESAOXA$ESAOXA_SD))
sd_temp <- subset(outletESAOXA, !is.na(outletESAOXA$ESAOXA_SD))
means_temp$ID <- NULL
sd_temp$ID <- NULL

head(sd_temp)
```

```
##      MOXA.ugL  MESA.ugL ESAOXA_SD ESAOXA_Mean
## 2   1.1414453 3.4972206        SD     AO-W0-1
## 4  10.1852510 3.0369845        SD     AO-W1-1
## 6   0.2430544 0.8533820        SD     AO-W1-2
## 8   1.1526489 2.8261924        SD     AO-W2-1
## 10  0.6100011 0.1910419        SD     AO-W2-2
## 12  2.6589421 0.3268637        SD     AO-W3-1
```

```
head(means_temp)
```

```
##      MOXA.ugL MESA.ugL ESAOXA_SD ESAOXA_Mean
## 1    4.824094 18.05531      <NA>     AO-W0-1
## 3   30.531235 45.98364      <NA>     AO-W1-1
## 5   32.492465 41.28052      <NA>     AO-W1-2
## 7  104.541255 98.56782      <NA>     AO-W2-1
## 9   26.885849 51.95245      <NA>     AO-W2-2
## 11  45.080673 24.04717      <NA>     AO-W3-1
```

```
outletESAOXA <- merge(means_temp, sd_temp, by = "ESAOXA_Mean", all = T)
outletESAOXA$ESAOXA_SD.x <- NULL
outletESAOXA$ESAOXA_SD.y <- NULL
split_ID <- strsplit(outletESAOXA$ESAOXA_Mean, "AO-", fixed = T)
outletESAOXA$ID <- sapply(split_ID, "[", 2)
outletESAOXA$ESAOXA_Mean <- NULL
outletESAOXA <- outletESAOXA[ , c("ID", "MOXA.ugL.x", "MOXA.ugL.y", "MESA.ugL.x", "MESA.ugL.y")]
colnames(outletESAOXA) <- c("WeekSubWeek", "OXA_mean", "OXA_SD", "ESA_mean",  "ESA_SD")
```

```
outletESAOXA$WeekSubWeek <- as.factor(outletESAOXA$WeekSubWeek)

head(outletESAOXA)
```

```
##   WeekSubWeek  OXA_mean      OXA_SD ESA_mean    ESA_SD
## 1        W0-1  4.824094  1.14144531 18.05531 3.4972206
## 2        W1-1 30.531235 10.18525095 45.98364 3.0369845
## 3        W1-2 32.492465  0.24305444 41.28052 0.8533820
## 4       W10-1 21.311423  0.05168437 82.87549 1.8167218
## 5       W10-2 13.095046  0.17703516 12.02387 0.3057521
## 6       W10-3 45.605808  1.92663562 11.31492 0.1763479
```

3. Isotope data

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 > 2.0.

```
# Outlet isotope data:

outletIso = read.csv2("Data/Outlet_Isotopes_W0toW17.csv", header = T)
if (length(outletIso) == 1){
  outletIso = read.csv("Data/Outlet_Isotopes_W0toW17.csv", header = T)
}
head(outletIso)
```

```
##   FileHeader..Filename ID Week Wnum SubWeek WeekSubWeek Repl d.13C.12C
## 1       AO_W2_2-1_.dxf AO   W2    2       2        W2-2    1   -28.609
## 2       AO_W2_2-2_.dxf AO   W2    2       2        W2-2    2   -28.894
## 3       AO_W2_2-3_.dxf AO   W2    2       2        W2-2    3   -28.503
## 4  AO_W3_1-1_-0001.dxf AO   W3    3       1        W3-1    1   -29.838
## 5  AO_W3_1-2_-0001.dxf AO   W3    3       1        W3-1    2   -29.840
## 6  AO_W3_1-3_-0001.dxf AO   W3    3       1        W3-1    3   -30.073
##   DD13...31.21. Ave...STDEV     Rt Ampl..44 Std.Ampl.    ng..C.    ng..N.
## 1         2.601   0.2022136 2656.2      127       658  5.790274 2.4601342
## 2         2.316          NA 2656.2      163       658  7.431611 2.5579959
## 3         2.707          NA 2655.3      176       658  8.024316 1.7404161
## 4         1.372          NA 2648.9      914       858 31.958042 1.5596397
## 5         1.370          NA 2649.3      905       858 31.643357 1.2796135
## 6         1.137          NA 2649.5      941       858 32.902098 0.1419031
```

```
colnames(outletIso)[colnames(outletIso) == "DD13...31.21."] <- "DD13"
colnames(outletIso)[colnames(outletIso) == "ng..C."] <- "ngC"
outletIso <- subset(outletIso, DD13 > 0 & DD13 < 10 & ngC >= 2)

# Filter isotope data:

filtersIso = read.csv2("Data/MESAlteck_FilterIsotopes.csv", header = T)
#filtersIso <- filtersIso[filtersIso$Level != "J+7", ]
if (length(filtersIso) == 1){
  filtersIso = read.csv("Data/MESAlteck_FilterIsotopes.csv", header = T)
}
filtersIso$WeekSubWeek = paste(filtersIso$Week, filtersIso$Num, sep = "-")
colnames(filtersIso)[colnames(filtersIso) == "DD13...31.21."] <- "DD13"
colnames(filtersIso)[colnames(filtersIso) == "ng..C."] <- "ngC"
```

```
head(filtersIso)
```

```
##    ID Week Wnum Num Levl Repl d.13C.12C  DD13       ngC WeekSubWeek
## 1 AFP   W2    1   1   NA    1   -25.154 6.056 0.7300885        W2-1
## 2 AFP   W2    1   1   NA    2   -28.187 3.023 0.8296460        W2-1
## 3 AFP   W2    1   1   NA    3   -28.283 2.927 0.8296460        W2-1
## 4 AFP   W2    2   2   NA    1   -30.618 0.592 0.6637168        W2-2
## 5 AFP   W2    2   2   NA    2   -26.304 4.906 0.7300885        W2-2
## 6 AFP   W2    2   2   NA    3   -26.024 5.186 0.7300885        W2-2
```

4. Hydrochemistry Data

```
hydroChem = read.csv2("Data/AO-Hydrochem.csv", header = T)
hydroChem = hydroChem[, c("WeekSubWeek",
                          "NH4.mM",
                          "TIC.ppm.filt",
                          "Cl.mM",
                          "NO3...mM",
                          "PO4..mM",
                          "NPOC.ppm" ,
                          "TIC.ppm.unfilt",
                          "TOC.ppm.unfilt" )]
head(hydroChem)
```

```
##   WeekSubWeek NH4.mM TIC.ppm.filt   Cl.mM NO3...mM PO4..mM NPOC.ppm
## 1        W1-1   0.05         51.8    1.48   616.00      NA      4.0
## 2        W1-2     NA         44.8 1574.00   778.00      NA      4.4
## 3       W10-1     NA         60.1    1.17   964.00      NA      2.0
## 4       W10-2   9.00         57.1 1013.00  1174.00      13      5.2
## 5       W10-3     NA         58.2  858.00     1.23      NA      5.0
## 6       W10-4  15.00         26.4  355.00  1409.00      NA      6.4
##   TIC.ppm.unfilt TOC.ppm.unfilt
## 1           44.8            4.7
## 2           26.4            5.4
## 3           63.2            2.0
## 4           55.9            4.0
## 5           60.4            4.3
## 6           24.5            6.4
```

Summarizing IRMS data

```
isoOutSummary = ddply(outletIso, c("WeekSubWeek"), summarise,
                          N    = length(d.13C.12C),
                          diss.d13C = mean(d.13C.12C),
                          SD.d13C = sd(d.13C.12C),
                          se.d13C = SD.d13C / sqrt(N),
                          N_ngC.diss = length(ngC),
                          ngC.mean.diss = mean(ngC),
                          ngC.SD.diss = sd(ngC))



head(isoOutSummary)
```

```
##   WeekSubWeek N diss.d13C   SD.d13C    se.d13C N_ngC.diss ngC.mean.diss
## 1        W1-1 3 -30.46867 0.1060016 0.06120004          3     42.692308
## 2        W1-2 3 -30.61967 0.1513550 0.08738484          3     54.696970
## 3       W10-1 2 -28.43800 0.5260874 0.37200000          2      9.811304
## 4       W10-2 3 -29.97667 0.6127261 0.35375761          3     44.807210
## 5       W10-3 3 -29.76967 0.3411749 0.19697744          3     19.092646
## 6       W10-4 3 -28.11367 0.4713240 0.27211905          3     16.921348
##   ngC.SD.diss
## 1   1.9211688
## 2   2.5407658
## 3   4.3931602
## 4  28.9991771
## 5   1.0603010
## 6   0.2430709
```

```
isoFiltSummary = ddply(filtersIso, c("WeekSubWeek"), summarise,
                       N    = length(d.13C.12C),
                       filt.d13C = mean(d.13C.12C),
                       filt.SD.d13C = sd(d.13C.12C),
                       filt.se.d13C = filt.SD.d13C / sqrt(N),
                       N_ngC.fl = length(ngC),
                       ngC.mean.fl = mean(ngC),
                       ngC.SD.fl = sd(ngC))
head(isoFiltSummary)
```

```
##   WeekSubWeek N filt.d13C filt.SD.d13C filt.se.d13C N_ngC.fl ngC.mean.fl
## 1        W2-1 3 -27.20800     1.779464    1.0273738        3   0.7964602
## 2        W2-2 3 -27.64867     2.575326    1.4868653        3   0.7079646
## 3        W6-3 3 -28.00667     1.593462    0.9199856        3   1.0619469
## 4        W9-1 2 -26.79150     1.745847    1.2345000        2   4.1783217
## 5        W9-2 3 -27.69633     2.013989    1.1627772        3   5.5594406
## 6        W9-3 3 -26.94633     1.685361    0.9730434        3   3.7645688
##    ngC.SD.fl
## 1 0.05747956
## 2 0.03831971
## 3 0.03318584
## 4 0.56865231
## 5 0.54280331
## 6 0.51189257
```

Merging and data wrangling stepts

1. Merge all data sets by the *WeekSubWeek* column ID, icluding:

```
# Dissolved
out.CoIs = merge(outletConc,  outletESAOXA, by = "WeekSubWeek", all = T)
out.CoIs = merge(out.CoIs, isoOutSummary, by = "WeekSubWeek", all = T)

# Filters (MES, Conc.MES)
out.CoIs = merge(out.CoIs, filters, by = "WeekSubWeek", all = T)
out.CoIs = merge(out.CoIs, isoFiltSummary, by= "WeekSubWeek", all = T)

# Pure and cuve isotope average
d13Co = -31.21
```

```
# Lab enrichment:
# epsilon = -1.61

# Lab enrichment:
# Alteck
epsilon_max = -1.5 # +/- 0.3 (@ 20C, 20% vwc)
epsilon_min = -2.0 # +/- 0.2 (@ 20C, 40% vwc)
epsilon_mean = -1.75

# Remaining fraction
out.CoIs$DD13C.diss <- (out.CoIs$diss.d13C - (d13Co))
out.CoIs$DD13C.filt <- (out.CoIs$filt.d13C - (d13Co))

out.CoIs$f.diss <- (((10**(-3)*out.CoIs$diss.d13C + 1)/(10**(-3)*d13Co + 1))**(1000/(epsilon_mean)))
out.CoIs$f.filt <- (((10**(-3)*out.CoIs$filt.d13C + 1)/(10**(-3)*d13Co + 1))**(1000/(epsilon_mean)))

out.CoIs$B.diss <- (1 - out.CoIs$f.diss)*100
out.CoIs$B.filt <- (1 - out.CoIs$f.filt)*100
#out.CoIs$invf <- 1/out.CoIs$f

# Discharge times
out.CoIs = merge(weeklyhydro, out.CoIs, by = "WeekSubWeek", all = T)

# Discharge summary
out.CoIs = merge(weeklyflux, out.CoIs, by = "WeekSubWeek", all = T)

# Hydrochemistrty
out.CoIs = merge(out.CoIs, hydroChem, by= "WeekSubWeek", all = T)


out.CoIs$tf <- as.POSIXct(out.CoIs$tf, "%Y-%m-%d %H:%M", tz = "EST")
out.CoIs$ti <- as.POSIXct(out.CoIs$ti, "%Y-%m-%d %H:%M", tz = "EST")
class(out.CoIs$tf)
```

```
## [1] "POSIXct" "POSIXt"
```

```
sum(is.na(out.CoIs$tf))
```

```
## [1] 7
```

```
# Temprarily remove Weeks 16 & 17 (need to get discharge data)
# No discharge data yet avaialble to multiply against...
out.CoIs <- out.CoIs[!is.na(out.CoIs$tf), ]
```

2. Weekly Exported Solids (Kg)

```
# V[m3] * MES [mg/L] * 1000 [L/m3] * [1 Kg/10^6 mg]
out.CoIs$ExpMES.Kg = out.CoIs$Volume.m3*out.CoIs$MES.mg.L/1000
```

Fork! Prepare Data for C-Q Hysteresis curves

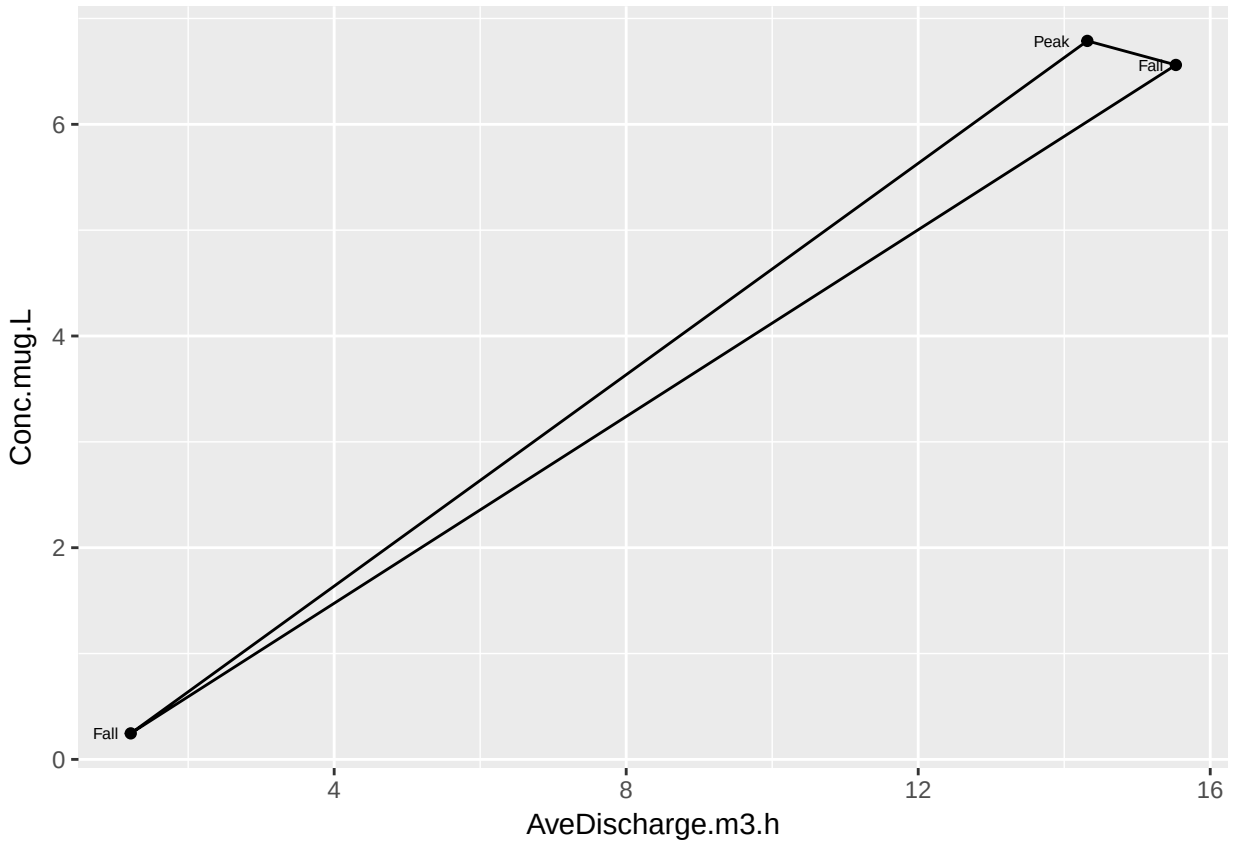
```
CQdata <- out.CoIs[with(out.CoIs, order(ti)), ]
CQdata$FlowType <- ifelse(is.na(CQdata$Event), "Fall", "Peak")
CQdata$Event[1:3]<- 0
```

```r
CQdata$EventMark <- NA

CQdata$EventMark <- na.locf(CQdata$Event)

CQdata$EventMark <- ifelse(is.na(CQdata$Event), CQdata$EventMark, CQdata$EventMark*10)
CQdata$Row <- seq.int(nrow(CQdata))

cq1 <- subset(CQdata[1:6, ])

cq1 <- cq1[cq1$Sampled != 'Not Sampled', ]

str(cq1)
```

```
## 'data.frame':    3 obs. of  60 variables:
##  $ WeekSubWeek           : Factor w/ 58 levels "W0-0x","W0-1",..: 2 4 5
##  $ ti                    : POSIXct, format: "2016-03-25 12:04:00" "2016-03-30 12:18:00" ...
##  $ tf                    : POSIXct, format: "2016-03-28 22:36:00" "2016-03-31 15:34:00" ...
##  $ iflux                 : num  1.12 1.46 16.33
##  $ fflux                 : num  1.31 16.45 15.18
##  $ changeflux            : num  0.189 14.989 -1.15
##  $ maxQ                  : num  1.38 38.4 18.67
##  $ minQ                  : num  1.08 1.45 13.2
##  $ Duration.Hrs          : num  82.5 27.3 23.1
##  $ chExtreme             : num  0.256 36.944 -3.133
##  $ Event                 : num  0 1 NA
##  $ Markers               : num  NA 16.9 NA
##  $ TimeDiff              : Factor w/ 18 levels "106","136","150",..: NA 10 NA
##  $ AveDischarge.m3.h     : num  1.21 14.32 15.53
##  $ Volume.m3             : num  100 390 359
##  $ Sampled.Hrs           : num  82.5 27.3 23.1
##  $ Sampled               : Factor w/ 2 levels "Not Sampled",..: 2 2 2
##  $ Conc.mug.L            : num  0.246 6.788 6.561
##  $ Conc.SD               : num  0.0193 0.2894 0.1906
##  $ OXA_mean              : num  4.82 30.53 32.49
##  $ OXA_SD                : num  1.141 10.185 0.243
##  $ ESA_mean              : num  18.1 46 41.3
##  $ ESA_SD                : num  3.497 3.037 0.853
##  $ N.x                   : int  NA 3 3
##  $ diss.d13C             : num  NA -30.5 -30.6
##  $ SD.d13C               : num  NA 0.106 0.151
##  $ se.d13C               : num  NA 0.0612 0.0874
##  $ N_ngC.diss            : int  NA 3 3
##  $ ngC.mean.diss         : num  NA 42.7 54.7
##  $ ngC.SD.diss           : num  NA 1.92 2.54
##  $ MES.mg.L              : num  53.4 62.5 22.5
##  $ MES.sd                : num  NA NA NA
##  $ MO.mg.L               : num  0e+00 1e-03 1e-04
##  $ Conc.Solids.mug.gMES  : num  0.645 0.126 0.436
##  $ Conc.Solids.ug.gMES.SD: num  0.0232 0.0271 0.1232
##  $ N.y                   : int  NA NA NA
##  $ filt.d13C             : num  NA NA NA
##  $ filt.SD.d13C          : num  NA NA NA
##  $ filt.se.d13C          : num  NA NA NA
##  $ N_ngC.fl              : int  NA NA NA
```

```
##  $ ngC.mean.fl           : num  NA NA NA
##  $ ngC.SD.fl             : num  NA NA NA
##  $ DD13C.diss            : num  NA 0.741 0.59
##  $ DD13C.filt            : num  NA NA NA
##  $ f.diss                : num  NA 0.646 0.706
##  $ f.filt                : num  NA NA NA
##  $ B.diss                : num  NA 35.4 29.4
##  $ B.filt                : num  NA NA NA
##  $ NH4.mM                : num  NA 0.05 NA
##  $ TIC.ppm.filt          : num  NA 51.8 44.8
##  $ Cl.mM                 : num  NA 1.48 1574
##  $ NO3...mM              : num  NA 616 778
##  $ PO4..mM               : int  NA NA NA
##  $ NPOC.ppm              : num  NA 4 4.4
##  $ TIC.ppm.unfilt        : num  NA 44.8 26.4
##  $ TOC.ppm.unfilt        : num  NA 4.7 5.4
##  $ ExpMES.Kg             : num  5.35 24.4 8.08
##  $ FlowType              : chr  "Fall" "Peak" "Fall"
##  $ EventMark             : num  0 10 1
##  $ Row                   : int  2 4 5
```

```
p <- ggplot(cq1) +
  geom_point(aes(x=AveDischarge.m3.h, y=Conc.mug.L), colour="black") +
  geom_polygon(aes(x=AveDischarge.m3.h, y=Conc.mug.L), colour="black", fill = NA) +

  geom_text(data = cq1,
            aes(x=AveDischarge.m3.h, y=Conc.mug.L, label=FlowType), hjust=1.5, vjust=0.5, size = 2)
p
```




```
#p <- ggplotly(p)
#p
```

Section to UPDATE!!!

3. Weekly exported S-metolachlor mass (mg)

This section converts the observed S-metolachlor concentrations to [mg] in dissolved water and suspended solids. For non-sampled subsets a linear interpolation value based on the trailing and leading observed concentrations was assumed. An approximative model will be tested at a later stage.

To revise: SD for filtered samples!!

```
# Assume first observation is equivalent to second for all measured values
out.CoIs[1, c("Conc.mug.L")] <- out.CoIs[2, c("Conc.mug.L")]
out.CoIs[1, c("Conc.SD")] <- out.CoIs[2, c("Conc.SD")]

out.CoIs[1, c("OXA_mean")] <- out.CoIs[2, c("OXA_mean")]
out.CoIs[1, c("OXA_SD")] <- out.CoIs[2, c("OXA_SD")]

out.CoIs[1, c("ESA_mean")] <- out.CoIs[2, c("ESA_mean")]
out.CoIs[1, c("ESA_SD")] <- out.CoIs[2, c("ESA_SD")]

out.CoIs[1, c("Conc.Solids.mug.gMES")] <- out.CoIs[2, c("Conc.Solids.mug.gMES")]
out.CoIs[1, c("Conc.Solids.ug.gMES.SD")] <- out.CoIs[2, c("Conc.Solids.ug.gMES.SD")]

out.CoIs[1, c("ExpMES.Kg")] <- out.CoIs[2, c("ExpMES.Kg")]
```

```
# Assign linear approximation of trailing and leading observed values
out.CoIs <- out.CoIs[with(out.CoIs , order(ti)), ]

out.CoIs$Conc.mug.L <- na.approx(out.CoIs$Conc.mug.L)
out.CoIs$Conc.SD <- na.approx(out.CoIs$Conc.SD)

out.CoIs$OXA_mean <- na.approx(out.CoIs$OXA_mean)
out.CoIs$OXA_SD <- na.approx(out.CoIs$OXA_SD)

out.CoIs$ESA_mean <- na.approx(out.CoIs$ESA_mean)
out.CoIs$ESA_SD <- na.approx(out.CoIs$ESA_SD)

out.CoIs$Conc.Solids.mug.gMES <- na.approx(out.CoIs$Conc.Solids.mug.gMES)
out.CoIs$Conc.Solids.ug.gMES.SD <- na.approx(out.CoIs$Conc.Solids.ug.gMES.SD)

out.CoIs$ExpMES.Kg <- na.approx(out.CoIs$ExpMES.Kg)
```

4. Add the application dates and merge the total mass to the nearest discharge event

The five application dates were:

- 2016-03-20
- 2016-04-05
- 2016-04-13 and 2016-04-14
- 2016-05-26

So the total applied mass mass is merged at the nearest sampling time marker available :

```
ti = c(as.POSIXct('2016-03-25 00:04:00' , tz="EST"),
#       as.POSIXct('2016-04-05 15:08:00' , tz="EST"),
       as.POSIXct('2016-04-14 13:52:00' , tz="EST"),
       as.POSIXct('2016-05-10 00:06:00' , tz="EST"))

Appl.Mass.g = c(9497.87, 4744.571, 4982.038)

applics = as.data.frame(ti)
applics$Appl.Mass.g = Appl.Mass.g

out.CoIs = merge(out.CoIs, applics, by = "ti", all = T)
out.CoIs$Appl.Mass.g <- ifelse(is.na(out.CoIs$Appl.Mass.g), 0.0, out.CoIs$Appl.Mass.g)

out.CoIs$timeSinceApp <- NA
for (i in 1:length(out.CoIs$Duration.Hrs)){
  if (out.CoIs[i, ]['Appl.Mass.g'] != 0){
    out.CoIs[i,]['timeSinceApp'] = out.CoIs[i, ]['Duration.Hrs']
  } else {
    out.CoIs[i, ]['timeSinceApp'] = out.CoIs[i ,]['Duration.Hrs'] + out.CoIs[i-1,]['timeSinceApp']
  }
}

out.CoIs$timeSinceApp <- round(out.CoIs$timeSinceApp/24, 1)

# Cumulative (Continous)
out.CoIs$CumAppMass.g = cumsum(out.CoIs$Appl.Mass.g)
```

Section to UPDATE!!!

5. This section is based on approximate carried-last-observation for the observed concentration data (if no model has been conducted yet).

```
# First simulate a mass out to deal with missing values
# Option 1, just assume 0.0

# Dissolved - [mg] S-metolachlor exported per sub-week
# Conc. [mu.g s-meto/L H20] * Vol[m3] * [10^3 L/m^3] * [1 mg/10^3 mu.g]
out.CoIs$DissSmeto.mg = out.CoIs$Conc.mug.L*out.CoIs$Volume.m3
out.CoIs$DissSmeto.mg.SD = out.CoIs$Conc.SD*out.CoIs$Volume.m3
out.CoIs$DissSmeto.g = out.CoIs$DissSmeto.mg/10^3
out.CoIs$DissSmeto.g.SD = out.CoIs$DissSmeto.mg.SD/10^3

out.CoIs$DissOXA.mg = out.CoIs$OXA_mean*out.CoIs$Volume.m3
out.CoIs$DissOXA.mg.SD = out.CoIs$OXA_SD*out.CoIs$Volume.m3
out.CoIs$DissOXA.g = out.CoIs$DissOXA.mg/10^3
out.CoIs$DissOXA.g.SD = out.CoIs$DissOXA.mg.SD/10^3

out.CoIs$DissESA.mg = out.CoIs$ESA_mean*out.CoIs$Volume.m3
out.CoIs$DissESA.mg.SD = out.CoIs$ESA_SD*out.CoIs$Volume.m3
out.CoIs$DissESA.g = out.CoIs$DissESA.mg/10^3
out.CoIs$DissESA.g.SD = out.CoIs$DissESA.mg.SD/10^3

# Solids - [mg] S-metolachlor in solids exported per sub-week
# Conc. [mu.g s-meto / g MES] * Kg MES * [10^3 g/Kg] * [1 mg/10^3 mu.g]
out.CoIs$FiltSmeto.mg = out.CoIs$Conc.Solids.mug.gMES*out.CoIs$ExpMES.Kg
out.CoIs$FiltSmeto.mg.SD = out.CoIs$Conc.Solids.ug.gMES.SD*out.CoIs$ExpMES.Kg
out.CoIs$FiltSmeto.g = out.CoIs$FiltSmeto.mg/10^3
out.CoIs$FiltSmeto.g.SD  = out.CoIs$FiltSmeto.mg.SD/10^3

# Total SM
out.CoIs$TotSMout.mg = out.CoIs$DissSmeto.mg + out.CoIs$FiltSmeto.mg
out.CoIs$TotSMout.mg.SD = sqrt(((out.CoIs$DissSmeto.mg.SD)^2 + (out.CoIs$FiltSmeto.mg.SD)^2)/2)
out.CoIs$TotSMout.g = out.CoIs$TotSMout.mg/10^3
out.CoIs$TotSMout.g.SD = out.CoIs$TotSMout.mg.SD/10^3

# Distribution dissolved vs suspended solids
out.CoIs$FracDiss = out.CoIs$DissSmeto.mg/out.CoIs$TotSMout.mg
out.CoIs$FracFilt = out.CoIs$FiltSmeto.mg/out.CoIs$TotSMout.mg

#out.CoIs$DissSmeto.g = ifelse(is.na(out.CoIs$DissSmeto.g), 0.0, out.CoIs$DissSmeto.g)
#out.CoIs$FiltSmeto.g = ifelse(is.na(out.CoIs$FiltSmeto.g), 0.0, out.CoIs$FiltSmeto.g)
#out.CoIs$TotSMout.g = out.CoIs$DissSmeto.g + out.CoIs$FiltSmeto.g

# Need to update this :
# out.CoIs$TotSMout.g.SD = out.CoIs$DissSmeto.g.SD

mw.SM <- 283.796 # g/mol
mw.MOXA <- 279.33 # g/ml
mw.MESA <- 329.1 # g/mol
out.CoIs$MELsm.g <-
  out.CoIs$TotSMout.g +
```

```
  out.CoIs$DissOXA.g * (mw.SM/mw.MOXA) +
  out.CoIs$DissESA.g * (mw.SM/mw.MESA)

# How to sum a standard deviation
# http://stats.stackexchange.com/questions/25848/how-to-sum-a-standard-deviation
out.CoIs$MELsm.g.SD <-
  sqrt((out.CoIs$TotSMout.g.SD^2 +
     (out.CoIs$DissOXA.g.SD * (mw.SM/mw.MOXA))^2 +
     (out.CoIs$DissESA.g.SD * (mw.SM/mw.MESA))^2)/3)

# Cumulative OUT
out.CoIs$CumOutDiss.g = cumsum(out.CoIs$DissSmeto.g)
out.CoIs$CumOutFilt.g = cumsum(out.CoIs$FiltSmeto.g)
out.CoIs$CumOutSmeto.g = out.CoIs$CumOutDiss.g + out.CoIs$CumOutFilt.g
out.CoIs$CumOutMELsm.g = cumsum(out.CoIs$MELsm.g)

# Balance
out.CoIs$BalMassDisch.g = out.CoIs$CumAppMass.g - out.CoIs$CumOutMELsm.g

# Mass fraction
massOUT = tail(out.CoIs$CumOutSmeto.g, n=1)
MELsmOUT = tail(out.CoIs$CumOutMELsm.g, n=1)

TotAppl = tail(out.CoIs$CumAppMass.g, n=1)

out.CoIs$prctMassOut = (out.CoIs$TotSMout.g / massOUT)
out.CoIs$FracDeltaOut = (out.CoIs$TotSMout.g / massOUT)*out.CoIs$diss.d13C
out.CoIs$FracDeltaOut = ifelse(is.na(out.CoIs$FracDeltaOut), 0.0, out.CoIs$FracDeltaOut)

BulkDeltaOut = sum(out.CoIs$FracDeltaOut)
```

The total mass discharged (up to Week 15) and bulk isotope signature (up to week 11) was:

```
# Cummulative S-metolachlor [g] discharged (before correction)
cat("SM mass sampled: " , as.character(91.10687))
```

```
## SM mass sampled:  91.10687
```

```
# Cummulative S-metolachlor [g] discharged
cat("SM mass sampled and non-sampled: ",  as.character(massOUT))
```

```
## SM mass sampled and non-sampled:  140.392784355072
```

```
# Cummulative MEL-sm [g] discharged
cat("MEL-sm [g] sampled and non-sampled: ",  as.character(MELsmOUT))
```

```
## MEL-sm [g] sampled and non-sampled:  3096.82107110135
```

```
cat("% Mass applied in discahrge [MEL-sm]: ",  (MELsmOUT/TotAppl)*100)
```

```
## % Mass applied in discahrge [MEL-sm]:  16.10874
```

```
# Bulk isotope signature
BulkDeltaOut
```

```
## [1] -18.32412
```

6. Testing a regression tree (ommitted for now)

Save files

```
names(out.CoIs)[names(out.CoIs) == "Event"] <- "Peak"

out.CoIs$Events <- as.factor(c("0-1", "0-2", "0-3",
                          "1-1", "1-2", "1-3",
                          "2-1", "2-2", "2-3",
                          "3-1",
                          "4-1", "4-2", "4-3", "4-4", "4-5",
                          "5-1",
                          "6-1", "6-2", "6-3",
                          "7-1",
                          "8-1", "8-2", "8-3",
                          "9-1", "9-2", "9-3", "9-4", "9-5",
                          "10-1", "10-2", "10-3", "10-4", "10-5",
                          "11-1",
                          "12-1", "12-2", "12-3",
                          "13-1",
                          "14-1",
                          "15-1", "15-2", "15-3", "15-4",
                          "16-1", "16-2",
                          "17-1", "17-2",
                          "18-1", "18-2", "18-3", "18-4"))

# Adding a Weeks column for labelling
out.CoIs$WeekSubWeek <- as.character(out.CoIs$WeekSubWeek)
Split <- strsplit(out.CoIs$WeekSubWeek, "-", fixed = TRUE)
out.CoIs$Weeks <- sapply(Split, "[", 1)

Split2 <- strsplit(as.character(out.CoIs$Events), "-", fixed = T)
out.CoIs$Event <- as.factor(sapply(Split2, "[", 1))

out.CoIs$WeekSubWeek <- factor(out.CoIs$WeekSubWeek, levels = unique(out.CoIs$WeekSubWeek))
out.CoIs$Weeks <- factor(out.CoIs$Weeks, levels = unique(out.CoIs$Weeks))

out.CoIs$Events <- factor(out.CoIs$Events, levels = unique(out.CoIs$Events))
out.CoIs$Event <- factor(out.CoIs$Event, levels = unique(out.CoIs$Event))

head(out.CoIs)
```

```
##                    ti WeekSubWeek                  tf     iflux     fflux
## 1 2016-03-25 00:04:00       W0-0x 2016-03-25 12:02:00  1.248600  1.129227
## 2 2016-03-25 12:04:00        W0-1 2016-03-28 22:36:00  1.124382  1.313125
## 3 2016-03-28 22:38:00       W0-2x 2016-03-30 12:16:00  1.308100  1.456349
## 4 2016-03-30 12:18:00        W1-1 2016-03-31 15:34:00  1.456080 16.445436
## 5 2016-03-31 15:36:00        W1-2 2016-04-01 14:44:00 16.334349 15.184536
## 6 2016-04-01 14:46:00       W1-3x 2016-04-05 15:06:00 15.203629  5.856380
##   changeflux      maxQ      minQ Duration.Hrs  chExtreme Peak  Markers
## 1 -0.1193728  1.248600  1.118296     11.96667 -0.1303036   NA       NA
## 2  0.1887431  1.380388  1.082199     82.53333  0.2560062   NA       NA
## 3  0.1482496  1.637782  0.929055     37.63333  0.3296817   NA       NA
## 4 14.9893566 38.399790  1.448977     27.26667 36.9437102    1 16.88972
## 5 -1.1498131 18.668972 13.201113     23.13333 -3.1332355   NA       NA
## 6 -9.3472489 15.895640  5.471042     96.33333 -9.7325862   NA       NA
```

```
##   TimeDiff AveDischarge.m3.h Volume.m3 Sampled.Hrs     Sampled Conc.mug.L
## 1     <NA>          1.204775  14.41714    11.96667 Not Sampled  0.2456594
## 2     <NA>          1.213511 100.15508    82.53333     Sampled  0.2456594
## 3     <NA>          1.284719  48.34827    37.63333 Not Sampled  3.5169528
## 4       24         14.316647 390.36726    27.26667     Sampled  6.7882463
## 5     <NA>         15.529299 359.24445    23.13333     Sampled  6.5609982
## 6     <NA>          9.107720 877.37700    96.33333 Not Sampled  8.0026500
##    Conc.SD  OXA_mean     OXA_SD ESA_mean   ESA_SD N.x diss.d13C   SD.d13C
## 1 0.019310  4.824094  1.1414453 18.05531 3.497221  NA        NA        NA
## 2 0.019310  4.824094  1.1414453 18.05531 3.497221  NA        NA        NA
## 3 0.154365 17.677665  5.6633481 32.01948 3.267103  NA        NA        NA
## 4 0.289420 30.531235 10.1852510 45.98364 3.036985   3 -30.46867 0.1060016
## 5 0.190640 32.492465  0.2430544 41.28052 0.853382   3 -30.61967 0.1513550
## 6 0.262090 68.516860  0.6978517 69.92417 1.839787  NA        NA        NA
##      se.d13C N_ngC.diss ngC.mean.diss ngC.SD.diss MES.mg.L MES.sd MO.mg.L
## 1         NA         NA            NA          NA       NA     NA      NA
## 2         NA         NA            NA          NA 53.44444     NA   0e+00
## 3         NA         NA            NA          NA       NA     NA      NA
## 4 0.06120004          3      42.69231    1.921169 62.50000     NA   1e-03
## 5 0.08738484          3      54.69697    2.540766 22.50000     NA   1e-04
## 6         NA         NA            NA          NA       NA     NA      NA
##   Conc.Solids.mug.gMES Conc.Solids.ug.gMES.SD N.y filt.d13C filt.SD.d13C
## 1            0.6447290             0.02323755  NA        NA          NA
## 2            0.6447290             0.02323755  NA        NA          NA
## 3            0.3853094             0.02515062  NA        NA          NA
## 4            0.1258897             0.02706369  NA        NA          NA
## 5            0.4357872             0.12323706  NA        NA          NA
## 6            0.2575699             0.06396039  NA        NA          NA
##   filt.se.d13C N_ngC.fl ngC.mean.fl ngC.SD.fl DD13C.diss DD13C.filt
## 1           NA       NA          NA        NA         NA         NA
## 2           NA       NA          NA        NA         NA         NA
## 3           NA       NA          NA        NA         NA         NA
## 4           NA       NA          NA        NA  0.7413333         NA
## 5           NA       NA          NA        NA  0.5903333         NA
## 6           NA       NA          NA        NA         NA         NA
##      f.diss f.filt   B.diss B.filt NH4.mM TIC.ppm.filt   Cl.mM NO3...mM
## 1        NA     NA       NA     NA     NA           NA      NA       NA
## 2        NA     NA       NA     NA     NA           NA      NA       NA
## 3        NA     NA       NA     NA     NA           NA      NA       NA
## 4 0.6459075     NA 35.40925     NA   0.05         51.8    1.48      616
## 5 0.7060321     NA 29.39679     NA     NA         44.8 1574.00      778
## 6        NA     NA       NA     NA     NA           NA      NA       NA
##   PO4..mM NPOC.ppm TIC.ppm.unfilt TOC.ppm.unfilt ExpMES.Kg Appl.Mass.g
## 1      NA       NA             NA             NA  5.352733     9497.87
## 2      NA       NA             NA             NA  5.352733        0.00
## 3      NA       NA             NA             NA 14.875343        0.00
## 4      NA      4.0           44.8            4.7 24.397953        0.00
## 5      NA      4.4           26.4            5.4  8.083000        0.00
## 6      NA       NA             NA             NA  7.935755        0.00
##   timeSinceApp CumAppMass.g DissSmeto.mg DissSmeto.mg.SD DissSmeto.g
## 1          0.5      9497.87     3.541705       0.2783949 0.003541705
## 2          3.9      9497.87    24.604033       1.9339946 0.024604033
## 3          5.5      9497.87   170.038598       7.4632812 0.170038598
## 4          6.6      9497.87  2649.909084     112.9800910 2.649909084
```

```
## 5          7.6      9497.87  2357.002211      68.4863626 2.357002211
## 6         11.6      9497.87  7021.341115     229.9517390 7.021341115
##   DissSmeto.g.SD  DissOXA.mg DissOXA.mg.SD   DissOXA.g DissOXA.g.SD
## 1   0.0002783949    69.54963      16.45637  0.06954963   0.01645637
## 2   0.0019339946   483.15756     114.32155  0.48315756   0.11432155
## 3   0.0074632812   854.68456     273.81310  0.85468456   0.27381310
## 4   0.1129800910 11918.39439    3975.98846 11.91839439   3.97598846
## 5   0.0684863626 11672.73795      87.31596 11.67273795   0.08731596
## 6   0.2299517390 60115.11746     612.27900 60.11511746   0.61227900
##   DissESA.mg DissESA.mg.SD  DissESA.g DissESA.g.SD FiltSmeto.mg
## 1   260.3058      50.41991  0.2603058   0.05041991     3.451062
## 2  1808.3308     350.26441  1.8083308   0.35026441     3.451062
## 3  1548.0863     157.95877  1.5480863   0.15795877     5.731609
## 4 17950.5083    1185.53932 17.9505083   1.18553932     3.071452
## 5 14829.7964     306.57276 14.8297964   0.30657276     3.522468
## 6 61349.8588    1614.18699 61.3498588   1.61418699     2.044012
##   FiltSmeto.mg.SD FiltSmeto.g FiltSmeto.g.SD TotSMout.mg TotSMout.mg.SD
## 1       0.1243844 0.003451062   0.0001243844    6.992766      0.2156098
## 2       0.1243844 0.003451062   0.0001243844   28.055095      1.3703661
## 3       0.3741240 0.005731609   0.0003741240  175.770206      5.2839633
## 4       0.6602985 0.003071452   0.0006602985 2652.980536     79.8903528
## 5       0.9961252 0.003522468   0.0009961252 2360.524679     48.4322936
## 6       0.5075740 0.002044012   0.0005075740 7023.385126    162.6008301
##    TotSMout.g TotSMout.g.SD  FracDiss     FracFilt     MELsm.g MELsm.g.SD
## 1 0.006992766  0.0002156098 0.5064812 0.4935188249   0.3021264 0.02689497
## 2 0.028055095  0.0013703661 0.8769898 0.1230101642   2.0783329 0.18683762
## 3 0.175770206  0.0052839633 0.9673915 0.0326085349   2.3790960 0.17885971
## 4 2.652980536  0.0798903528 0.9988423 0.0011577363  30.2413655 2.40621294
## 5 2.360524679  0.0484322936 0.9985078 0.0014922393  27.0082117 0.16340841
## 6 7.023385126  0.1626008301 0.9997090 0.0002910294 121.0040582 0.88525127
##   CumOutDiss.g CumOutFilt.g CumOutSmeto.g CumOutMELsm.g BalMassDisch.g
## 1  0.003541705  0.003451062   0.006992766     0.3021264       9497.568
## 2  0.028145738  0.006902124   0.035047862     2.3804594       9495.490
## 3  0.198184336  0.012633733   0.210818068     4.7595554       9493.110
## 4  2.848093419  0.015705185   2.863798604    35.0009209       9462.869
## 5  5.205095630  0.019227652   5.224323282    62.0091326       9435.861
## 6 12.226436745  0.021271664  12.247708409   183.0131909       9314.857
##    prctMassOut FracDeltaOut Events Weeks Event
## 1 4.980859e-05    0.0000000    0-1    W0     0
## 2 1.998329e-04    0.0000000    0-2    W0     0
## 3 1.251989e-03    0.0000000    0-3    W0     0
## 4 1.889684e-02   -0.5757616    1-1    W1     1
## 5 1.681372e-02   -0.5148304    1-2    W1     1
## 6 5.002668e-02    0.0000000    1-3    W1     1
```

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

# out.CoIs = read.csv2("Data/WeeklyHydroContam_R.csv")
# out.CoIs$ti = as.POSIXct(out.CoIs$ti, "%Y-%m-%d %H:%M", tz = "EST")
```