

Mass Discharge - Outlet Alteck. 2016

PAZ

27 octobre 2016

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      dryHrs Duration.Hrs  chExtreme Event
## 1 -0.1193728  1.248600  1.118296  0.01666667    11.96667 -0.1303036    NA
## 2  0.1887431  1.380388  1.082199  6.01666667    82.53333  0.2560062    NA
## 3  0.1482496  1.637782  0.929055 47.30000000    37.63333  0.3296817    NA
## 4 14.9893566 38.399790  1.448977 66.13333333    27.26667 36.9437102     1
## 5 -1.1498131 18.668972 13.201113  1.65000000    23.13333 -3.1332355    NA
## 6 -9.3472489 15.895640  5.471042  6.26666667    96.33333 -9.7325862    NA
##   Markers TimeDiff
## 1      NA    <NA>
## 2      NA    <NA>
## 3      NA    <NA>
## 4 16.88972     24
## 5      NA    <NA>
## 6      NA    <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$M0.mg.L = ifelse(filters$M0.mg.L < 0, 0.0001, filters$M0.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:

- The isotope shift was not largely beyond (2x) Streitwieser theoretical limits (i.e. > 10)
- Isotope shift was non-negative
- 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      AQ_W2_2-1_.dxf AQ  W2  2      2      W2-2      1  -28.609
## 2      AQ_W2_2-2_.dxf AQ  W2  2      2      W2-2      2  -28.894
## 3      AQ_W2_2-3_.dxf AQ  W2  2      2      W2-2      3  -28.503
## 4     AQ_W3_1-1_-0001.dxf AQ  W3  3      1      W3-1      1  -29.838
## 5     AQ_W3_1-2_-0001.dxf AQ  W3  3      1      W3-1      2  -29.840
## 6     AQ_W3_1-3_-0001.dxf AQ  W3  3      1      W3-1      3  -30.073
##   DD13...31.21. Ave...STDEV      Rt Ampl...44 Std.Ampl.      ng..C. no.ng10
## 1      2.601  0.2022136 2656.2      127      658  5.790274      0
## 2      2.316      NA 2656.2      163      658  7.431611      0
## 3      2.707      NA 2655.3      176      658  8.024316      0
## 4      1.372  0.1351037 2648.9      914      858 31.958042      1
## 5      1.370      NA 2649.3      905      858 31.643357      1
## 6      1.137      NA 2649.5      941      858 32.902098      1
```

```
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$Levl != "J+7", ]
if (length(filtersIso) == 1){
  filtersIso = read.csv("Data/MESAlteck_FilterIsotopes.csv", header = T)
}
filtersIso$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 Lev1 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/A0-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 = ddpIy(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 steps

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

```
# 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

# Temporarily remove Weeks 16 & 17 (need to get discharge data)
# No discharge data yet avaiable 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/106 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

```

```

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  61 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
##  $ dryHrs            : num  6.02 66.13 1.65
##  $ 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

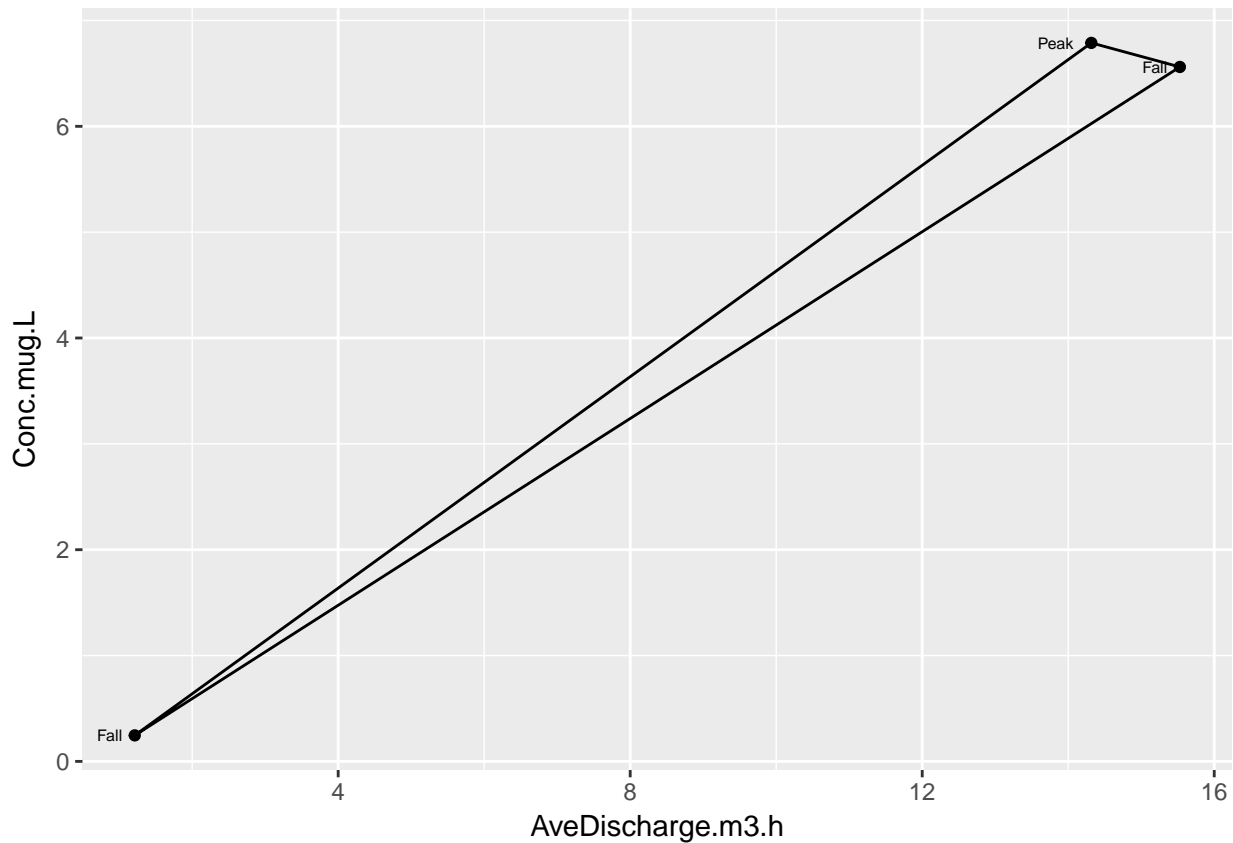
```



```
## $ 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 (Continuous)
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. [ $\mu\text{g s-meto/L H}_2\text{O}$ ] * Vol[m3] * [ $10^3 \text{ L/m}^3$ ] * [ $1 \text{ mg}/10^3 \mu\text{g}$ ]
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. [ $\mu\text{g s-meto} / \text{g MES}$ ] * Kg MES * [ $10^3 \text{ g/Kg}$ ] * [ $1 \text{ mg}/10^3 \mu\text{g}$ ]
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:

```

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

## SM mass sampled: 91.10687

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

## SM mass sampled and non-sampled: 140.392784355072

# Cumulative 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 discharge [MEL-sm]: ", (MELsmOUT/TotAppl)*100)

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

# Bulk isotope signature
BulkDeltaOut

## [1] -18.39794

```

6. Testing a regression tree (omitted 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      dryHrs Duration.Hrs  chExtreme Peak
## 1 -0.1193728  1.248600  1.118296  0.01666667    11.96667 -0.1303036   NA
## 2  0.1887431  1.380388  1.082199  6.01666667    82.53333  0.2560062   NA
## 3  0.1482496  1.637782  0.929055 47.30000000    37.63333  0.3296817   NA
## 4 14.9893566 38.399790  1.448977 66.13333333    27.26667 36.9437102    1
## 5 -1.1498131 18.668972 13.201113  1.65000000    23.13333 -3.1332355   NA
## 6 -9.3472489 15.895640  5.471042  6.26666667    96.33333 -9.7325862   NA
```

| ## | Markers | TimeDiff | AveDischarge.m3.h | Volume.m3 | Sampled.Hrs | Sampled | | |
|------|--------------|--------------|----------------------|---------------------|-----------------|---------------|--------------|-----------|
| ## 1 | NA | <NA> | 1.204775 | 14.41714 | 11.96667 | Not Sampled | | |
| ## 2 | NA | <NA> | 1.213511 | 100.15508 | 82.53333 | Sampled | | |
| ## 3 | NA | <NA> | 1.284719 | 48.34827 | 37.63333 | Not Sampled | | |
| ## 4 | 16.88972 | 24 | 14.316647 | 390.36726 | 27.26667 | Sampled | | |
| ## 5 | NA | <NA> | 15.529299 | 359.24445 | 23.13333 | Sampled | | |
| ## 6 | NA | <NA> | 9.107720 | 877.37700 | 96.33333 | Not Sampled | | |
| ## | Conc.mug.L | Conc.SD | OXA_mean | OXA_SD | ESA_mean | ESA_SD | N.x | diss.d13C |
| ## 1 | 0.2456594 | 0.019310 | 4.824094 | 1.1414453 | 18.05531 | 3.497221 | NA | NA |
| ## 2 | 0.2456594 | 0.019310 | 4.824094 | 1.1414453 | 18.05531 | 3.497221 | NA | NA |
| ## 3 | 3.5169528 | 0.154365 | 17.677665 | 5.6633481 | 32.01948 | 3.267103 | NA | NA |
| ## 4 | 6.7882463 | 0.289420 | 30.531235 | 10.1852510 | 45.98364 | 3.036985 | 3 | -30.46867 |
| ## 5 | 6.5609982 | 0.190640 | 32.492465 | 0.2430544 | 41.28052 | 0.853382 | 3 | -30.61967 |
| ## 6 | 8.0026500 | 0.262090 | 68.516860 | 0.6978517 | 69.92417 | 1.839787 | NA | NA |
| ## | SD.d13C | se.d13C | N_ngC.diss | ngC.mean.diss | ngC.SD.diss | MES.mg.L | | |
| ## 1 | NA | NA | NA | NA | NA | NA | | |
| ## 2 | NA | NA | NA | NA | NA | 53.44444 | | |
| ## 3 | NA | NA | NA | NA | NA | NA | | |
| ## 4 | 0.1060016 | 0.06120004 | 3 | 42.69231 | 1.921169 | 62.50000 | | |
| ## 5 | 0.1513550 | 0.08738484 | 3 | 54.69697 | 2.540766 | 22.50000 | | |
| ## 6 | NA | NA | NA | NA | NA | NA | | |
| ## | MES.sd | MO.mg.L | Conc.Solids.mug.gMES | Conc.Solids.ug.gMES | SD | N.y | filt.d13C | |
| ## 1 | NA | NA | 0.6447290 | | 0.02323755 | NA | NA | |
| ## 2 | NA | 0e+00 | 0.6447290 | | 0.02323755 | NA | NA | |
| ## 3 | NA | NA | 0.3853094 | | 0.02515062 | NA | NA | |
| ## 4 | NA | 1e-03 | 0.1258897 | | 0.02706369 | NA | NA | |
| ## 5 | NA | 1e-04 | 0.4357872 | | 0.12323706 | NA | NA | |
| ## 6 | NA | NA | 0.2575699 | | 0.06396039 | NA | NA | |
| ## | filt.SD.d13C | filt.se.d13C | N_ngC.fl | ngC.mean.fl | ngC.SD.fl | DD13C.diss | | |
| ## 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 | NA | 0.7413333 | | |
| ## 5 | NA | NA | NA | NA | NA | 0.5903333 | | |
| ## 6 | NA | NA | NA | NA | NA | NA | | |
| ## | DD13C.filt | f.diss | f.filt | B.diss | B.filt | NH4.mM | TIC.ppm.filt | Cl.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 | NA | 0.6459075 | NA | 35.40925 | NA | 0.05 | 51.8 | 1.48 |
| ## 5 | NA | 0.7060321 | NA | 29.39679 | NA | NA | 44.8 | 1574.00 |
| ## 6 | NA | NA | NA | NA | NA | NA | NA | NA |
| ## | N03...mM | P04...mM | NPOC.ppm | TIC.ppm.unfilt | TOC.ppm.unfilt | ExpMES.Kg | | |
| ## 1 | NA | NA | NA | | NA | NA 5.352733 | | |
| ## 2 | NA | NA | NA | | NA | NA 5.352733 | | |
| ## 3 | NA | NA | NA | | NA | NA 14.875343 | | |
| ## 4 | 616 | NA | 4.0 | | 44.8 | 4.7 24.397953 | | |
| ## 5 | 778 | NA | 4.4 | | 26.4 | 5.4 8.083000 | | |
| ## 6 | NA | NA | NA | | NA | NA 7.935755 | | |
| ## | Appl.Mass.g | timeSinceApp | CumAppMass.g | DissSmeto.mg | DissSmeto.mg.SD | | | |
| ## 1 | 9497.87 | | 0.5 | 9497.87 | 3.541705 | 0.2783949 | | |
| ## 2 | 0.00 | | 3.9 | 9497.87 | 24.604033 | 1.9339946 | | |
| ## 3 | 0.00 | | 5.5 | 9497.87 | 170.038598 | 7.4632812 | | |
| ## 4 | 0.00 | | 6.6 | 9497.87 | 2649.909084 | 112.9800910 | | |

```

## 5      0.00      7.6      9497.87 2357.002211      68.4863626
## 6      0.00     11.6      9497.87 7021.341115      229.9517390
##   DissSmeto.g DissSmeto.g.SD DissOXA.mg DissOXA.mg.SD DissOXA.g
## 1 0.003541705 0.0002783949 69.54963 16.45637 0.06954963
## 2 0.024604033 0.0019339946 483.15756 114.32155 0.48315756
## 3 0.170038598 0.0074632812 854.68456 273.81310 0.85468456
## 4 2.649909084 0.1129800910 11918.39439 3975.98846 11.91839439
## 5 2.357002211 0.0684863626 11672.73795 87.31596 11.67273795
## 6 7.021341115 0.2299517390 60115.11746 612.27900 60.11511746
##   DissOXA.g.SD DissESA.mg DissESA.mg.SD DissESA.g DissESA.g.SD
## 1 0.01645637 260.3058 50.41991 0.2603058 0.05041991
## 2 0.11432155 1808.3308 350.26441 1.8083308 0.35026441
## 3 0.27381310 1548.0863 157.95877 1.5480863 0.15795877
## 4 3.97598846 17950.5083 1185.53932 17.9505083 1.18553932
## 5 0.08731596 14829.7964 306.57276 14.8297964 0.30657276
## 6 0.61227900 61349.8588 1614.18699 61.3498588 1.61418699
##   FiltSmeto.mg FiltSmeto.mg.SD FiltSmeto.g FiltSmeto.g.SD TotSMout.mg
## 1 3.451062 0.1243844 0.003451062 0.0001243844 6.992766
## 2 3.451062 0.1243844 0.003451062 0.0001243844 28.055095
## 3 5.731609 0.3741240 0.005731609 0.0003741240 175.770206
## 4 3.071452 0.6602985 0.003071452 0.0006602985 2652.980536
## 5 3.522468 0.9961252 0.003522468 0.0009961252 2360.524679
## 6 2.044012 0.5075740 0.002044012 0.0005075740 7023.385126
##   TotSMout.mg.SD TotSMout.g TotSMout.g.SD FracDiss FracFilt
## 1 0.2156098 0.006992766 0.0002156098 0.5064812 0.4935188249
## 2 1.3703661 0.028055095 0.0013703661 0.8769898 0.1230101642
## 3 5.2839633 0.175770206 0.0052839633 0.9673915 0.0326085349
## 4 79.8903528 2.652980536 0.0798903528 0.9988423 0.0011577363
## 5 48.4322936 2.360524679 0.0484322936 0.9985078 0.0014922393
## 6 162.6008301 7.023385126 0.1626008301 0.9997090 0.0002910294
##   MELsm.g MELsm.g.SD CumOutDiss.g CumOutFilt.g CumOutSmeto.g
## 1 0.3021264 0.02689497 0.003541705 0.003451062 0.006992766
## 2 2.0783329 0.18683762 0.028145738 0.006902124 0.035047862
## 3 2.3790960 0.17885971 0.198184336 0.012633733 0.210818068
## 4 30.2413655 2.40621294 2.848093419 0.015705185 2.863798604
## 5 27.0082117 0.16340841 5.205095630 0.019227652 5.224323282
## 6 121.0040582 0.88525127 12.226436745 0.021271664 12.247708409
##   CumOutMELsm.g BalMassDisch.g prctMassOut FracDeltaOut Events Weeks
## 1 0.3021264 9497.568 4.980859e-05 0.0000000 0-1 W0
## 2 2.3804594 9495.490 1.998329e-04 0.0000000 0-2 W0
## 3 4.7595554 9493.110 1.251989e-03 0.0000000 0-3 W0
## 4 35.0009209 9462.869 1.889684e-02 -0.5757616 1-1 W1
## 5 62.0091326 9435.861 1.681372e-02 -0.5148304 1-2 W1
## 6 183.0131909 9314.857 5.002668e-02 0.0000000 1-3 W1
##   Event
## 1 0
## 2 0
## 3 0
## 4 1
## 5 1
## 6 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")
```