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 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
```

```
# 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)
head(outletIso)
```

```
##   FileHeader..Filename ID Week Wnum SubWeek WeekSubWeek Repl d.13C.12C
## 1        AO_W0_1-1.dxf AO   W0    0       1        W0-1    1   -26.035
## 2        AO_W0_1-2.dxf AO   W0    0       1        W0-1    2   -27.740
## 3  AO_W0_1-3_-0001.dxf AO   W0    0       1        W0-1    3   -26.219
## 4       AO_W2_2-1_.dxf AO   W2    2       2        W2-2    1   -28.609
## 5       AO_W2_2-2_.dxf AO   W2    2       2        W2-2    2   -28.894
## 6       AO_W2_2-3_.dxf AO   W2    2       2        W2-2    3   -28.503
##   DD13...31.21. Ave...STDEV     Rt Ampl..44 Std.Ampl.    ng..C.
## 1         5.175   0.9357993 2651.2      239       858  8.356643
## 2         3.470          NA 2649.3      296       858 10.349650
## 3         4.991          NA 2649.7      302       858 10.559441
## 4         2.601   0.2022136 2656.2      127       658  5.790274
## 5         2.316          NA 2656.2      163       658  7.431611
## 6         2.707          NA 2655.3      176       658  8.024316
```

```
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$WeekSubWeek = paste(filtersIso$Week, filtersIso$Num, sep = "-")
filtersIso <- filtersIso[filtersIso$Levl != "J+7", ]
head(filtersIso)
```

```
##    ID Week Wnum Num Levl Repl d.13C.12C WeekSubWeek
## 1 AFP   W2    1   1         1   -25.154        W2-1
## 2 AFP   W2    1   1         2   -28.187        W2-1
## 3 AFP   W2    1   1         3   -28.283        W2-1
## 4 AFP   W2    2   2         1   -30.618        W2-2
## 5 AFP   W2    2   2         2   -26.304        W2-2
## 6 AFP   W2    2   2         3   -26.024        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))

head(isoOutSummary)
```

```
##   WeekSubWeek N diss.d13C   SD.d13C    se.d13C
## 1        W0-1 3 -26.66467 0.9357993 0.54028398
## 2        W1-1 3 -30.46867 0.1060016 0.06120004
## 3        W1-2 3 -30.61967 0.1513550 0.08738484
## 4       W10-1 2 -29.47350 1.9905056 1.40750000
## 5       W10-2 3 -29.27067 0.6003202 0.34659502
## 6       W10-3 3 -29.76967 0.3411749 0.19697744
```

```
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))
head(isoFiltSummary)
```

```
##   WeekSubWeek N filt.d13C filt.SD.d13C filt.se.d13C
## 1        W2-1 3 -27.20800     1.779464    1.0273738
## 2        W2-2 3 -27.64867     2.575326    1.4868653
## 3        W6-3 3 -28.00667     1.593462    0.9199856
## 4        W9-1 2 -26.79150     1.745847    1.2345000
## 5        W9-2 3 -27.69633     2.013989    1.1627772
## 6        W9-3 3 -26.94633     1.685361    0.9730434
```

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
```

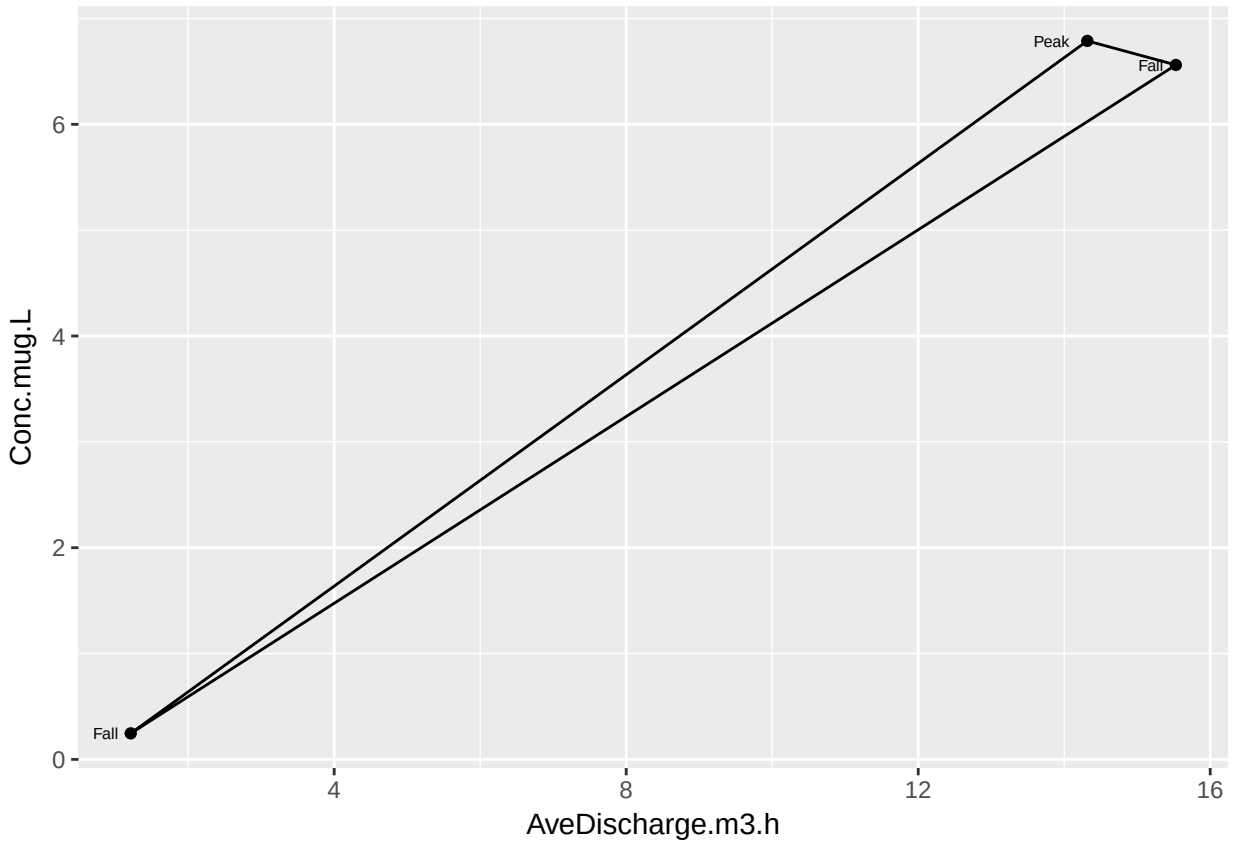
Fork! Prepare Data for C-Q Hysteresis curves

```
CQdata <- out.CoIs[with(out.CoIs, order(ti)), ]
CQdata$FlowType <- ifelse(is.na(CQdata$Event), "Fall", "Peak")
CQdata$Event[1:3]<- 0
CQdata$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  53 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  3 3 3
##  $ diss.d13C           : num  -26.7 -30.5 -30.6
```

```
##  $ SD.d13C             : num  0.936 0.106 0.151
##  $ se.d13C             : num  0.5403 0.0612 0.0874
##  $ 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
##  $ 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
##  $ DD13C.diss          : num  4.545 0.741 0.59
##  $ DD13C.filt          : num  NA NA NA
##  $ f.diss              : num  0.0689 0.6459 0.706
##  $ f.filt              : num  NA NA NA
##  $ B.diss              : num  93.1 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.

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

# Assign trailing observed value
# out.CoIs$Conc.mug.L.sim = na.locf(out.CoIs$Conc.mug.L.sim, na.rm = TRUE)


# 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$DissOXA.mg = out.CoIs$OXA_mean*out.CoIs$Volume.m3
out.CoIs$DissOXA.mg.SD = out.CoIs$OXA_SD*out.CoIs$Volume.m3

out.CoIs$DissESA.mg = out.CoIs$ESA_mean*out.CoIs$Volume.m3
out.CoIs$DissESA.mg.SD = out.CoIs$ESA_SD*out.CoIs$Volume.m3

# 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$ExpMES.Kg
################
# SD for MES S-meto mass (mg)
###############
# mg = Conc. [mu.g s-meto / g MES] * MES.sd [mg/L] * Vol [m3] * [10^3 L/1 m3]* [mg/10^3mug]
# out.CoIs$Conc.Solids.mug.gMES * out.CoIs$MES.sd * out.CoIs$Volume.m3... check calculation

# Total
out.CoIs$TotMassOut.mg = out.CoIs$DissSmeto.mg + out.CoIs$FiltSmeto.mg


# Proportion in dissolved and suspended solids
out.CoIs$FracDiss = out.CoIs$DissSmeto.mg/out.CoIs$TotMassOut.mg
out.CoIs$FracFilt = out.CoIs$FiltSmeto.mg/out.CoIs$TotMassOut.mg
```

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('2016-05-31 12:00:00' , tz="EST"))

Appl.Mass.g = c(6369.396, 3128.475, 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)

# 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
out.CoIs$SimOutDiss.g = out.CoIs$DissSmeto.mg/10^3
out.CoIs$SimOutFilt.g = out.CoIs$FiltSmeto.mg/10^3
out.CoIs$SimOutOXA.g = out.CoIs$DissOXA.mg/10^3
out.CoIs$SimOutESA.g = out.CoIs$DissESA.mg/10^3

out.CoIs$DissSmeto.g.SD = out.CoIs$DissSmeto.mg.SD/10^3
out.CoIs$DissOXA.g.SD = out.CoIs$DissOXA.mg.SD/10^3
out.CoIs$DissESA.g.SD = out.CoIs$DissESA.mg.SD/10^3

out.CoIs$SimOutDiss.g = ifelse(is.na(out.CoIs$SimOutDiss.g), 0.0, out.CoIs$SimOutDiss.g)
out.CoIs$SimOutFilt.g = ifelse(is.na(out.CoIs$SimOutFilt.g), 0.0, out.CoIs$SimOutFilt.g)
out.CoIs$SimOutSmeto.g = out.CoIs$SimOutDiss.g + out.CoIs$SimOutFilt.g

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

mw.SM <- 283.796 # g/mol
mw.MOXA <- 279.33 # g/ml
mw.MESA <- 329.1 # g/mol
out.CoIs$SimMELsm.g <-
  out.CoIs$SimOutSmeto.g +
  out.CoIs$SimOutOXA.g * (mw.SM/mw.MOXA) +
  out.CoIs$SimOutESA.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$SimMELsm.g.SD <-
  sqrt((out.CoIs$SimOutSmeto.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$CumOutDiss.g = cumsum(out.CoIs$SimOutDiss.g)
out.CoIs$CumOutFilt.g = cumsum(out.CoIs$SimOutFilt.g)
out.CoIs$CumOutSmeto.g = out.CoIs$CumOutDiss.g + out.CoIs$CumOutFilt.g
out.CoIs$CumOutMELsm.g = cumsum(out.CoIs$SimMELsm.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$prctMassOut = (out.CoIs$SimOutSmeto.g / massOUT)
out.CoIs$FracDeltaOut = (out.CoIs$SimOutSmeto.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:  140.392784358867
```

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

```
## MEL-sm [g] sampled and non-sampled:  3096.82107110515
```

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

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

```
# Bulk isotope signature
BulkDeltaOut
```

```
## [1] -18.24983
```

6. Testing a regression tree (ommitted for now)

Save files

```
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 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 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   3 -26.66467 0.9357993
## 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 MES.mg.L MES.sd MO.mg.L Conc.Solids.mug.gMES N.y filt.d13C
## 1         NA       NA     NA      NA            0.6447290  NA        NA
## 2 0.54028398 53.44444     NA   0e+00            0.6447290  NA        NA
## 3         NA       NA     NA      NA            0.3853094  NA        NA
## 4 0.06120004 62.50000     NA   1e-03            0.1258897  NA        NA
## 5 0.08738484 22.50000     NA   1e-04            0.4357872  NA        NA
## 6         NA       NA     NA      NA            0.2575699  NA        NA
##   filt.SD.d13C filt.se.d13C DD13C.diss DD13C.filt     f.diss f.filt
## 1           NA           NA         NA         NA         NA     NA
## 2           NA           NA  4.5453333         NA 0.06892489     NA
## 3           NA           NA         NA         NA         NA     NA
## 4           NA           NA  0.7413333         NA 0.64590754     NA
## 5           NA           NA  0.5903333         NA 0.70603206     NA
## 6           NA           NA         NA         NA         NA     NA
##     B.diss B.filt NH4.mM TIC.ppm.filt   Cl.mM NO3...mM PO4..mM NPOC.ppm
## 1       NA     NA     NA           NA      NA       NA      NA       NA
## 2 93.10751     NA     NA           NA      NA       NA      NA       NA
## 3       NA     NA     NA           NA      NA       NA      NA       NA
## 4 35.40925     NA   0.05         51.8    1.48      616      NA      4.0
## 5 29.39679     NA     NA         44.8 1574.00      778      NA      4.4
## 6       NA     NA     NA           NA      NA       NA      NA       NA
##   TIC.ppm.unfilt TOC.ppm.unfilt ExpMES.Kg DissSmeto.mg DissSmeto.mg.SD
## 1             NA             NA  5.352733     3.541705       0.2783949
## 2             NA             NA  5.352733    24.604033       1.9339946
## 3             NA             NA 14.875343   170.038598       7.4632812
## 4           44.8            4.7 24.397953  2649.909084     112.9800910
## 5           26.4            5.4  8.083000  2357.002211      68.4863626
## 6             NA             NA  7.935755  7021.341115     229.9517390
##    DissOXA.mg DissOXA.mg.SD DissESA.mg DissESA.mg.SD FiltSmeto.mg
## 1    69.54963      16.45637   260.3058      50.41991     3.451062
```

```
## 2   483.15756     114.32155  1808.3308     350.26441     3.451062
## 3   854.68456     273.81310  1548.0863     157.95877     5.731609
## 4 11918.39439    3975.98846 17950.5083    1185.53932     3.071452
## 5 11672.73795      87.31596 14829.7964     306.57276     3.522468
## 6 60115.11746     612.27900 61349.8588    1614.18699     2.044012
##   TotMassOut.mg  FracDiss     FracFilt Appl.Mass.g CumAppMass.g
## 1      6.992766 0.5064812 0.4935188248    6369.396     6369.396
## 2     28.055095 0.8769898 0.1230101641       0.000     6369.396
## 3    175.770206 0.9673915 0.0326085349       0.000     6369.396
## 4   2652.980536 0.9988423 0.0011577363       0.000     6369.396
## 5   2360.524679 0.9985078 0.0014922393       0.000     6369.396
## 6   7023.385126 0.9997090 0.0002910294       0.000     6369.396
##   SimOutDiss.g SimOutFilt.g SimOutOXA.g SimOutESA.g DissSmeto.g.SD
## 1  0.003541705  0.003451062  0.06954963   0.2603058   0.0002783949
## 2  0.024604033  0.003451062  0.48315756   1.8083308   0.0019339946
## 3  0.170038598  0.005731609  0.85468456   1.5480863   0.0074632812
## 4  2.649909084  0.003071452 11.91839439  17.9505083   0.1129800910
## 5  2.357002211  0.003522468 11.67273795  14.8297964   0.0684863626
## 6  7.021341115  0.002044012 60.11511746  61.3498588   0.2299517390
##   DissOXA.g.SD DissESA.g.SD SimOutSmeto.g SimOutSmeto.g.SD  SimMELsm.g
## 1   0.01645637   0.05041991   0.006992766     0.0002783949   0.3021264
## 2   0.11432155   0.35026441   0.028055095     0.0019339946   2.0783329
## 3   0.27381310   0.15795877   0.175770206     0.0074632812   2.3790960
## 4   3.97598846   1.18553932   2.652980536     0.1129800910  30.2413655
## 5   0.08731596   0.30657276   2.360524679     0.0684863626  27.0082117
## 6   0.61227900   1.61418699   7.023385126     0.2299517390 121.0040582
##   SimMELsm.g.SD CumOutDiss.g CumOutFilt.g CumOutSmeto.g CumOutMELsm.g
## 1    0.02689516  0.003541705  0.003451062   0.006992766     0.3021264
## 2    0.18683928  0.028145738  0.006902124   0.035047862     2.3804594
## 3    0.17888559  0.198184336  0.012633733   0.210818068     4.7595554
## 4    2.40665496  2.848093419  0.015705185   2.863798604    35.0009209
## 5    0.16578261  5.205095630  0.019227652   5.224323282    62.0091326
## 6    0.89021500 12.226436745  0.021271664  12.247708409   183.0131909
##   BalMassDisch.g  prctMassOut FracDeltaOut
## 1       6369.094 4.980859e-05  0.000000000
## 2       6367.016 1.998329e-04 -0.005328477
## 3       6364.636 1.251989e-03  0.000000000
## 4       6334.395 1.889684e-02 -0.575761639
## 5       6307.387 1.681372e-02 -0.514830439
## 6       6186.383 5.002668e-02  0.000000000
```

```
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")
```