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**
- **fluxAlteck2016_R.csv**
- **OutletConc_W0toW17.csv**
- **MESAlteckWater.csv**
- **Outlet_Isotopes_W0toW17.csv**
- **MESAlteck_FilterIsotopes.csv**
- **AO-Hydrochem.csv**

Generates:

- **WeeklyHydroContam_R.csv**

Required R-packages:

```
library("plyr")
library("dplyr")
```

Working directory

```
# setwd("D:/Documents/these_pablo/Alteckendorf2016/R")
# setwd("/Users/DayTightChunks/Documents/PhD/Routput/Alteck/R")
# setwd("D:/Documents/these_pablo/Alteckendorf2016/00_TransparencyFolder")
getwd()
```

```
## [1] "D:/Documents/these_pablo/Alteckendorf2016/00_TransparencyFolder"
```

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      peak    valley    tdiff  chExtreme
## 1 -0.1193728  1.248600  1.118296 11.96667 -0.1303036
## 2  0.1887431  1.380388  1.082199 82.53333  0.2560062
## 3  0.1482496  1.637782  0.929055 37.63333  0.3296817
## 4 14.9893566 38.399790  1.448977 27.26667 36.9437102
## 5 -1.1498131 18.668972 13.201113 23.13333 -3.1332355
## 6 -9.3472489 15.895640  5.471042 96.33333 -9.7325862
```

2. Concentration data (dissolved and suspended solids)

```
outletConc = read.csv2("Data/OutletConc_W0toW17.csv", header = T)
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
```

3. Isotope data

```
# 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_W1_1-1_-0001.dxf AO   W1    1       1        W1-1    1   -30.591
## 5  AO_W1_1-2_-0001.dxf AO   W1    1       1        W1-1    2   -30.411
## 6  AO_W1_1-3_-0001.dxf AO   W1    1       1        W1-1    3   -30.404
```

```
# 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:

```r
# Dissolved
out.CoIs = merge(outletConc, 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

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

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"
```

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

```
## [1] 4
```

```r
# Temprarily remove Weeks 16 & 17 (need to get discharge data)
out.CoIs <- out.CoIs[!is.na(out.CoIs$tf), ]
```

2. Weekly Exported Solids (Kg)

```r
# 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
```

3. Weekly exported S-metolachlor mass (mg)

```
# 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

# 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

# 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('2016-05-24 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)
```

5. This section converts the observed S-metolachlor concentrations to [g] in dissolved water and suspended solids, assuming 0 for the values where no sample was taken. An approximative model will be tested at a later stage.

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

# 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$SimOutDiss.g = ifelse(is.na(out.CoIs$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

# 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

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

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

```
## [1] 91.10687
```

```
# Bulk isotope signature
BulkDeltaOut
```

```
## [1] -23.8942
```

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      peak    valley    tdiff  chExtreme AveDischarge.m3.h
## 1 -0.1193728  1.248600  1.118296 11.96667 -0.1303036          1.204775
## 2  0.1887431  1.380388  1.082199 82.53333  0.2560062          1.213511
```

```
## 3  0.1482496  1.637782  0.929055 37.63333  0.3296817          1.284719
## 4 14.9893566 38.399790  1.448977 27.26667 36.9437102         14.316647
## 5 -1.1498131 18.668972 13.201113 23.13333 -3.1332355         15.529299
## 6 -9.3472489 15.895640  5.471042 96.33333 -9.7325862          9.107720
##   Volume.m3 Sampled.Hrs     Sampled Conc.mug.L Conc.SD N.x diss.d13C
## 1  14.41714    11.96667 Not Sampled         NA      NA  NA        NA
## 2 100.15508    82.53333     Sampled  0.2456594 0.01931   3 -26.66467
## 3  48.34827    37.63333 Not Sampled         NA      NA  NA        NA
## 4 390.36726    27.26667     Sampled  6.7882463 0.28942   3 -30.46867
## 5 359.24445    23.13333     Sampled  6.5609982 0.19064   3 -30.61967
## 6 877.37700    96.33333 Not Sampled         NA      NA  NA        NA
##     SD.d13C    se.d13C MES.mg.L MES.sd MO.mg.L Conc.Solids.mug.gMES N.y
## 1        NA         NA       NA     NA      NA                   NA  NA
## 2 0.9357993 0.54028398 53.44444     NA   0e+00            0.6447290  NA
## 3        NA         NA       NA     NA      NA                   NA  NA
## 4 0.1060016 0.06120004 62.50000     NA   1e-03            0.1258897  NA
## 5 0.1513550 0.08738484 22.50000     NA   1e-04            0.4357872  NA
## 6        NA         NA       NA     NA      NA                   NA  NA
##   filt.d13C filt.SD.d13C filt.se.d13C DD13C.diss DD13C.filt     f.diss
## 1        NA           NA           NA         NA         NA         NA
## 2        NA           NA           NA  4.5453333         NA 0.05462172
## 3        NA           NA           NA         NA         NA         NA
## 4        NA           NA           NA  0.7413333         NA 0.62181820
## 5        NA           NA           NA  0.5903333         NA 0.68498131
## 6        NA           NA           NA         NA         NA         NA
##   f.filt   B.diss B.filt NH4.mM TIC.ppm.filt   Cl.mM NO3...mM PO4..mM
## 1     NA       NA     NA     NA           NA      NA       NA      NA
## 2     NA 94.53783     NA     NA           NA      NA       NA      NA
## 3     NA       NA     NA     NA           NA      NA       NA      NA
## 4     NA 37.81818     NA   0.05         51.8    1.48      616      NA
## 5     NA 31.50187     NA     NA         44.8 1574.00      778      NA
## 6     NA       NA     NA     NA           NA      NA       NA      NA
##   NPOC.ppm TIC.ppm.unfilt TOC.ppm.unfilt ExpMES.Kg DissSmeto.mg
## 1       NA             NA             NA        NA           NA
## 2       NA             NA             NA  5.352733     24.60403
## 3       NA             NA             NA        NA           NA
## 4      4.0           44.8            4.7 24.397953   2649.90908
## 5      4.4           26.4            5.4  8.083000   2357.00221
## 6       NA             NA             NA        NA           NA
##   FiltSmeto.mg TotMassOut.mg  FracDiss    FracFilt Appl.Mass.g
## 1           NA            NA        NA          NA    6369.396
## 2     3.451062       28.0551 0.8769898 0.123010164       0.000
## 3           NA            NA        NA          NA       0.000
## 4     3.071452     2652.9805 0.9988423 0.001157736       0.000
## 5     3.522468     2360.5247 0.9985078 0.001492239       0.000
## 6           NA            NA        NA          NA       0.000
##   CumAppMass.g SimOutDiss.g SimOutFilt.g SimOutSmeto.g CumOutDiss.g
## 1     6369.396   0.00000000  0.000000000     0.0000000   0.00000000
## 2     6369.396   0.02460403  0.003451062     0.0280551   0.02460403
## 3     6369.396   0.00000000  0.000000000     0.0000000   0.02460403
## 4     6369.396   2.64990908  0.003071452     2.6529805   2.67451312
## 5     6369.396   2.35700221  0.003522468     2.3605247   5.03151533
## 6     6369.396   0.00000000  0.000000000     0.0000000   5.03151533
##   CumOutFilt.g CumOutSmeto.g BalMassDisch.g  FracMassOut FracDeltaOut
```

```
## 1  0.000000000     0.0000000       6369.396 0.0000000000  0.000000000
## 2  0.003451062     0.0280551       6369.368 0.0003079361 -0.008211013
## 3  0.003451062     0.0280551       6369.368 0.0000000000  0.000000000
## 4  0.006522514     2.6810356       6366.715 0.0291194331 -0.887230300
## 5  0.010044982     5.0415603       6364.354 0.0259094025 -0.793337267
## 6  0.010044982     5.0415603       6364.354 0.0000000000  0.000000000
```

```r
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")
```