Carbon mass balance of French vertical flow treatment wetlands

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This notebook describes the carbon mass balance estimation for French Vertical Flow (VF) wetlands. It is based on the first LCA inventory carried out by Risch *et al.* (2010). This updated version aims to take better account of experimental data. In particular, it focuses on data collected from a large number of full-scale French VF wetlands.

The mass balance is expressed in $g C⋅pe^{−1}d^{−1}$.

## Incoming carbon flux

The estimation of the incoming carbon flux is based on the COD inlet flux. Mercoiret *et al.* (2009) estimated the incoming COD flux to 157.2 $gO\_{2}d^{−1}$.

$$F\_{COD}^{inlet}=157.2 \left[g⋅d^{−1}⋅pe^{−1}\right]  \left(1\right)$$

COD <- list(inlet = list(total = set\_units(157.2, g/d/pe)))

## Unit surface area

The maximum recommended surface load ($L\_{COD}^{inlet}$) is 350 $gCODm^{−2}d^{−1}$ (Molle et al., 2023). Considering [Equation 1](#eq-incoming_COD), one can derived the minimum required surface per people equivalent ($S\_{pe}$):

$$S\_{pe}=\frac{F\_{COD}^{inlet}}{L\_{COD}^{inlet}}×nb.filter \left[m^{2}⋅pe^{−1}\right]  \left(2\right)$$

where $nb.filter$ is the number of filter in parallel and fed alternativelly. The recommended value for $nb.filter$ is 3 for the first stage and 2 for the second stage.

CCTP.load <- set\_units(350, g/m^2/d)
surface <- list(first.stage = list(unit = COD$inlet$total/CCTP.load,
 nb.filter = 3),
 second.stage = list(unit = COD$inlet$total/CCTP.load,
 nb.filter = 2)
 )
surface$first.stage$total <-
 surface$first.stage$unit\*surface$first.stage$nb.filter
surface$second.stage$total <-
 surface$second.stage$unit\*surface$second.stage$nb.filter

The recommended surface are 1.35 $m^{2}/pe$ for the first stage and 0.9 $m^{2}/pe$.

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|  Note |
| The resulting surface is larger than the value usually presented in the literature: 1.2 $m^{2}⋅pe^{−1}$ (Molle et al., 2005). |

## Conversion from COD to carbon equivalent

COD, BOD and TOC are all measures that can be used to estimate the quantity of organic matter present in the environment, although they are not sensitive to the same constituents (Thomas and Burgess, 2017).

### Stocheometric approaches

#### Molar mass ratio

In Risch *et al.* (2010), conversion from COD to carbon is based on the following assumption. The degradation of the organic matter by microorganisms can be approximated by the following simplified equation:

$$Organic Matter+O\_{2}\rightarrow CO\_{2}  \left(3\right)$$

Assuming that the consumption of 1 mole of $O\_{2}$ results in the emission of 1 mole of $CO\_{2}$, the amount of carbon present in the organic matter being degraded is equal to the molar mass ratio $CO\_{2}−C/O\_{2}$ (12/32) times the COD concentration. The conversion factor is then equal to $2.67g COD/g C$.

#### Equivalent chemical formula

In Langergraber *et al.* (2007), two calculations are presented according to the equivalent chemical formula taken for the biomass ($C\_{5}H\_{7}O\_{2}N$ or $C\_{8}H\_{14}O\_{4}N$).

langergraber.convert <- tibble(formula = c("C5H7O2N", "C8H14O4N"),
 `conversion factor (g C0D/g C)` = set\_units(c(2.667, 2.917), g/g)
)
kable(langergraber.convert)

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| Table 1: conversion table from COD to C

| formula | conversion factor (g C0D/g C) |
| --- | --- |
| C5H7O2N | 2.667 [g/g] |
| C8H14O4N | 2.917 [g/g] |

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#### TOC equivalence

An alternative approach consists in converting COD into TOC. Dubber and Gray (2010) suggest the following equation:

$$COD=49.2+3.00×TOC  \left(4\right)$$

The slope of the obtained relationship: 3, is very close to that of the second formula in [Table 1](#tbl-conversion) . The value of 3 ($K$) will therefore be retained for the time being.

COD\_2\_C <- set\_units(1/3, g/g)

In the rest of the document, all calculations will first be performed in COD and then converted to their C equivalent using the conversion factor above.

## COD inlet fractionation

The inlet COD is composed of an inert fraction and a biodegradable fraction . For the inert fraction, Gillot and Choubert (2010) indicate that it consists of:

* a soluble fraction representing 4% of the total COD
* a particulate fraction representing 25% of the total COD

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| Figure 1: COD inlet fractionation according to (2010) |

COD$inlet$inert\_soluble <- 4/100\*COD$inlet$total
COD$inlet$inert\_particulate <- 25/100\*COD$inlet$total
COD$inlet$biodegradable <- COD$inlet$total - COD$inlet$inert\_soluble -
 COD$inlet$inert\_particulate

Next we convert these values into their C-equivalent:

bilan.C$inlet[1] <- COD$inlet$biodegradable\*COD\_2\_C
bilan.C$inlet[2] <- COD$inlet$inert\_soluble\*COD\_2\_C
bilan.C$inlet[3] <- COD$inlet$inert\_particulate\*COD\_2\_C

## First treatment stage

### COD removal

The COD removal rate between the inlet and the outlet of the first treatment stage is obtained from Morvannou *et al.* (2015) : 77%.

$$F\_{COD}^{out}=\left(1−0.77\right)\*F\_{COD}^{in}  \left(5\right)$$

COD$first.stage$effluent <- (1-0.77)\*COD$inlet$total

It is assumed that the inert soluble fraction is entirely transferred to the first stage outlet. It is also assumed that the inert particular fraction is completely removed by filtration:

$$COD\_{out}^{soluble inert}=DCO\_{in}^{soluble inert}  \left(6\right)$$

$$COD\_{out}^{particulate inert}=0  \left(7\right)$$

$$COD\_{out}^{biodegradable}=COD\_{out}−COD\_{out}^{soluble inert}  \left(8\right)$$

COD$first.stage$inert\_soluble <- COD$inlet$inert\_soluble
COD$first.stage$inert\_particulate <- set\_units(0,g/pe/d)
COD$first.stage$biodegradable <- COD$first.stage$effluent -
 COD$first.stage$inert\_soluble

#### Conversion to C

bilan.C$inlet[1] <- COD$inlet$biodegradable\*COD\_2\_C
bilan.C$inlet[2] <- COD$inlet$inert\_soluble\*COD\_2\_C
bilan.C$inlet[3] <- COD$inlet$inert\_particulate\*COD\_2\_C

bilan.C$first.stage[1] <- COD$first.stage$biodegradable\*COD\_2\_C
bilan.C$first.stage[2] <- COD$first.stage$inert\_soluble\*COD\_2\_C
bilan.C$first.stage[3] <- COD$first.stage$inert\_particulate\*COD\_2\_C

### Biosolids

The degraded organic matter is partly transformed into biomass and partly used to produce energy (and transformed to $CO\_{2}$) ([Figure 2](#fig-biomass_growth)).

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| Figure 2: COD biodegradation pathways |

The yield coefficient ($Y\_{H}$) for heterotrophic bacteria is equal to 0.67 $mg COD/mg COD$ (Henze et al., 2015). For sake of simplicity, new biomass, storage and adsorption will be looped into a simple term called biomass that we directly convert into C.

$$biomass=Y\_{H}\*\left(F\_{COD}^{in}−F\_{COD}^{out}\right)\*K  \left(9\right)$$

$$F\_{C−CO\_{2}}^{biomass}=\left(1−Y\_{H}\right)\*\left(F\_{COD}^{in}−F\_{COD}^{out}\right)\*K  \left(10\right)$$

COD.degraded <- COD$inlet$biodegradable-COD$first.stage$biodegradable
YH <- set\_units(0.67, g/g)
biomass <- YH\*COD.degraded\*COD\_2\_C
CO2.degradation <- (set\_units(1, g/g)-YH)\*COD.degraded\*COD\_2\_C

There are two sources of biosolid accumulation:

* The biomass associated to the organic matter degradation (estimated above)
* The inert particulate COD

It is assumed that biosolids only significantly accumulates on the surface of the 1st treatment stage.

$$biosolids=biomass+F\_{COD}^{inert\_{p}articulate}\*K  \left(11\right)$$

biosolids <- biomass + COD$inlet$inert\_particulate\*COD\_2\_C

However, accumulated biosolids are partly mineralized over time. This mineralization will in turn produces $CO\_{2}$ and $CH\_{4}$. In order to estimate the mineralized fraction, an estimate of the actual surface deposit accumulation rate will be used. Molle *et al.* (2014) reported an average accumulation rate of 2.5 $cm/m^{2}/y$. Therefore, the volume of biosolids produced can be calculated:

$$V\_{biosolids}=2.5 cm/y×S\_{total}  \left(12\right)$$

biosolids.growth.rate <- set\_units(2.5/365.5, cm/d)
V.biosolids <- biosolids.growth.rate\*surface$first.stage$total

The biosolids density is assumed to be equal to 300 $kg DM/m^{3}$ ((Vincent, 2011))

$$M\_{biosolids}=d\_{biosolids}×V\_{biosolids}  \left(13\right)$$

density.biosolids <- set\_units(300, kg/m^3)
M.biosolids <- density.biosolids\*V.biosolids

The biosolids COT content has been estimated to ~ 25% (Kania et al., 2019)

$$M\_{C biosolids}=0.25×M\_{biosolids}  \left(14\right)$$

biosolids.C.content <- 0.25

bilan.C$first.stage[6] <- set\_units(biosolids.C.content\*M.biosolids,g/d/pe)

The difference between the stored biosolids ([Equation 14](#eq-COT_content)) and the produced biosolids ([Equation 11](#eq-produced_biosolids)) gives an estimate of the fraction of biosolids that have been mineralized and then turned into methane or $CO\_{2}$.

biosolids.degraded <- biosolids - bilan.C$first.stage[6]

### Gaseous emission

Methane emission have been measured by Molle *et al.* (2008). For the fist stage, it has been measured:

* 0.1 g C-CH4/m2/d during resting period
* 0.25 g C-CH4/m2/d during feeding period

CH4.emission.feed <- set\_units(0.25, g/m^2/d)
CH4.emission.rest <- set\_units(0.1, g/m^2/d)

Consequently, over an entire feeding/resting cycle, the methane production is:

$$Production C-CH4=\frac{\left(feeding duration×feeding production rate+resting duration×resting production rate\right)}{feeding duration+resting duration}\left[g⋅m^{2}⋅d\right]  \left(15\right)$$

feed.duration <- set\_units(3.5, d)
rest.duration <- set\_units(7, d)

CH4.emission.cycle <- (feed.duration\*CH4.emission.feed+rest.duration\*CH4.emission.rest)/(rest.duration+feed.duration)

Then the production per square meter is transformed into the production per people equivalent:

$$Production C-CH4/EH=Production C-CH4×Surface per PE \left[g⋅PE^{−1}⋅d^{−1}\right]$$

bilan.C$first.stage[5] <- CH4.emission.cycle\*surface$first.stage$total

If the mass of carbon transformed into methane is removed from degraded biomass estimated earlier, we obtain the mass of the biosolids that have been turned into $CO\_{2}$ to which we need to add the mass of $CO\_{2}$ produced during the biomass formation to obtain the total $CO\_{2}$ emission.

bilan.C$first.stage[4] <-biosolids.degraded - bilan.C$first.stage[5] + CO2.degradation

### Carbon storage in reeds

It is assumed that reeds only captured atmospheric $CO\_{2}$ which in turn will be transformed into atmospheric $CO\_{2}$ during composting. This lead to a neutral mass balance (biogenic $CO\_{2}$).

bilan.C$first.stage[7] <- set\_units(0,g/d/pe)

Cette hypothèse tend à négliger la quantité de carbone stockée au niveau des rizhomes et le carbone stocké au final après compostage. Pascal cherche le quantité de C stockée dans les roseaux et Karine cherche la quantité de C capté par photosynthèse par les roseaux

## 2nd treatment stage

### Effluent

#### COD removal

The COD removal rate between the inlet and the outlet of the second treatment stage is obtained from Morvannou et al. (2015): 87%

COD$second.stage$effluent <- (1-0.87)\*COD$inlet$total

It is assumed that the quantity of inert soluble COD remains unchanged between the inlet and the outlet of the second treatment stage.

COD$second.stage$inert\_soluble <- COD$first.stage$inert\_soluble
COD$second.stage$inert\_particulate <- COD$first.stage$inert\_particulate
COD$second.stage$biodegradable <- COD$second.stage$effluent-COD$second.stage$inert\_soluble-COD$second.stage$inert\_particulate

#### Conversion to C

bilan.C$second.stage[1] <- COD$second.stage$biodegradable\*COD\_2\_C
bilan.C$second.stage[2] <- COD$second.stage$inert\_soluble\*COD\_2\_C
bilan.C$second.stage[3] <- COD$second.stage$inert\_particulate\*COD\_2\_C

### Carbon storage in reeds

Similarly to the first stage, the storage in reeds can be neglected.

bilan.C$second.stage[7] <- set\_units(0,g/d/pe)

### Gaseous emission

There has been no measurement performed on the second treatment stage. Therefore, it has been assumed that for both treatment stages, the methane production is proportional to the quantity of organic carbon degraded and that the ratio observed for the first treatment stage can be applied to the second treatment stage.

bilan.C$second.stage[5] <- (bilan.C$first.stage[1]-bilan.C$second.stage[1])/
 (bilan.C$inlet[1] - bilan.C$first.stage[1])\*bilan.C$first.stage[5]

CO2 emission are computed by difference:

bilan.C$second.stage[4] <- sum(bilan.C$first.stage[1:3])-sum(bilan.C$second.stage[-4])

## Summary

kable(bilan.C)

|  | inlet | first.stage | second.stage |
| --- | --- | --- | --- |
| water - biodegradable | 37.204 [g/d/pe] | 9.9560000 [g/d/pe] | 4.71600000 [g/d/pe] |
| water - inert soluble | 2.096 [g/d/pe] | 2.0960000 [g/d/pe] | 2.09600000 [g/d/pe] |
| water - inert particulate | 13.100 [g/d/pe] | 0.0000000 [g/d/pe] | 0.00000000 [g/d/pe] |
| gas - CO2-C | 0.000 [g/d/pe] | 33.2336324 [g/d/pe] | 5.20113187 [g/d/pe] |
| gas - CH4-C | 0.000 [g/d/pe] | 0.2021143 [g/d/pe] | 0.03886813 [g/d/pe] |
| solid - biosolids | 0.000 [g/d/pe] | 6.9122533 [g/d/pe] | 0.00000000 [g/d/pe] |
| solid - reed | 0.000 [g/d/pe] | 0.0000000 [g/d/pe] | 0.00000000 [g/d/pe] |

Results can also be presented using a Sankey plot:

Inputs <- as.numeric(c(bilan.C$inlet[1],
 bilan.C$inlet[2]+bilan.C$inlet[3]))
Inputs <- round(Inputs,2)
Losses <- as.numeric(c(
 bilan.C$second.stage[5]+bilan.C$first.stage[5],
 bilan.C$second.stage[4]+bilan.C$first.stage[4],
 bilan.C$second.stage[1],
 bilan.C$second.stage[2],
 bilan.C$first.stage[6]
 ))
Losses <- round(Losses,2)
Labels <- c("CODb-C", "CODi-C",
 "CH4-C", "CO2-C",
 "CODb-C", "CODi-C",
 "biosolids-C")

SankeyR(inputs = Inputs,
 losses = Losses,
 unit = "g/d/pe",
 labels = Labels
 )



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