

# Anoxia in the Scheldt estuary

Exercises Accompanying the Course Reaction Transport Modelling in the Hydrosphere

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## Problem formulation

One of the major pollution problems in European rivers and estuaries is the input of untreated municipal waste water. A major chemical component of such wastewater is ammonia ( $NH_3$ ). Here we will make a case study of the Scheldt estuary, in the Southwestern part of the Netherlands. This estuary receives its water from the Scheldt river.

In the twentieth century, the Scheldt river and estuary were highly polluted, causing hypoxic and even anoxic conditions in the water. It has been postulated that the massive amounts of ammonia input to this river were responsible for the low oxygen conditions. More recently, the ammonia concentration in the inflow of the river into the estuary has drastically decreased; from  $0.6 \text{ mol N m}^{-3}$  in 1975 to  $0.1 \text{ mol N m}^{-3}$  in 2002. In contrast, there was no change in the input concentration of oxygen, which remained at  $0.1 \text{ mol O}_2 \text{ m}^{-3}$ . The reduction of the input of ammonia led to significant improvement of the water quality, and the restoration of oxic conditions.

In this exercise, you will investigate this by means of a biogeochemical model of the Scheldt estuary. The model will include both the transport and reaction processes. Of interest will be the concentrations of ammonia, nitrate and oxygen in the river water.

Regarding *reactions*, assume that the dominant pathway of oxygen consumption in the Scheldt is the nitrification process (oxidation of ammonia to nitrate), which consumes 2 moles of oxygen per mole of ammonia:



Although this process can happen abiotically, its rate is much greater if it is mediated by bacteria, which can use it to gain energy for growth.<sup>1</sup> Another important reaction is the exchange of oxygen across the air-water interface (re-aeration).

Regarding *transport*, oxygen, nitrate and ammonia are transported by the river flow (advection) and are mixed by the tides (tidal dispersion).

## Assumptions

- The estuary connects the Scheldt river (upstream boundary) to the sea (downstream boundary), and it is  $100 \text{ km}$  long. To make the model simple, assume a considerably *simplified* estuarine morphology, where its cross-sectional area  $A = 20000 \text{ m}^2$ , and the water depth  $d = 10 \text{ m}$ , are *constant* along the entire length of the estuary.

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<sup>1</sup>In fact, the overall process is a two-step process. The first step is ammonia oxidation to nitrite, mediated by one type of bacteria, and the second step is nitrite oxidation to nitrate, mediated by another type of bacteria. We will, however, neglect this aspect in our model.

- The discharge of river water is constant at  $Q = 100 \text{ m}^3 \text{ s}^{-1}$ .
- The water is mixed by the tides, and this tidal mixing is described by the dispersion coefficient  $D = 350 \text{ m}^2 \text{ s}^{-1}$ .
- The rate of nitrification is modelled as follows:

$$\text{Nitrification} = r_{nit} \cdot [NH_3] \cdot \frac{[O_2]}{[O_2] + k_{sO_2}},$$

where the nitrification rate constant is  $r_{nit} = 0.10 \text{ d}^{-1}$ , and the half-saturation concentration is  $k_{sO_2} = 0.001 \text{ mol } O_2 \text{ m}^{-3}$ . Note that this rate expression only considers  $O_2$  in the Michaelis-Menten term, indicating that  $O_2$  is the rate-limiting substrate. Although nitrification is a microbially mediated process (see above), there is no “worker” (i.e., bacteria) in the rate expression. In this expression, we assume that the concentration of  $NH_3$  is a *proxy* for the bacterial concentration—the more ammonia is available, the more bacteria is present, and therefore the faster the rate of nitrification will be. This substitution of the “worker” by the “resource” is a common assumption that we employ in biogeochemical models. Specifically, we assume that the “workers” are “adjusting” themselves to match the concentration of the resource that is (presumably) always present, and this adjustment is so rapid that we do *not* need to model the worker explicitly. This is similar to the local equilibrium assumption that we employed in models of chemical reactions comprising a fast equilibration reaction coupled to a slower process. Essentially, we assume that the “worker” is in a local “equilibrium” with the available resource (here  $NH_3$ ).

- The oxygen exchange with the atmosphere (aeration) is driven by the “distance” from the equilibrium. Thus, the aeration rate ( $\text{mol } O_2 \text{ m}^{-3} \text{ d}^{-1}$ ) is expressed as

$$\text{Aeration} = -\frac{v_d}{d} \cdot ([O_2] - O_{2,sat}).$$

This expression assumes that the aeration flux is *instantaneously* homogenized over the entire water depth ( $d$ ). Assume a value of  $v_d = 1 \text{ m d}^{-1}$  for the rate constant (called ‘piston-velocity’), and  $O_{2,sat} = 0.3 \text{ mol } O_2 \text{ m}^{-3}$  for the equilibrium concentration of dissolved oxygen in water (called ‘solubility’).

- The model is completely specified only if we prescribe what happens at the boundaries with the outside world (i.e., the boundary conditions). For the estuary, the outside world is the river (distance  $x = 0$ ) and the sea (distance  $x = 100 \text{ km}$ ). In the current situation, the concentrations of oxygen, nitrate and ammonia in the river are 0.1, 0.3 and  $0.1 \text{ mol N m}^{-3}$ , respectively. At the sea boundary, they are 0.3, 0.05 and  $0.010 \text{ mol m}^{-3}$ , respectively.

## Tasks

### Mass balance equations

- Write down the mass balance equations for all relevant substances. Do not forget to specify the boundary conditions. Not all components that feature in the chemical reactions need to be modeled. Which ones can be ignored and why?

### Model implementation

- Implement the model, using the R-markdown file `RTM_1D.Rmd` as a template.<sup>2</sup>

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<sup>2</sup>You can obtain this file from Rstudio: File → new File → Rmarkdown → from template → `RTM_1D`. Save this file under a different name. Do not forget to change the heading of this file.

- Ensure that the parameters have the correct units. You have a mix of units and they need to be made consistent.
- Also think about the units of the transport parameters. Check the function `tran.1D` from the `ReacTran` package to find these units.
- Find a steady-state solution to the model, using the function `steady.1D` from the R-package `rootSolve` (Soetaert, 2009). You will need to specify that the state variables should be positive.<sup>3</sup>

## Comparison of the 1970s and current situation

The previous simulation corresponded to a scenario where the condition in the estuary was not very eutrophic. In the 1970s the loading of ammonia to the Belgian rivers was much higher, and the nitrate concentrations in the inflowing water were much lower.

- Run the model again using these different boundary conditions:
  - For nitrate, use 0.050 and 0.020  $\text{mol N m}^{-3}$  as concentrations in the river and sea, respectively.
  - For ammonia, use 0.600 and 0.020  $\text{mol N m}^{-3}$  as a concentrations in the river and sea, respectively.
  - For oxygen, the conditions do not change. Do not forget to store the output in a different variable.
- Plot the results from the two model runs in one graph.
  - What is the minimal oxygen concentration in both scenarios? (Tip: the function `steady.1D` returns a list that contains a matrix called “y” that contains the state variables, and the ordinary variables.)

## Creating budgets

- Make a budget of nitrate, ammonia and oxygen for the entire estuary and for the two modelled periods.
  - You will do this by integrating all rates over the estuarine length, and taking into account the estuarine cross-sectional surface area.
  - Output the integrated rates in  $\text{Mmol yr}^{-1}$  ( $10^6 \text{ mol yr}^{-1}$ ).
  - Draw a conceptual diagram that represents the flows of nitrogen and oxygen in the entire estuary, including the import and export. (Tip: in this diagram, the boxes will represent the pools of nitrogen and oxygen in the entire estuary.)
  - Add the budget rates next to each arrow. If your model is consistent, then the rates in and out of one compartment should add to 0.

## The impact of ammonia reduction in inflowing waters — sensitivity analysis

Previous model runs demonstrated that the oxygen concentration in the estuary is a function of the ammonia concentration in the inflowing water. The *minimal* oxygen concentration in the estuary is especially important, as this value determines whether organisms will be able to survive or not. As the removal of ammonia is a costly process, it is worthwhile to use the model to determine the maximal ammonia concentration that still keeps oxygen concentrations above a certain threshold. Here is how to do this.

- Write an R-function, called *Sens*, that estimates the minimal oxygen concentration as a function of the upstream ammonia concentration.
  - The R-function should have the upstream ammonia concentration as an input argument, put this value in the model parameters, solve for the steady-state (using `rootSolve` function `steady.1D`; see above), and finally return the minimal oxygen concentration in the steady-state solution.

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<sup>3</sup>The function `steady.1D` estimates the root of the model function via an iterative technique. Often several roots may exist, of which some can also comprise negative values. While this can make sense mathematically, we do not accept such results when modeling concentrations. Thus, by setting the input parameter “positive = TRUE”, we ensure that a solution with only positive values is found.

- Now create a sequence of  $NH_3$  concentrations ranging from 0 to  $0.8 \text{ mol N m}^{-3}$  (call this sequence `NH3_vect`). For each of these values, call the R-function `Sens` and store the results in a vector called `O2_vect`. (Hint: use a *for* loop here. When doing so, it is convenient to initially define a NULL object called `O2_vect`, and then for each  $NH_3$  value, concatenate to this the corresponding minimal  $O_2$  concentration).
- Plot the minimal oxygen concentration in the estuary as a function of the upstream ammonia concentration.

# Answers

## Mass balance equations

The mass balances for ammonia ( $NH_3$ ), nitrate ( $NO_3^-$ ) and oxygen ( $O_2$ ) can be written as the following differential equations:

$$\begin{aligned}\frac{\partial[NO_3^-]}{\partial t} &= D \frac{\partial^2[NO_3^-]}{\partial x^2} - v \frac{\partial[NO_3^-]}{\partial x} + \text{Nitrification} \\ \frac{\partial[NH_3]}{\partial t} &= D \frac{\partial^2[NH_3]}{\partial x^2} - v \frac{\partial[NH_3]}{\partial x} - \text{Nitrification} \\ \frac{\partial[O_2]}{\partial t} &= D \frac{\partial^2[O_2]}{\partial x^2} - v \frac{\partial[O_2]}{\partial x} + \text{Aeration} - 2 \cdot \text{Nitrification}\end{aligned}$$

Here,  $D$  is the dispersion coefficient due to tidal mixing, and  $v$  is the advective velocity (in  $m\ s^{-1}$ ), calculated from the discharge ( $Q$ ) and cross-sectional area ( $A$ ) as  $v = Q/A$ . Thus, the 1st and 2nd term in the differential equations describe the rate of change due to transport by dispersion (diffusion-like) and advection, respectively. Note that the parameters characterizing the magnitude of this change are the *same* for each component, which is because all components are *dissolved* substances affected in the same way by the water flow. Also note that we assumed that  $D$  and  $u$  are *not* varying along the estuary, which is why we could take them out of the spatial derivatives.

The boundary conditions at the upper boundary (river side):  $[O_2]_{x=0} = 0.1$ ,  $[NO_3^-]_{x=0} = 0.3$ ,  $[NH_3]_{x=0} = 0.1$ . The boundary conditions at the lower boundary (sea side):  $[O_2]_{x=1e5} = 0.3$ ,  $[NO_3^-]_{x=1e5} = 0.050$ ,  $[NH_3]_{x=1e5} = 0.010$ . All values are in  $mol\ m^{-3}$ .

It is not necessary to model the proton ( $H^+$ ) or water ( $H_2O$ ) concentrations in this exercise.

## R implementation

Note how the vector of state variables is defined in models with transport. From zero-dimensional models (models without transport), we are used to define state variables in a vector with *named* components, for example like this:

```
# state variables in a zero-dimensional models
state <- c(O2=0.1, NO3=0.3, NH3=0.1)
```

This made it easy to refer to the state variables in the model function using the `with(as.list(...` function.

In models with transport, each state variable is a *vector* by itself! Thus, this “trick” is *no longer* possible. Instead, we concatenate the vectors for each state variable into a *long* vector called *state*, and then “unpack” the individual vectors from this variable within the model function.

```
require(ReacTran) # package with solution methods

# Note: units are: m, days, mol/m3.

# model grid
Length <- 100000 # m
N <- 500 # - number of boxes
dx <- Length/N # m grid size
x <- seq(dx/2, by = dx, length.out = N) # m position of cells
Area <- 20000 # m2, cross-sectional area of the estuary
day2sec <- 24*3600 # number of seconds in a day
```

```

# State variables, each is a vector of length=N - initial concentrations set to 0
Oxygen <- rep(0, times = N)
Nitrate <- rep(0, times = N)
Ammonia <- rep(0, times = N)
state <- c(Oxygen, Nitrate, Ammonia)
SVnames <- c("Oxygen", "Nitrate", "Ammonia")

# model parameters
pars <- c(
  riverO2 = 0.1,          # river oxygen conc [mol/m3]
  seaO2   = 0.3,          # marine oxygen conc [mol/m3]
  riverNit = 0.3,         # river nitrate conc [mol/m3]
  seaNit  = 0.05,         # marine nitrate conc
  riverAmm = 0.1,         # river ammonium conc
  seaAmm  = 0.01,         # marine ammonium conc
  depth   = 10,           # [m]
  v        = 100/Area*day2sec, # advection velocity [m/d], discharge/cross-sect. area
  Ddisp    = 350*day2sec,   # dispersion coefficient [m2/d], tidal dispersion
  rnitri   = 0.1,          # nitrification rate constant, [/d]
  ksO2     = 1e-3,         # Monod ct for O2 limitation of nitrification [mol/m3]
  piston   = 1.0,          # piston velocity [m/day]
  O2sat    = 0.3           # saturated oxygen concentration [mol/m3], solubility
)

# Model function
Scheldt1D <- function(t, C, pars) {          # C is a LONG vector of state variables
  with (as.list(pars),{

    # here we "unpack" the vectors of individual state variables from the LONG input vector
    Oxygen <- C[ 1 : N]
    Nitrate <- C[ (N+1) : (2*N)] # note parentheses around (N+1) and (2*N)!!
    Ammonia <- C[(2*N+1) : (3*N)]

    # Transport - tran.1D solves the "transport terms" (spatial derivatives).
    # It also implements the boundary conditions!
    TranOxygen <- tran.1D(C = Oxygen,
      C.up = riverO2, C.down = seaO2, # upstream and downstream concentrations
      D = Ddisp, v = v, dx = dx)

    TranNitrate <- tran.1D(C = Nitrate,
      C.up = riverNit, C.down = seaNit,
      D = Ddisp, v = v, dx = dx)

    TranAmmonia <- tran.1D(C = Ammonia,
      C.up = riverAmm, C.down = seaAmm,
      D = Ddisp, v = v, dx = dx)

    # Nitrification rate (calculated in every location)
    Nitrification <- rnitri * Ammonia * Oxygen/(Oxygen+ksO2)

    # air-water exchange rate (calculated in every location)
    Aeration <- -piston/depth * (Oxygen - O2sat)
  })
}

```

```

# the rates of change = transport + net reaction
dNitrate <- TranNitrate$dC + Nitrification
dAmmonia <- TranAmmonia$dC - Nitrification
dOxygen <- TranOxygen$dC - 2*Nitrification + Aeration

list(c(dOxygen, dNitrate, dAmmonia), # the rates of change
     TotalNitrogen = mean(Nitrate + Ammonia),
     Nitrification = Nitrification,
     Aeration = Aeration,
     NH3influx = TranAmmonia$flux.up,
     NO3influx = TranNitrate$flux.up,
     O2influx = TranOxygen$flux.up,
     NH3efflux = TranAmmonia$flux.down,
     NO3efflux = TranNitrate$flux.down,
     O2efflux = TranOxygen$flux.down,
     # total fluxes in-out and integrated rates
     TotNinflux = TranAmmonia$flux.up + TranNitrate$flux.up,
     TotNefflux = TranAmmonia$flux.down + TranNitrate$flux.down,
     TotalNitrification = sum(Nitrification * dx),
     TotalAeration = sum(Aeration*dx)
)
})
}

```

## Comparison of the 1970s and the current situation

We estimate the steady-state solution for the current situation and for the 1970s.

```

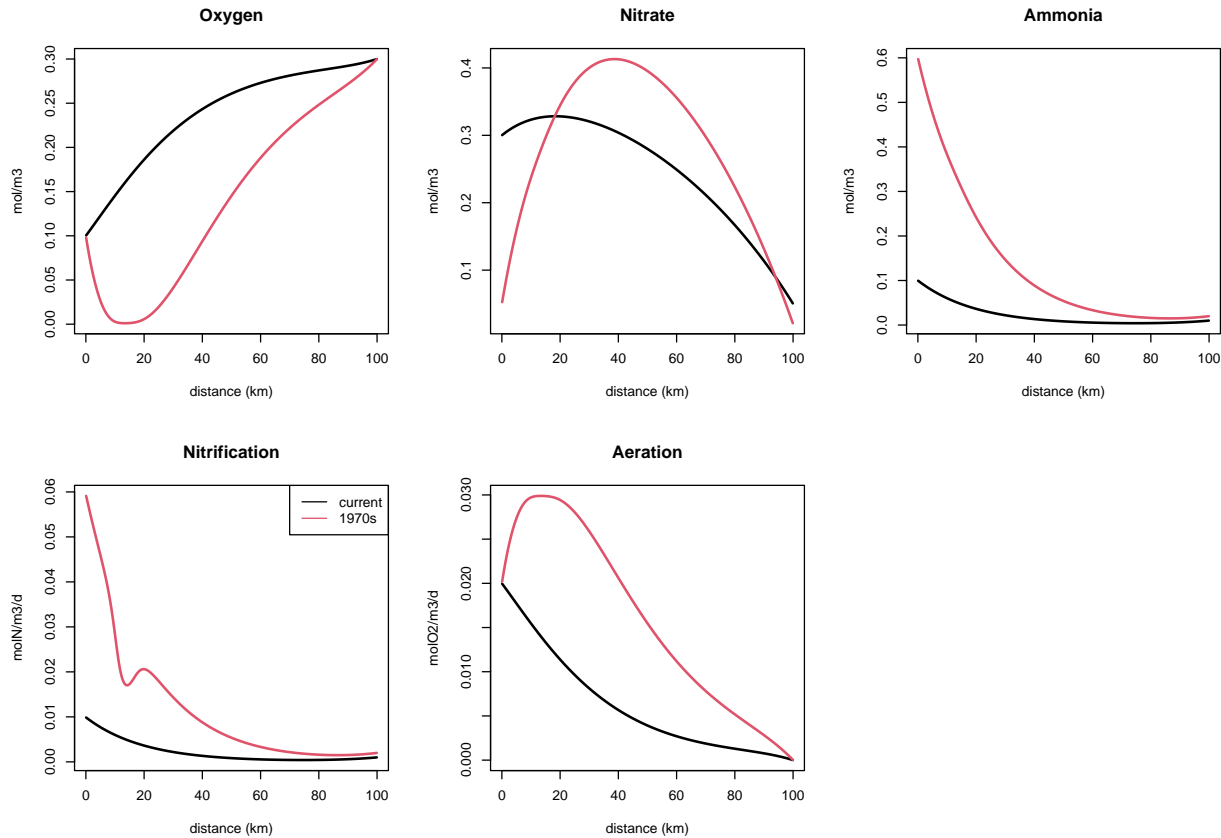
Scheldt00 <- steady.1D(y = state, parms = pars, func = Scheldt1D, positive = TRUE,
                      nspec = length(SVnames), dimens = N, names = SVnames)

# The parameters for the 1970s
par70 <- pars
par70["riverNit"] <- 0.05 # river nitrate conc
par70["seaNit"] <- 0.02 # marine nitrate conc
par70["riverAmm"] <- 0.60 # river ammonium conc
par70["seaAmm"] <- 0.02 # marine ammonium conc

Scheldt70 <- steady.1D(y = state, parms = par70, func = Scheldt1D, positive = TRUE,
                      nspec = length(SVnames), dimens = N, names = SVnames)

plot(Scheldt00, Scheldt70, grid=x/1000, lwd=2, lty=1,
     mfrow=c(2,3), ylab="mol/m3", xlab="distance (km)")
plot(Scheldt00, Scheldt70, grid=x/1000, lwd=2, lty=1, mfrow=NULL,
     which = "Nitrification", ylab="molN/m3/d", xlab="distance (km)")
legend("topright", legend = c("current", "1970s"), lty = 1, col = 1:2)
plot(Scheldt00, Scheldt70, grid=x/1000, lwd=2, lty=1, mfrow=NULL,
     which = "Aeration", ylab="molO2/m3/d", xlab="distance (km)")

```



## Budget in Mmol/year

The current model function returns the fluxes in  $\text{mol m}^{-2} \text{d}^{-1}$ . To construct the budget for the entire estuary, we converts the values to  $10^6 \text{ mol yr}^{-1}$ . These budget values can be added to a diagram that represents the relevant state variables for the *entire* estuary as boxes, similar to the one shown in Figure 1.

```
f1      <- Area/1e6*365      # from mol m-2 d-1 to 106 mol yr-1
toselect <- c("NH3influx", "NO3influx", "O2influx",
              "NH3efflux", "NO3efflux", "O2efflux",
              "TotalNitrification", "TotalAeration" )
BUDGET <- data.frame(Megamol_per_yr_2000 = unlist(Scheldt00[toselect]),
                    Megamol_per_yr_1970s = unlist(Scheldt70[toselect]))*f1
knitr::kable(BUDGET, digits = 0)
```

	Megamol_per_yr_2000	Megamol_per_yr_1970s
NH3influx	1433	8144
NO3influx	168	-5487
O2influx	-675	5013
NH3efflux	-96	-116
NO3efflux	1696	2773
O2efflux	713	182
TotalNitrification	1528	8260
TotalAeration	4445	11689



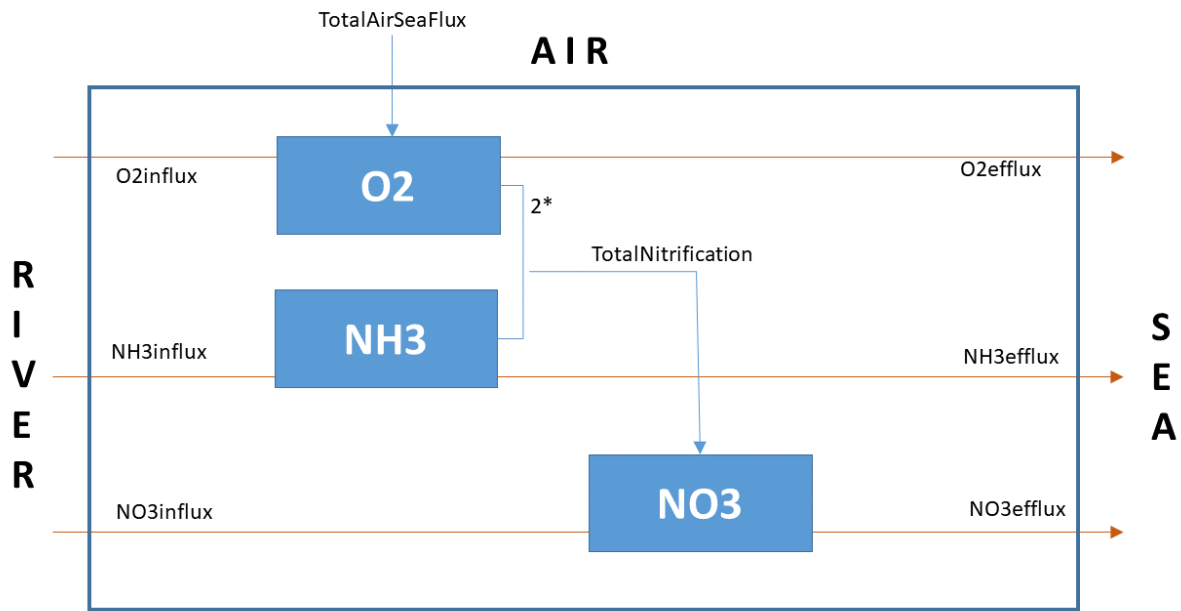


Figure 1: Nitrogen budget for the entire Western Scheldt estuary. Values are shown in the table above.

## The impact of ammonia concentration in inflowing waters

The sensitivity analysis is run using a for-loop, where the minimal value in the steady state solution is found for each run of the loop.

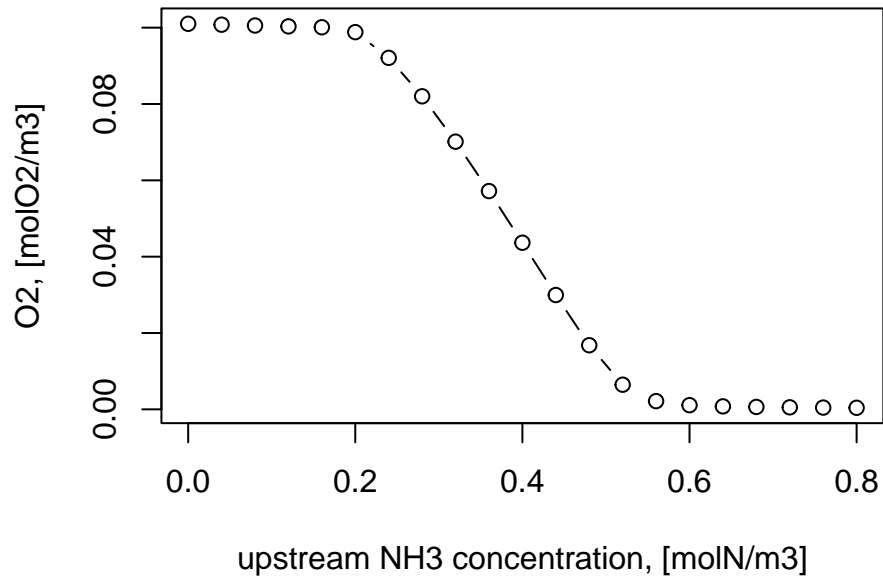
```
Sens <- function(NH3up){
  parsNH3 <- pars
  parsNH3["riverAmm"] <- NH3up # river ammonium conc
  ScheldtNH3 <- steady.1D(y = state, parms = parsNH3, func = Scheldt1D, positive = TRUE,
    nspec = length(SVnames), dimens = N, names = SVnames)
  return(min(ScheldtNH3$y[, "Oxygen"]))
}

NH3_vect <- seq(from = 0, to = 0.8, by = 0.04)
O2_vect <- NULL

# use for-loop to find the minimal O2 concentration for each value in NH3_vect
for (NH3up in NH3_vect)
  O2_vect <- c(O2_vect, Sens(NH3up))

plot(NH3_vect, O2_vect, type="b", xlab = "upstream NH3 concentration, [molN/m3]",
  ylab = "O2, [molO2/m3]", main = "Minimal O2 concentration in the estuary")
```

## Minimal O2 concentration in the estuary



## References

R Core Team (2020). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <https://www.R-project.org/>.

Soetaert Karline (2009). rootSolve: Nonlinear root finding, equilibrium and steady-state analysis of ordinary differential equations. R-package version 1.6

Soetaert, Karline and Meysman, Filip, (2012). Reactive transport in aquatic ecosystems: Rapid model prototyping in the open source software R Environmental Modelling & Software, 32, 49-60.