
# Efficient Operation of Urban Wastewater Treatment Plants (EOLI)

**Work Package 2**

# WP2 – Model Selection and Parameter Identification

## *EM2 Associated to C/N Removal Processes*

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# Introduction

This report presents the results of the parameter identification of the carbon-nitrogen removal EM2 models of the SBR's operated in France (LBE/ INRA) and Italy (POLIMI).

The model selection of these processes deals is in line with the monitoring and control objectives, i.e. in particular to optimize the SBR's operation, e.g. via appropriate phase-switching strategies. The phases that are considered to be potentially controlled are the anoxic phase and the aerobic phase. These correspond to denitrification and nitrification activities, respectively. For this reason, the parameter identification is only applied to these two phases.

The following procedure has been applied in order to provide suitable models.

1) The model equations including the parameters to be identified are proposed.
2) All the experimental data generated and used for the parameter identification are studied and analysed for each phase. This step allows the distribution of the data in two sets (one for parameter calibration, one for model validation).
3) The parameter identification is performed by following the procedure [BAS 90] defined at the meeting of Mexico and recalled at the meeting in Compiègne, i.e. independent identification of the yield coefficients, of the kinetic parameters, and of the transfer coefficients.
4) A sensitivity analysis of the parameters is performed prior to the parameter calibration in order to distinguish between sensitive and insensitive parameters, and possibly simplify the identification procedure.
5) An analysis of the parameter identification results is then performed, in particular confidence intervals for each parameter, as well as all the assumptions and steps followed during the identification to provide the most reliable model possible with respect to the objectives of the project and the data available (this includes detailed explanations about possible choices of model structures and/or (non-)selection of some (bio)chemical reactions or physical phenomena).

It has been agreed at the meeting of Compiègne that two sub-models are considered to describe appropriately the studied processes; the first one, called EM2-a, is related to the Italian wastewater treatment process in which 2-step models of denitrification and nitrification are introduced; the second one, called EM2-b, corresponds to the French wastewater treatment with 1-step models of denitrification and nitrification. Therefore, this report will be presented in two parts: the parameter identification of the EM2-a model and of the EM2-b model.

## 1. EM2-a: Carbon/Nitrogen removal model of the POLIMI SBR

The POLIMI data show that the denitrification takes place in 2 steps :

1) $NO_3$ reduction into $NO_2$
2) $NO_2$ reduction into $N_2$

Therefore, a 2-step model is considered for describing the POLIMI process. For the model representation, let us denote $S_C$, $S_{NO3}$, $S_{NO2}$, $S_{NH}$, $S_N$, $S_O$, $X_h$ and $X_a$, the biodegradable substrate concentration (i.e. carbon, mg COD/L), the nitrate nitrogen concentration (mg N/L), the nitrite nitrogen concentration (mg N/L), the ammonia nitrogen concentration (mg N/L), the soluble

organic nitrogen concentration (mg N/L), the concentration of the dissolved oxygen (DO) in the water (mg/L) and the concentration of the heterotroph and autotroph bacteria, respectively.

### *1.1. Anoxic Phase with Two-step denitrification model*

The two-step denitrification in the anoxic phase of the POLIMI process can be described, according to the IWA notations [BOU 96, DOC 01], as follows:

- First step: $NO_3$ reduction,

$$\frac{1}{Y_{h1}} S_C + \frac{1}{1.17}\frac{1-Y_{h1}}{Y_{h1}} S_{NO_3} \xrightarrow{r_{h1}} X_h + \frac{1}{1.71}\frac{1-Y_{h2}}{Y_{h2}} S_{NO_2} \tag{1}$$

where $r_{h1}$ is its reaction rate, equal to $\mu_{h1} X_h$, with

$$\mu_{h1} = \mu_{h1\max} \frac{S_C}{K_{Ch1} + S_C} \frac{S_{NO_3}}{K_{NO_3 h} + S_{NO_3}} \tag{2}$$

- Second step: $NO_2$ reduction,

$$\frac{1}{Y_{h2}} S_C + \frac{1}{1.71}\frac{1-Y_{h2}}{Y_{h2}} S_{NO_2} \xrightarrow{r_{h2}} X_h + N_2 \tag{3}$$

with its reaction rate $r_{h2} = \mu_{h2} X_h$, where

$$\mu_{h2} = \mu_{h2\max} \frac{S_C}{K_{Ch2} + S_C} \frac{S_{NO_2}}{K_{NO_2 h} + S_{NO_2}} \tag{4}$$

Ammonification activities that also occur in the anoxic phase can be described by:

$$S_N \xrightarrow{r_N} S_{NH} \tag{5}$$

where $S_N$ = TKN – $S_{NH}$, is the soluble organic nitrogen concentration with the reaction rate: $r_N = \mu_0 S_N$, where $\mu_0$ is constant.

The endogenous respiration in the anoxic phase is described by the following reaction :

$$C_X + S_{NO_3} \xrightarrow{r_{e1}} \ldots \tag{6}$$

with a reaction rate $r_{e1}$. $C_X$ is the organic carbon produced from dead biomass.

The biomass decay is represented by the following reaction scheme:

$$\begin{cases} X_h \xrightarrow{r_{d1}} X_d \\ X_a \xrightarrow{r_{d2}} X_d \end{cases} \text{ and } X_d \xrightarrow{r_{dX}} C_X \tag{7}$$

where $X_d$ is the dead biomass. The organic carbon $C_X$ will then hydrolyze into new organic carbon, via the following reaction:

$$C_X \xrightarrow{r_{Cx}} S_C \tag{8}$$

The system dynamics can be then represented by the following differential equations:

$$\frac{dS_C}{dt} = -k_1 \eta_{h1} X_h - k_2 \eta_{h2} X_h + k_{Cx} r_{Cx} \quad (9)$$

$$\frac{dS_{NO_3}}{dt} = -k_3 \eta_{h1} X_h - k_{e1} r_{e1} \quad (10)$$

$$\frac{dS_{NO_2}}{dt} = k_4 \eta_{h1} X_h - k_5 \eta_{h2} X_h \quad (11)$$

$$\frac{dS_{NH}}{dt} = k_6 r_N \quad (12)$$

$$\frac{dS_N}{dt} = -r_N \quad (13)$$

The biomass dynamics are given by the following equations:

$$\frac{dX_h}{dt} = \eta_{h1} X_h + \eta_{h2} X_h - r_{d1} \text{ with } r_{d1} = k_{d1} X_h \quad (14)$$

$$\frac{dX_a}{dt} = -r_{d2} \text{ with } r_{d2} = k_{d2} X_h \quad (15)$$

$$\frac{dX_d}{dt} = r_{d1} + r_{d2} - k_{dX} r_{dX} \quad (16)$$

$$\frac{dC_X}{dt} = r_{dX} - r_{Cx} - k_{e2} r_{e1} \quad (17)$$

In the above equations, the yield coefficients $k_i$ ($i$ = 1 to 5) are related to the IWA notations in the previous reactions as follows:

$$k_1 = \frac{1}{Y_{h1}},\ k_2 = \frac{1}{Y_{h2}},\ k_3 = \frac{1 - Y_{h1}}{1.17 Y_{h1}},\ k_4 = k_5 = \frac{1 - Y_{h2}}{1.71 Y_{h2}} \quad (18)$$

It is worth noting that the above model contains some parameters that are not directly identifiable due to the lack of measurement accessibility for some processs components (like dead biomass $X_d$, or the organic carbon produced from dead biomass $C_x$). It is therefore essential to simplify the model. This can be done by considering the following observations and assumptions based on the knowledge and on the scientific literature.

The available data show that there is always some remaining carbon at the end of each phase. This corresponds to the organic carbon produced from dead biomass $C_x$. As this component is not accessible for measurement, we have assumed the existence of a "non-biodegradable" carbon in the model, denoted $S_{Cmin}$. By this assumption, the hydrolysis reaction is removed as well as the corresponding term containing "$r_{Cx}$" from the organic carbon mass balance equation (9), since it is already taken into account in the non-biodegradable carbon. Therefore equation (9) can be rewritten as follows:

$$\frac{dS_C}{dt} = -k_1 \eta_{h1} X_h - k_2 \eta_{h2} X_h \quad (19)$$

with $\mu_{h1}$ corresponding to:

$$\mu_{h1} = \mu_{h1\max} \frac{S_C - S_{C\min}}{K_{Ch1} + S_C - S_{C\min}} \frac{S_{NO_3}}{K_{NO_3 h} + S_{NO_3}} \tag{20}$$

and $\mu_{h2}$ to:

$$\mu_{h2} = \mu_{h2\max} \frac{S_C - S_{C\min}}{K_{Ch2} + S_C - S_{C\min}} \frac{S_{NO_2}}{K_{NO_2 h} + S_{NO_2}} \tag{21}$$

The same phenomenon can also be noted in the soluble organic nitrogen, $S_N$. Therefore we can also make assumption of a non-degradable $S_N$, denoted $S_{N\min}$, such that the ammonification rate can be now expressed as follows:

$$r_N = \rho_0 (S_N - S_{N\min}) \tag{22}$$

Since the $NO_3$ consumption by the endogenous respiration is quite low, let us also assume that we can neglect this term in the $NO_3$ mass balance equation (10), which becomes :

$$\frac{dS_{NO_3}}{dt} = -k_3 \mu_{h1} X_h \tag{23}$$

Since there is no significant experimental evidence of biomass decay from the available data, the biomass death reactions are assumed to be negligible and the related kinetic terms "$r_{d1}$" and "$r_{d2}$" are removed from the biomass dynamical equations. In the anoxic phase, the biomass growth follows then only the expressions:

$$\frac{dX_h}{dt} = \mu_{h1} X_h + \mu_{h2} X_h \tag{24}$$

$$\frac{dX_a}{dt} = 0 \tag{25}$$

without taking into account the evolution of $X_d$ and $C_X$.

After extensive sensitivity analysis, the parameters to be identified in this phase are the following:

1) yield coefficients : $Y_{h1}$, $Y_{h2}$ and $k_6$,
2) kinetic parameters : $\mu_{h1\max}$, $\mu_{h2\max}$, $K_{Ch1}$, $K_{Ch2}$, $K_{NO3h}$, $K_{NO2h}$ and $\mu_0$

### 1.1.1. Data selection

As mentioned in the introduction, the data are treated and analyzed for each phase. This task aims at distributing the data between those that will be used for the parameter calibration and those that will used for the parameter validation. The first step of data selection is to plot all the given data. This operation can help to visualize the link between the data and the process behaviour, and to possibly detect some incoherence between the modelling assumptions and the data. In the present instance, data corresponding to experiments where reactions have not reached their completion have not be used for the calibration, due to the risk to result to poor kinetics

parameter identification. Yet these data can possibly be used for the validation. It has been agreed that the proportion of data for the calibration related to those for the validation is 2 to 3, i.e. two third of the data used for parameter calibration. More details about the identification procedure can be found in the file "EM2a_identification.xls".

### 1.1.2. Yield coefficients

The yield coefficients to be identified are $Y_{h1}$, $Y_{h2}$ and $k_6$. Based on the previous assumptions, we can write the following sub-models:

$$\frac{d}{dt}\begin{bmatrix} S_C \\ S_{NO_3} \\ S_{NO_2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{Y_{h1}} & -\frac{1}{Y_{h2}} \\ \frac{1}{1.17}\frac{1-Y_{h1}}{Y_{h1}} & 0 \\ \frac{1}{1.71}\frac{1-Y_{h2}}{Y_{h2}} & -\frac{1}{1.71}\frac{1-Y_{h2}}{Y_{h2}} \end{bmatrix} \begin{bmatrix} \rho_{h1} X_h \\ \rho_{h2} X_h \end{bmatrix} \tag{26}$$

and

$$\frac{d}{dt}\begin{bmatrix} S_{NH} \\ S_N \end{bmatrix} = \begin{bmatrix} k_6 \\ -1 \end{bmatrix} r_N \tag{27}$$

Equation (26) can be viewed as a system of 3 equations with 2 "unknowns" (the two kinetic terms, $\rho_{h1}X_h$ and $\rho_{h2}X_h$, that are not accessible for measurement) : we can eliminate both kinetic terms $\rho_{h1}X_h$ and $\rho_{h2}X_h$ and rewrite the 3 equations into the following unique equation :

$$-\frac{1-Y_{h2}}{1.71}\frac{dS_C}{dt} + \frac{1.17}{1.71}\frac{1-Y_{h2}}{1-Y_{h1}}\left(1+\frac{Y_{h1}}{Y_{h2}}\right)\frac{dS_{NO_3}}{dt} + \frac{dS_{NO_2}}{dt} = 0 \tag{28}$$

which is in a standard linear regression form :

$$y = \theta^T \varphi \tag{29}$$

with :

$$y = \frac{dS_{NO_2}}{dt}, \quad \varphi = \begin{bmatrix} \frac{dS_C}{dt} \\ \frac{dS_{NO_3}}{dt} \end{bmatrix}$$
$$\theta = \begin{bmatrix} \theta_1 \\ \theta_2 \end{bmatrix} = \begin{bmatrix} -\frac{1-Y_{h2}}{1.71} \\ \frac{1.17}{1.71}\frac{1-Y_{h2}}{1-Y_{h1}}\left(1+\frac{Y_{h1}}{Y_{h2}}\right) \end{bmatrix} \tag{30}$$

the unknown parameters $\alpha_1$ and $\alpha_2$ are calculated from any linear regression technique, and the yield coefficients $Y_{h1}$ and $Y_{h2}$ by inverting the above definition of $\alpha$.

The same approach can be applied to equation (27), which becomes by eliminating $r_N$ :

$$\frac{dS_{NH}}{dt} + k_6 \frac{dS_N}{dt} = 0 \tag{31}$$

Equation (31) is then used to estimate $k_6$.

The calibration of the coefficients $Y_{h1}$, $Y_{h2}$ and $k_6$ has been carried out using the Microsoft Excel software. Each experiment gives a set of parameters. Therefore $n$ experiments will give $n$ sets of parameters, from which we can compute their mean values, standard deviations and also deduce their confidence intervals (see **Appendix 2**). Note here that we apply a confidence level of 95%.

The identification results are given in Table 1-1. We can see that the confidence intervals are low except for $k_6$ (about 20%).

Table 1-1. EM2-a yield coefficients in the anoxic phase

| Yield coefficient | Unity | Value | Confidence Interval |
|---|---|---|---|
| $Y_{h1}$ | mg VSS/mg COD | 0.616 | 0.152 |
| $Y_{h2}$ | mg VSS/mg COD | 0.788 | 0.129 |
| $k_6$ | mg N-NH/mg N | 0.706 | 0.143 |

### 1.1.3. Kinetics parameters

The corresponding kinetics parameters of the two-step denitrification to be identified are $\mu_{h1\max}$, $\mu_{h2\max}$, $K_{Ch1}$, $K_{Ch2}$, $K_{NO3h}$ and $K_{NO2h}$. Since the yield coefficients are already identified, let us use the model equations (9)(10)(11)(24) to generate model predictions based on the estimated values of the kinetic parameters:

$$\frac{d}{dt}\begin{bmatrix}\hat{S}_C\\ \hat{S}_{NO_3}\\ \hat{S}_{NO_2}\\ \hat{X}_h\end{bmatrix} = \begin{bmatrix} -\frac{1}{Y_{h1}} & -\frac{1}{Y_{h2}} \\ \frac{1}{1.17}\frac{1-Y_{h1}}{Y_{h1}} & 0 \\ \frac{1}{1.71}\frac{1-Y_{h2}}{Y_{h2}} & -\frac{1}{1.71}\frac{1-Y_{h2}}{Y_{h2}} \\ 1 & 1 \end{bmatrix} \begin{bmatrix} \mu_{h1\max}\dfrac{\hat{S}_C - S_{C\min}}{K_{Ch1}+\hat{S}_C - S_{C\min}}\dfrac{\hat{S}_{NO_3}}{K_{NO_3h}+\hat{S}_{NO_3}}\hat{X}_h \\ \mu_{h2\max}\dfrac{\hat{S}_C - S_{C\min}}{K_{Ch2}+\hat{S}_C - S_{C\min}}\dfrac{\hat{S}_{NO_2}}{K_{NO_2h}+\hat{S}_{NO_2}}\hat{X}_h \end{bmatrix} \tag{32}$$

Since the values of $S_C(0)$, $S_{NO3}(0)$, $S_{NO2}(0)$ and $X_h(0)$ are known, a parameter optimization method, such as Levenberg-Marquardt or Gauss-Newton algorithm, is considered that minimizes the following criterion:

$$\min J\left(\mu_{h1\max}, K_{Ch1}, K_{NO_3h}, \mu_{h2\max}, K_{Ch2}, K_{NO_2h}\right) = \min \frac{1}{N}\sum_i \left[S_C, S_{NO_3}, S_{NO_2}\right] - \left[\hat{S}_C, \hat{S}_{NO_3}, \hat{S}_{NO_2}\right] \tag{33}$$

Similarly equation (13) allows us to identify the kinetics constant of the ammonification, $\mu_0$, by using the following model predictor :

$$\frac{d}{dt}\hat{S}_N = \mu_0 \hat{S}_N \tag{34}$$

and minimizing the following criterion:

$$\min J_N(\mu_0) = \min \frac{1}{N} \sum_i \left(S_N - \hat{S}_N\right)^2 \tag{35}$$

We have applied the identification procedure to the POLIMI calibration data using the Matlab function “lsqnonlin”. This leads to the following set of parameters (Table 1-2).

Table 1-2. EM2a kinetic parameters in anoxic phase

| Kinetics parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $\mu_{h1\,max}$ | $min^{-1}$ | 0.012 | 0.003 |
| $K_{Ch1}$ | mg COD/L | 57.45 | 21.15 |
| $K_{NO3h}$ | mg N/L | 44.65 | 7.87 |
| $\mu_{h2\,max}$ | $min^{-1}$ | 0.0015 | 0.0007 |
| $K_{Ch2}$ | mg COD/L | 21.17 | 16.05 |
| $K_{NO2h}$ | mg N/L | 4.99 | 4.22 |
| $\mu_0$ | $min^{-1}$ | 0.0527 | 0.0017 |

As previously, we have computed the mean values, standard deviations and confidence intervals by using the same method of the MS Excel software (see **Appendix 2**).

### *1.2. Aerobic Phase with Two-step nitrification model*

The aerobic phase is related, on one hand, to a nitrifying activity that related to the POLIMI data can be described by a two-step nitrification according to the IWA [PET 00, DOC 01]:

- First step: $NH_4$ oxidation to nitrite ($NO_2$), of which concentration is denoted $S_{NO2}$ (*mg* N/*L*),

$$\frac{1}{Y_{a1}} S_{NH} + \frac{3.43 - Y_{a1}}{Y_{a1}} S_O \xrightarrow{r_{a1}} X_a + \frac{1}{Y_{a1}} S_{NO_2} \tag{36}$$

where $r_{a1}$ is the first step nitrification rate, with $r_{a1} = \mu_{a1} X_a$ and

$$\mu_{a1} = \mu_{a1\max} \frac{S_{NH}}{K_{NH} + S_{NH}} \frac{S_O}{K_{Oa1} + S_O} \tag{37}$$

- Second step: $NO_2$ oxidation to nitrate ($NO_3$) with concentration $S_{NO3}$ (*mg* N/*L*),

$$\frac{1}{Y_{a2}} S_{NO_2} + \frac{1.14 - Y_{a2}}{Y_{a2}} S_O \xrightarrow{r_{a2}} X_a + \frac{1}{Y_{a2}} S_{NO_3} \tag{38}$$

and $r_{a2}$ is the second step nitrification rate, with $r_{a2} = \mu_{a2} X_a$ and

$$\mu_{a2} = \mu_{a2\max} \frac{S_{NO_2}}{K_{NO_2 a} + S_{NO_2}} \frac{S_O}{K_{Oa2} + S_O} \tag{39}$$

On the other hand, the aerobic phase also includes the following C-removal reaction:

$$\frac{1}{Y_h} S_C + \frac{1 - Y_h}{Y_h} S_O \xrightarrow{r_h} X_h \tag{40}$$

with the reaction rate, $r_h = \mu_h X_h$ that takes into account the non-degradable C, i.e.:

$$\mu_h = \mu_{h\max} \frac{S_C - S_{C\min}}{K_{Ch} + S_C - S_{C\min}} \frac{S_O}{K_{Oh} + S_O} \tag{41}$$

The ammonification is still active in the aerobic phase:

$$S_N \xrightarrow{r_N} S_{NH} \tag{42}$$

where the ammonification rate is described by:

$$r_N = \mu_0 (S_N - S_{N\min}) \text{ with } \mu_0 \text{ constant} \tag{43}$$

with a non-degradable term of $N$.

Here, the endogeneous respiration is associated to:

$$C_X + S_O \xrightarrow{r_{e2}} \dots \tag{44}$$

with a reaction rate of $r_{e2}$.

The biomass mortality is associated to the following reactions:

$$\begin{cases} X_h \xrightarrow{r_{a1}} X_d \\ X_a \xrightarrow{r_{a2}} X_d \end{cases} \text{ and } X_d \xrightarrow{r_{dX}} C_X \tag{45}$$

As previously, the terms corresponding to the biomass decay are assumed to be included in the biomass growth. Therefore we do not put these terms in the model equations.

The organic carbon $C_X$ also hydrolyses into new organic carbon:

$$C_X \xrightarrow{r_{Cx}} S_C \tag{46}$$

This term is already taken into account in the non-biodegradability assumption.

Therefore the dynamical model is given by the following equations:

$$\frac{dX_h}{dt} = \mu_h X_h \tag{47}$$

$$\frac{dX_a}{dt} = \mu_{a1} X_a + \mu_{a2} X_a \tag{48}$$

$$\frac{dS_C}{dt} = -k_7 \mu_h X_h \tag{49}$$

$$\frac{dS_O}{dt} = -k_8 \mu_h X_h - k_9 \mu_{a1} X_a - k_{10} \mu_{a2} X_a - r_{e2} + k_L a\,(S_{Os} - S_O) \quad (50)$$

$$\frac{dS_{NO3}}{dt} = k_{11} \mu_{a2} X_a \quad (51)$$

$$\frac{dS_{NO2}}{dt} = k_{13} \mu_{a1} X_a - k_{12} \mu_{a2} X_a \quad (52)$$

$$\frac{dS_{NH}}{dt} = -k_{14} \mu_{a1} X_a + k_{6b}\, r_N \quad (53)$$

$$\frac{dS_N}{dt} = -r_N \quad (54)$$

In equation (50), there is a term, denoted $r_{e2}$, corresponding to the aerobic endogeneous respiration of the biomass. Indeed this term is small compared to the others and is almost constant. Therefore we have assumed that it is constant and can be associated with a gap to the DO saturation constant in the liquid medium, that is equal to ($r_{e2}/k_La$). Consequently, we can simplify the model by removing the term $r_{e2}$ and putting $S_{O\max}$ instead of $S_{Os}$ that represents the maximal DO in the liquid medium, where:

$$S_{O\max} = S_{Os} - \frac{r_{e2}}{k_L a} \quad (55)$$

This assumption allows us to simplify the expression (50) such as:

$$\frac{dO}{dt} = -k_8 \mu_h X_h - k_9 \mu_{a1} X_a - k_{10} \mu_{a2} X_a + k_L a\,(S_{O\max} - S_O) \quad (56)$$

This equation is simpler then the previous one as the value of $S_{O\max}$ can be directly deduced from the available data.

Related to the standard IWA notations, the yield coefficients $k_i$ ($i$ = 7 to 14) correspond to the following expressions:

$$k_7 = \frac{1}{Y_h},\ k_8 = \frac{1 - Y_h}{Y_h} \quad (57)$$

$$k_9 = \frac{3.43 - Y_{a1}}{Y_{a1}},\ k_{13} = k_{14} = \frac{1}{Y_{a1}},\ k_{10} = \frac{1.14 - Y_{a2}}{Y_{a2}},\ k_{11} = k_{12} = \frac{1}{Y_{a2}} \quad (58)$$

Thus, the parameters to be identified are the following yield coefficients: $Y_h$, $Y_{a1}$, $Y_{a2}$ and $k_{6b}$, and the following kinetics parameters: $\mu_{h\max}$, $\mu_{a1\max}$, $\mu_{a2\max}$, $K_{Ch}$, $K_{Oh}$, $K_{NH}$, $K_{Oa1}$, $K_{NO2a}$, $K_{Oa2}$ and $\mu_0$.

### 1.2.1. Data selection

As the aerobic phase is independent of the anoxic one, the data used for the calibration in the aerobic phase are not necessarily considered in the same dataset than the one used for the anoxic phase. A set of data is selected according to the following criteria:

- The data must be issued from the experiments with the same operation conditions, e.g. the same $k_La$ and $S_{Os}$ (or $S_{Omax}$) values;
- The initial values of the kinetics parameters before the optimization procedure are determined by a random number technique, such as Monte Carlo procedure allowing to approximate as close as possible to the global optimum;
- The identified parameters in one set must be of the same order of magnitude after the parameters optimization procedure.

### 1.2.2. Gas transfer parameters

Due to a change in the aeration system, the transfer coefficients have identified independently over two periods of time, i.e. before and after Christmas stop, as well as globally over both periods. The techniques used for $k_La$ identification are based on hydrodynamic tests (see the first annual report of EOLI).

Table 1-3. EM2a gas parameters before Christmas stop

| Parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $k_La$ | $min^{-1}$ | 0.363 | 0.0485 |
| $S_{Omax}$ | mg DO/L | 7.793 | 0.2038 |

Table 1-4. EM2a gas parameters after Christmas stop

| Parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $k_La$ | $min^{-1}$ | 0.119 | 0.0080 |
| $S_{Omax}$ | mg DO/L | 6.515 | 0.1150 |

The transfer parameters corresponding to each period are presented in the Tables 1-3 and 1-4 while the unique set of parameters is given in Table 1-5. Confidence intervals are computed as described in **Appendix 2**.

Table 1-5. EM2-a common gas transfer parameters

| Parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $k_La$ | $min^{-1}$ | 0.252 | 0.079 |
| $S_{Omax}$ | mg DO/L | 7.383 | 0.359 |

### 1.2.3. Yield coefficients

The yield coefficients to be identified are $Y_h$, $Y_{a1}$, $Y_{a2}$ and $k_{6b}$. Some experiment evidence has shown that the value of $k_{6b}$ is equal to that of $k_6$ in the anoxic phase. Therefore, three parameters are to be identified here. A sub-model corresponding to the state variables $S_C$, $S_{NH}$, $S_{NO3}$, $S_{NO2}$ and $S_O$, can be written in the form of the following model:

$$\frac{d}{dt}\begin{bmatrix} S_C \\ S_{NH} \\ S_{NO_3} \\ S_{NO_2} \\ S_O \end{bmatrix} = \begin{bmatrix} -\frac{1}{Y_h} & 0 & 0 \\ 0 & -\frac{1}{Y_{a1}} & 0 \\ 0 & 0 & \frac{1}{Y_{a2}} \\ 0 & \frac{1}{Y_{a1}} & -\frac{1}{Y_{a2}} \\ \frac{1-Y_h}{Y_h} & -\frac{3.43-Y_{a1}}{Y_{a1}} & -\frac{1.14-Y_{a2}}{Y_{a2}} \end{bmatrix} \begin{bmatrix} \mu_h X_h \\ \mu_{a1} X_a \\ \mu_{a2} X_h \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ k_L a(S_{O\max} - S_O) \end{bmatrix} \tag{59}$$

By using the state transformation given in [BAS 90], if we consider the following model partition:

$$\xi_a^T = [S_C \quad S_{NH} \quad S_{NO3}] \text{ and } \xi_b^T = [S_{NO2} \quad S_O] \tag{60}$$

involving:

$$K_a = \begin{bmatrix} -\frac{1}{Y_h} & 0 & 0 \\ 0 & -\frac{1}{Y_{a1}} & 0 \\ 0 & 0 & \frac{1}{Y_{a2}} \end{bmatrix}, \quad K_b = \begin{bmatrix} 0 & \frac{1}{Y_{a1}} & -\frac{1}{Y_{a2}} \\ \frac{1-Y_h}{Y_h} & -\frac{3.43-Y_{a1}}{Y_{a1}} & -\frac{1.14-Y_{a2}}{Y_{a2}} \end{bmatrix} \tag{61}$$

then we obtain:

$$A_0 = \begin{bmatrix} 0 & 1 & 1 \\ Y_h - 1 & Y_{a1} - 3.43 & 1.14 - Y_{a2} \end{bmatrix} \tag{62}$$

This leads to the following equation independent of the kinetics and that will be used to identify (some of) the yield coefficients separately :

$$(Y_h - 1)\frac{dS_C}{dt} + (Y_{a1} - 3.43)\frac{dS_{NH}}{dt} + (1.14 - Y_{a2})\frac{dS_{NO_3}}{dt} + \frac{dS_O}{dt} = k_L a(S_{O\max} - S_O) \tag{63}$$

To complete the model structure that will be used to identify the yields coefficients, we consider the following state partition:

$$\xi_a^T = [S_C \quad S_{NO2} \quad S_O] \text{ and } \xi_b^T = [S_{NH} \quad S_{NO3}] \tag{64}$$

which involves

$$K_a = \begin{bmatrix} -\frac{1}{Y_h} & 0 & 0 \\ 0 & \frac{1}{Y_{a1}} & -\frac{1}{Y_{a2}} \\ \frac{1-Y_h}{Y_h} & -\frac{3.43-Y_{a1}}{Y_{a1}} & -\frac{1.14-Y_{a2}}{Y_{a2}} \end{bmatrix}; \quad K_b = \begin{bmatrix} 0 & -\frac{1}{Y_{a1}} & 0 \\ 0 & 0 & \frac{1}{Y_{a2}} \end{bmatrix} \tag{65}$$

Hence, after the state transformation, we will obtain:

$$\begin{cases} (Y_h - 1)\dfrac{dS_C}{dt} + (Y_{a2} - 1.14)\dfrac{dS_{NO_2}}{dt} + \dfrac{dS_O}{dt} + \dfrac{dS_{NH}}{dt} = -(4.57 - Y_{a2} - Y_{a1})k_L a(S_{O\max} - S_O) \\ (1 - Y_h)\dfrac{dS_C}{dt} + (Y_{a1} - 3.43)\dfrac{dS_{NO_2}}{dt} - \dfrac{dS_O}{dt} + \dfrac{dS_{NO_3}}{dt} = (4.57 - Y_{a2} - Y_{a1})k_L a(S_{O\max} - S_O) \end{cases} \quad (66)$$

Table 1-6. EM2a yield coefficients in the aerobic phase, after and before Christmas stop

| Yield coefficient | Unity | Value | Confidence Interval |
|---|---|---|---|
| $Y_h$ | mg VSS/mg COD | 0.75 | 0.067 |
| $Y_{a1}$ | mg VSS/mg N | 1.69 | 0.37 |
| $Y_{a2}$ | mg VSS/mg N | 0.187 | 0.09 |
| $k_{6b} = k_6$ | mg N-NH/mg N | 0.706 | 0.143 |

By using the calibration data (see EM2a_identification.xls in the worksheet "summary") and the Matlab function "lsqnonlin", the method results in the set of parameter values summarized in Table 1-6. Note that these confidence values have been computed according to the method given in **Appendix 2**.

### 1.2.4. Kinetics parameters

The 2-step nitrification involves 9 kinetics parameters to be identified: $\mu_{h\max}$, $\mu_{a1\max}$, $\mu_{a2\max}$, $K_{Ch}$, $K_{Oh}$, $K_{NH}$, $K_{Oa1}$, $K_{NO2a}$ and $K_{Oa2}$. During the data analysis, it has been noticed that the ammonification rate constant $\mu_0$ is invariant in both phases.

The prediction equations are the following:

$$\frac{d}{dt}\begin{bmatrix}\hat{S}_C\\ \hat{S}_{NH}\\ \hat{S}_{NO_3}\\ \hat{S}_{NO_2}\\ \hat{S}_O\\ \hat{X}_h\\ \hat{X}_a\end{bmatrix} = \begin{bmatrix} -\frac{1}{Y_h} & 0 & 0\\ 0 & -\frac{1}{Y_{a1}} & 0\\ 0 & 0 & \frac{1}{Y_{a2}}\\ 0 & \frac{1}{Y_{a1}} & -\frac{1}{Y_{a2}}\\ \frac{1-Y_h}{Y_h} & -\frac{3.43-Y_{a1}}{Y_{a1}} & -\frac{1.14-Y_{a2}}{Y_{a2}}\\ 1 & 0 & 0\\ 0 & 1 & 1\end{bmatrix}\begin{bmatrix}\mu_h\hat{X}_h\\ \mu_{a1}\hat{X}_a\\ \mu_{a2}\hat{X}_a\end{bmatrix} + \begin{bmatrix}0\\0\\0\\0\\-k_L a(S_{O\max}-\hat{S}_O)\\0\\0\end{bmatrix} \quad (67)$$

with:

$$\mu_h = \mu_{h\max}\frac{\hat{S}_C - S_{C\min}}{K_{Ch} + \hat{S}_C - S_{C\min}}\frac{\hat{S}_O}{K_{Oh} + \hat{S}_O} \quad (68)$$

$$\mu_{a1} = \mu_{a1\max}\frac{\hat{S}_{NH}}{K_{NH} + \hat{S}_{NH}}\frac{\hat{S}_O}{K_{Oa1} + \hat{S}_O} \quad (69)$$

$$\mu_{a2} = \mu_{a2\max} \frac{\hat{S}_{NO_2}}{K_{NO_2a} + \hat{S}_{NO_2}} \frac{\hat{S}_O}{K_{Oa2} + \hat{S}_O} \tag{70}$$

And we consider the following cost function to be minimized :

$$\min J_{aer}(\theta) = \min \frac{1}{N} \sum_i (x - \hat{x}) \tag{71}$$

where $\theta$ represents the vector of the parameters to be identified, and x (= [$S_C$ $S_{NH}$ $S_{NO3}$ $S_{NO2}$ $S_O$ $X_h$ $X_a$]$^T$) is the state variables vector. The results are given in Table 1-7. The values of the confidence intervals have been computed according to the method presented in **Appendix 2**.

Table 1-7. EM2a kinetic parameters in the aerobic phase, after and before Christmas stop

| Kinetics parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $\mu_{h\,max}$ | $min^{-1}$ | 0.0122 | $1.5 \cdot 10^{-10}$ |
| $K_{Ch}$ | mg COD/L | 18.96 | 7.42 |
| $K_{Oh}$ | mg DO/L | 40 | 10.34 |
| $\mu_{a1\,max}$ | $min^{-1}$ | 0.0235 | $1.74 \cdot 10^{-10}$ |
| $K_{NH}$ | mg N/L | 0.479 | 0.208 |
| $K_{Oa1}$ | mg DO/L | 29. 9 | 9.47 |
| $\mu_{a2\,max}$ | $min^{-1}$ | 0.0117 | $1.5 \cdot 10^{-10}$ |
| $K_{NO2a}$ | mg N/L | 4.963 | 2.74 |
| $K_{Oa2}$ | mg DO/L | 24.9 | 7.75 |
| $\mu_0$ | $min^{-1}$ | 0.0529 | 0.011 |

### *1.3. Non-biodegradable substrates*

As it has been done previously, we assume that the non-biodegradable substrates involve the parameters $S_{C\min}$ and $S_{N\min}$, which are about 20 mg COD/L, and 3 mg N/L, respectively. In order to know the reproducibility of these parameters related to some load changes in normal conditions, we have computed their confidence intervals. A statistical analysis on the data (see **Appendix 2**) has been performed and the results are summarized in Table 1-8.

Table 1-8. EM2a non-biodegradable substrates parameters

| Parameter | Value | Confidence Interval |
|---|---|---|
| $S_{C\,min}$ (mg COD/L) | 19.92 | 1.4 |
| $S_{N\,min}$ (mg N/L) | 3.16 | 0.44 |

### *1.4. Heterotrophic and autotrophic biomasses*

The data only provide the total biomass with no distinction between the heterotrophic and autotrophic bacteria. In the scientific literature [BAR 83], the following proportion between these two bacterial populations is proposed, which is based on the coefficient $F_N$:

$$F_N = \frac{X_a}{X_a + X_h} \quad \text{with } F_N \text{ constant} \tag{72}$$

It is assumed in particular that in steady state, the ratio of the growth of the nitrifiers over the sum of the growth of the nitrifiers and heterotrophs is equal to:

$$F_N = \frac{Y_A(TKN_{ox})}{Y_A(TKN_{ox}) + Y_h(S_{C\,ox})} = \frac{1}{1 + Y_h/Y_A\,(S_{C\,ox})/(TKN_{ox})} \tag{73}$$

where $S_{C\,ox}$ represents the oxidized organic substrate (denoted $S_C$ in the aerobic phase in the model), $TKN_{ox}$ is the oxidized $TKN$, which is the sum of $S_N$ and $S_{NH}$ in the aerobic phase; $Y_h$ is the heterotrophic yield coefficient and is usually assumed to be around 0.5 gVSS/gCOD, and $Y_A$, the autotrophic yield, is usually assumed to be 0.16667 gVSS/gN oxidized from stoichiometry of nitrification and refers to both populations (i.e.: both ammonia and nitrite oxidizing bacteria).

This means that the ratio $Y_h/Y_A$ is assumed to be about 0.5/0.16667, i.e. 3. If $S_{C\,ox}$ is around 300 mgCOD/L, $TKN_{ox}$ is around 50 mg/L, then we can deduce that the percentage of autotrophic bacteria $X_a/(X_h + X_a)$ should be equal to :

$$F_N = \frac{1}{1 + 3\left(\frac{300}{50}\right)} = 1/19 = 5.3\% \tag{74}$$

i.e. about 5% of the total VSS.

### *1.5. EM2-a model validation*

Some numerical simulations based on the calibration data have been performed and compared to the validation data to validate the model. In order to measure the reliability of the model, an error criterion is applied, as follows:

$$\varepsilon_y = \frac{1}{N}\sum_{i=1}^{N}(\hat{y}_i - y_i) \tag{75}$$

where $\hat{y}_i$ and $y_i$ denote the predicted and the actual values, respectively, of the variable $y$ at the sample time $t_i$ with $i \in [1, N]$; $N$ is the sample size. Or, in the non-dimensional form, we can also write the previous criterion as follows:

$$\varepsilon_y^{\circ} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\hat{y}_i - y_i}{\bar{y}}\right) \tag{76}$$

where $\bar{y}$ is the average value of the variable $y$ in the time interval $[t_1, t_N]$.

The validation has been done in two steps :

1) with the unique set of transfer coefficients on all the validation data;
2) with each set of transfer coefficients on the corresponding validation data.

## *1.6. Validation 1*

### 1.6.1. Validation set 1

The first validation is related to the experimental data of November 20, 2003. The comparisons between the measurement values and the simulation values are illustrated in the following figures and tables indicating the model error.

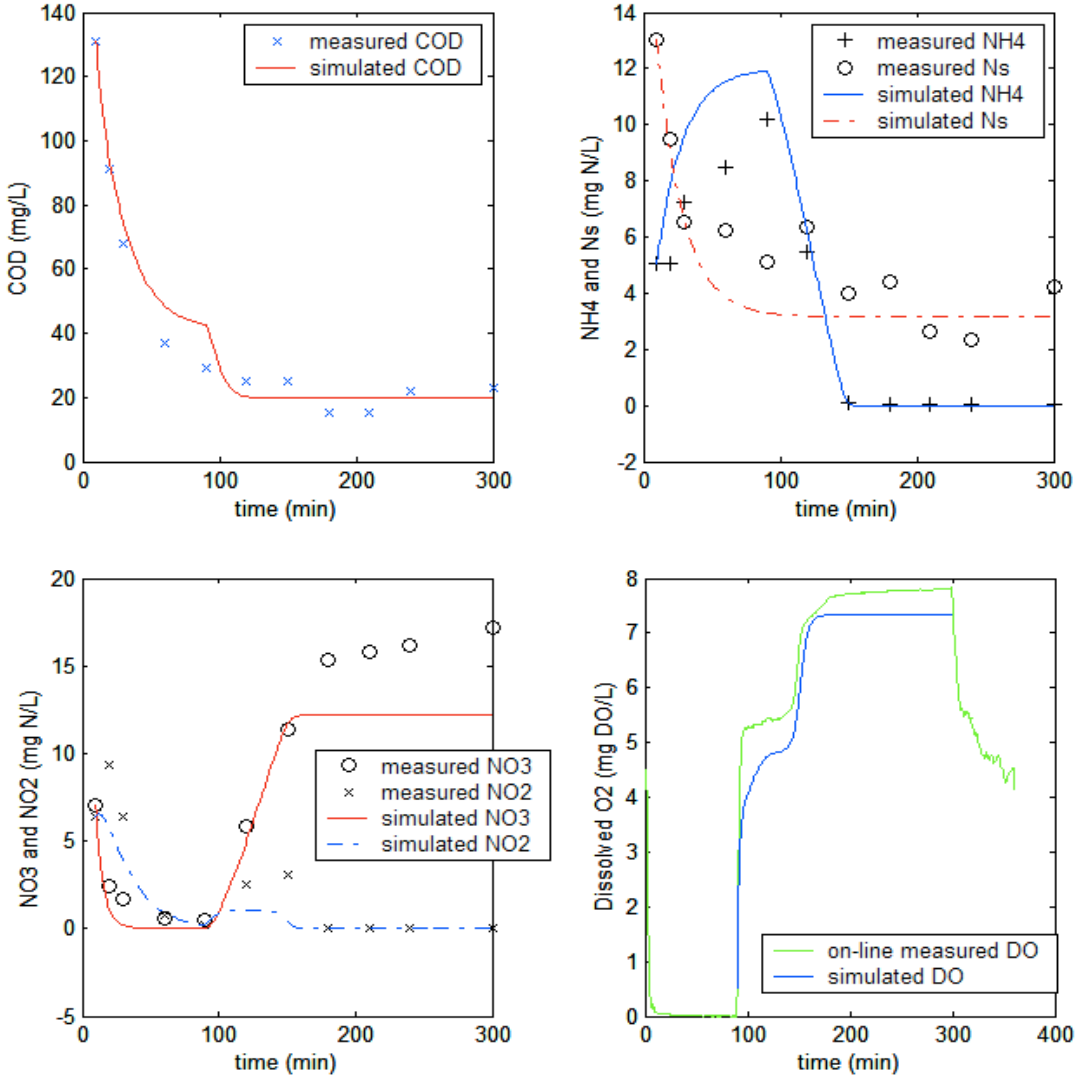


Figure 1-1. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of November 20, 2003

Table 1-9. EM2-a error for the validation of November 20, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | *Absolute Error Average* |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | 2.641 | 0.953 | -0.879 | -1.835 | -0.904 | -0.519 | 1.288 |
| | □° (%) | 6.041 | 25.103 | -15.017 | -21.493 | -34.687 | -7.416 | 18.293 |

### 1.6.2. Validation set 2

The second validation is related to the experimental data of November 26, 2003.

Table 1-10. EM2-a error for the validation of November 26, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | Δ (mg/L) | 1.662 | 0.185 | -0.301 | -1.988 | 0.382 | -0.620 | 0.856 |
| | Δ° (%) | 8.504 | 14.381 | -7.518 | -11.494 | 45.755 | -8.211 | 15.977 |

These data are related to the following figures.

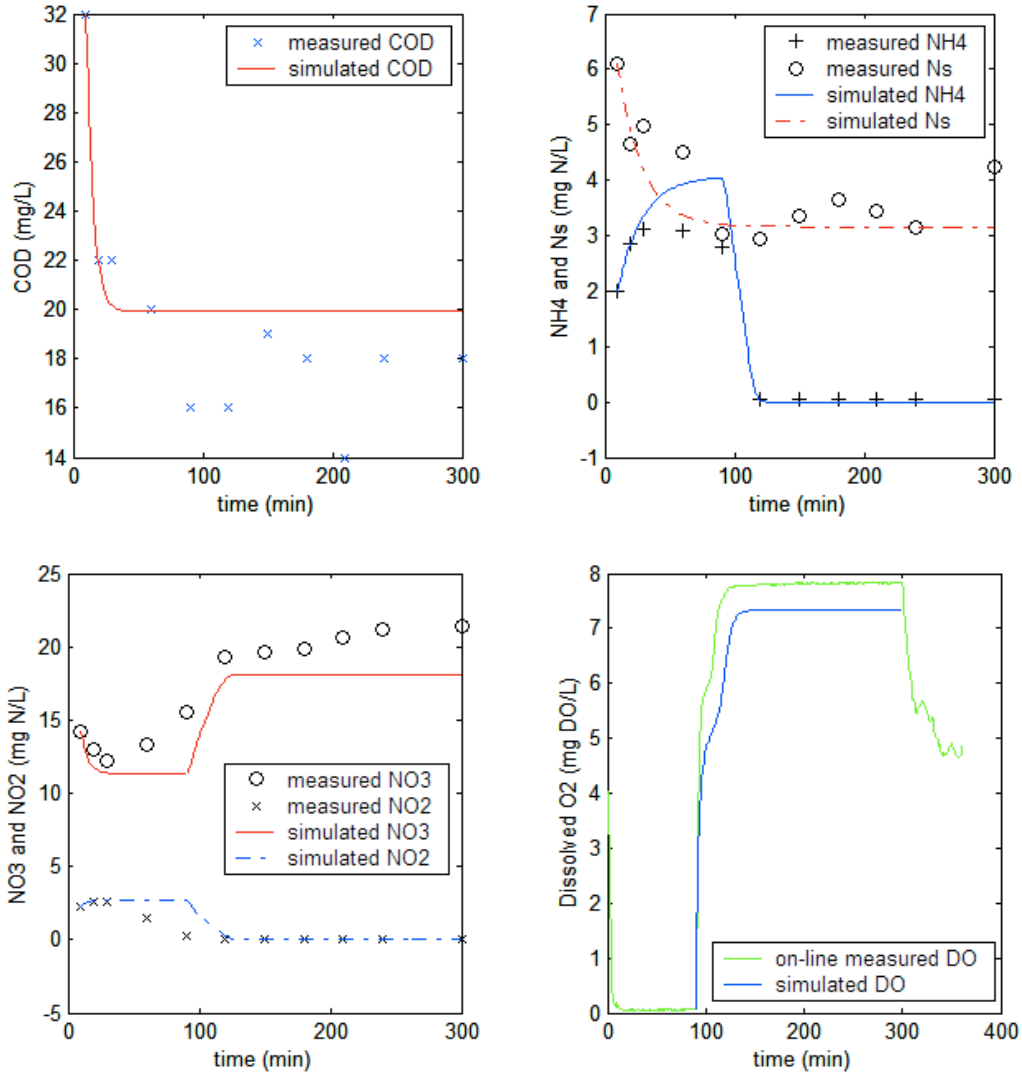


Figure 1-2. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of November 26, 2003

### 1.6.3. Validation set 3

Consider the experimental data of December 4, 2003 before the Christmas stop. The following errors are given in Table 1-11.

Table 1-11. EM2-a error for the validation of December 4, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | Δ (mg/L) | -0.482 | 2.160 | 1.841 | 0.003 | -0.484 | -0.553 | 0.921 |
| | Δ° (%) | -1.592 | 57.836 | 42.527 | 0.031 | -23.848 | -8.006 | 22.307 |

These data are related to the following figures.

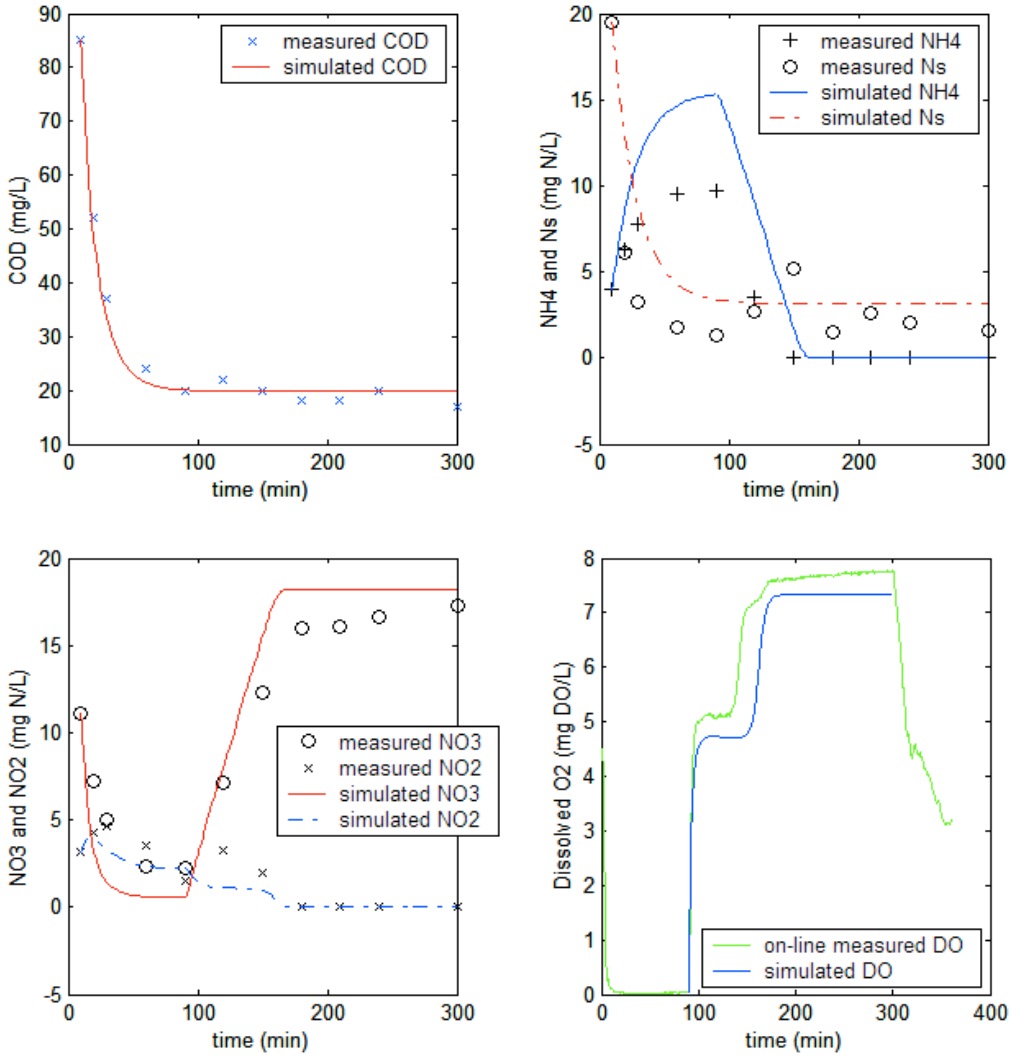


Figure 1-3. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of December 4, 2003

### 1.6.4. Validation set 4

Consider the experimental data of December 10, 2003. The following errors are given in Table 1-12.

Table 1-12. EM2-a error for the validation of December 10, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | -4.286 | 0.015 | -0.106 | -2.658 | -0.976 | -0.636 | 1.446 |
| | □° (%) | -13.170 | 0.481 | -2.326 | -24.561 | -37.970 | -8.650 | 14.526 |

These data are related to the following figures.

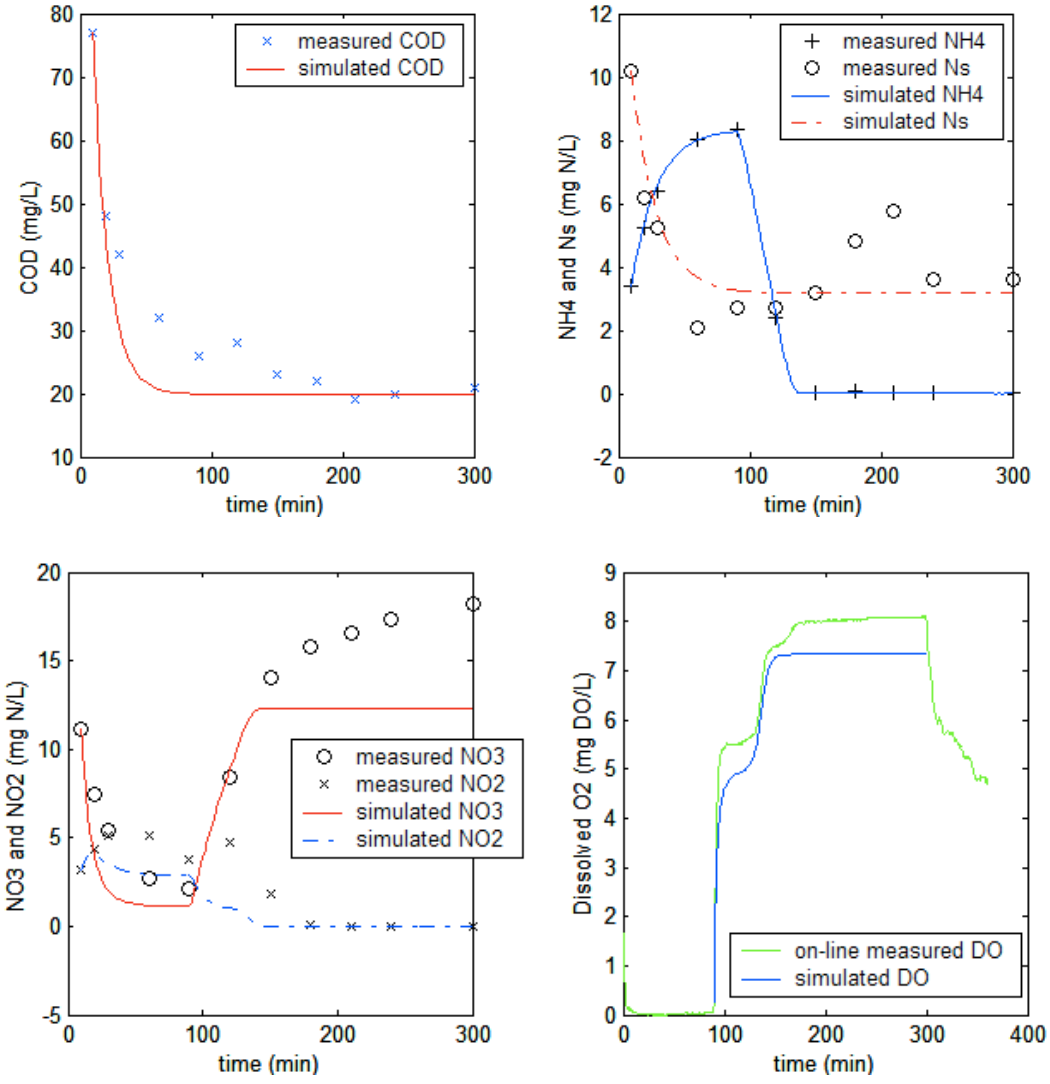


Figure 1-4. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of December 10, 2003

### 1.6.5. Validation set 5

Consider now the experimental data of January 27, 2004 after the Christmas stop. The following errors are given in Table 1-13.

Table 1-13. EM2-a error for the validation of January 27, 2004

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | 1.635 | -0.478 | 0.031 | -0.310 | -0.322 | 0.568 | 0.557 |
| | □° (%) | 7.000 | -17.333 | 0.832 | -4.919 | 18.345 | 9.073 | 9.584 |

These data are related to the following figures.

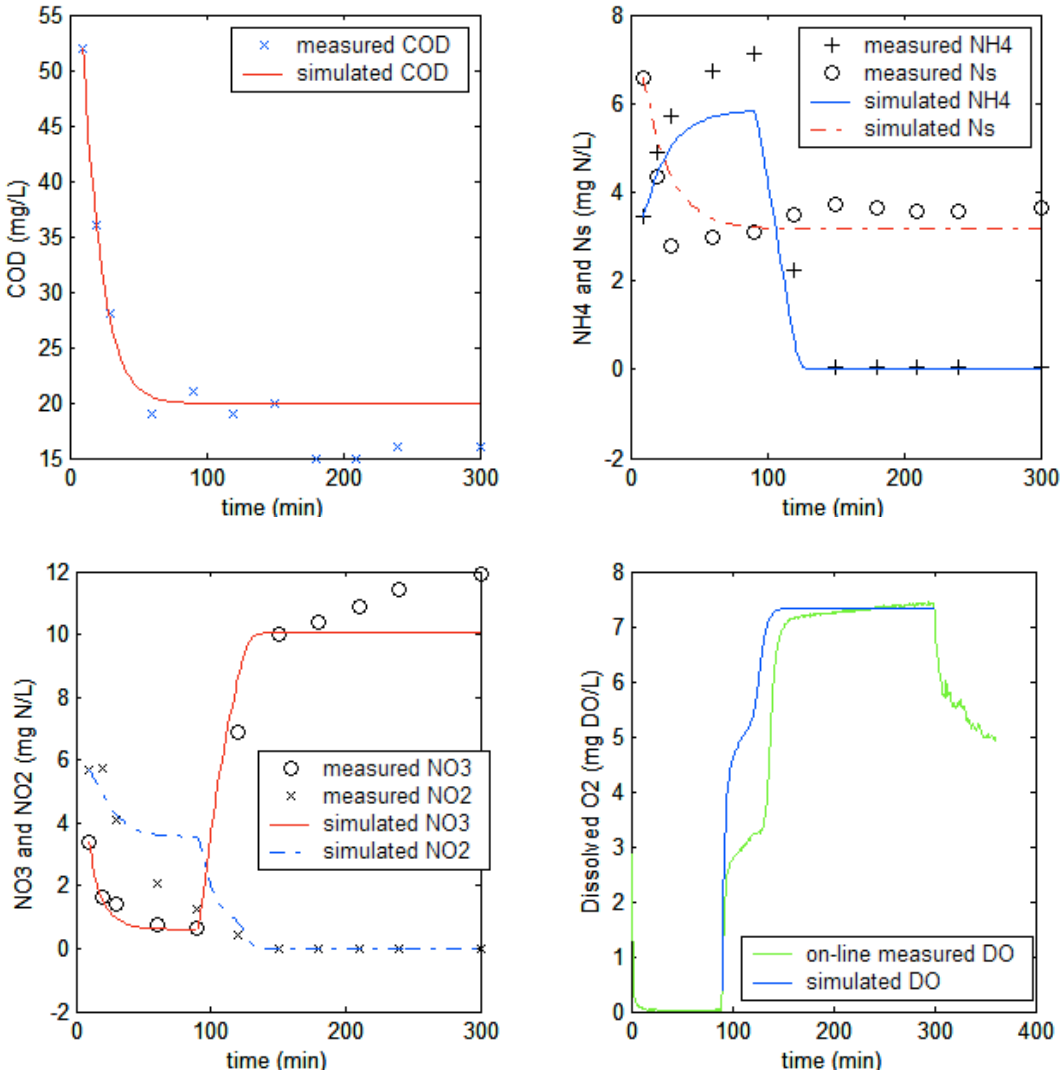


Figure 1-5. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of January 27, 2004

### 1.6.6. Validation set 6

Consider the experimental data of January 29, 2004 after the Christmas stop. The following errors are given in Table 1-14.

Table 1-14. EM2-a error for the validation of February 26, 2004

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | -0.821 | -1.094 | 0.368 | -0.848 | -0.583 | 2.582 | 1.049 |
| | □° (%) | -3.283 | -35.129 | 11.671 | -10.196 | -18.362 | 60.626 | 23.211 |

These data are related to the following figures.

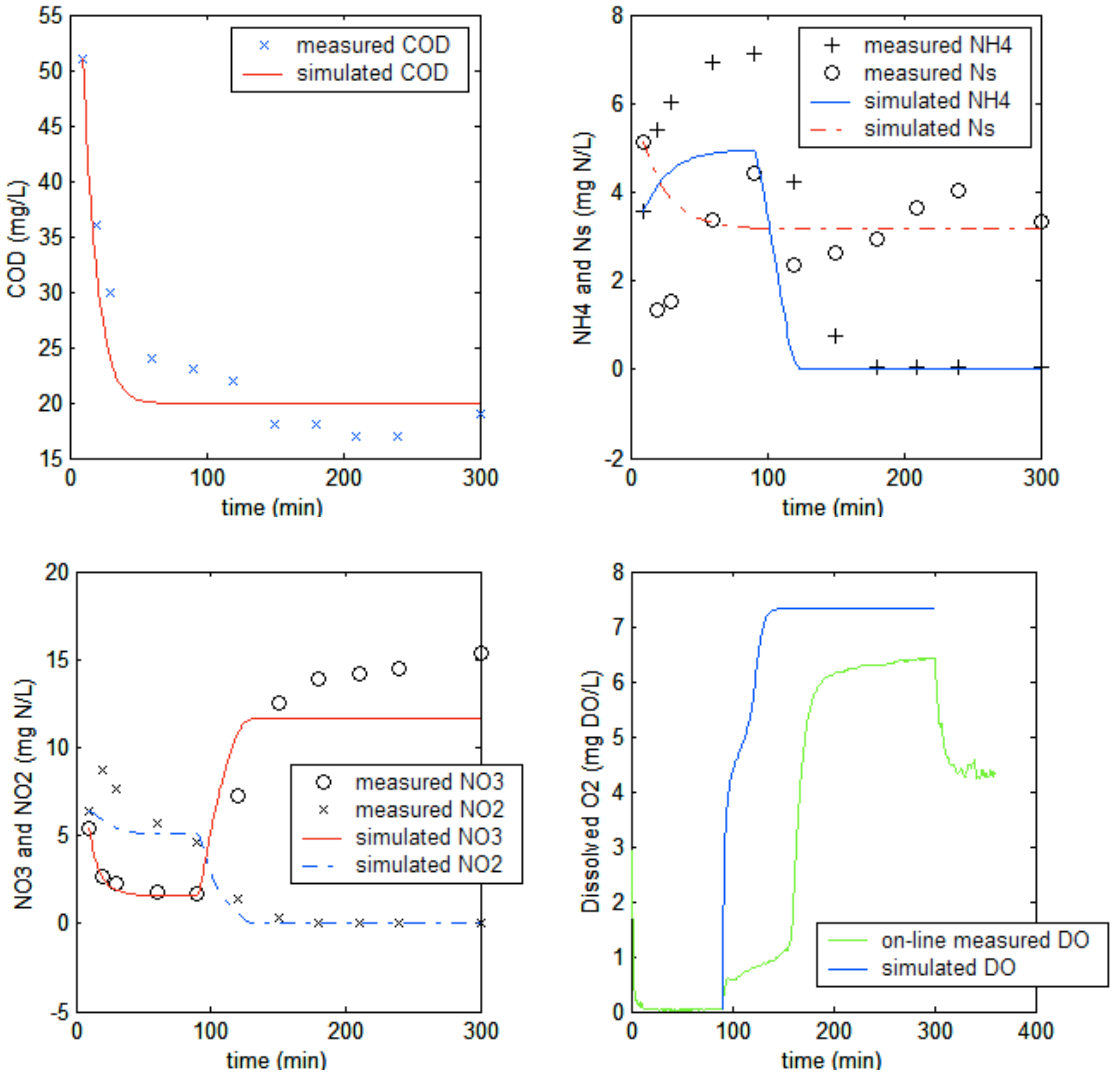


Figure 1-6. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of February 26, 2004

### 1.6.7. Validation set 7

Consider finally the experimental data of February 26, 2004 after the Christmas stop. The following errors are given in Table 1-15.

Table 1-15. EM2-a error for the validation of February 26, 2004

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | 1.483 | -0.789 | 1.138 | -1.400 | -0.028 | 1.801 | 1.106 |
| | □° (%) | 6.018 | -25.466 | 43.804 | -23.652 | -3.384 | 35.548 | 22.979 |

These data are related to the following figures.

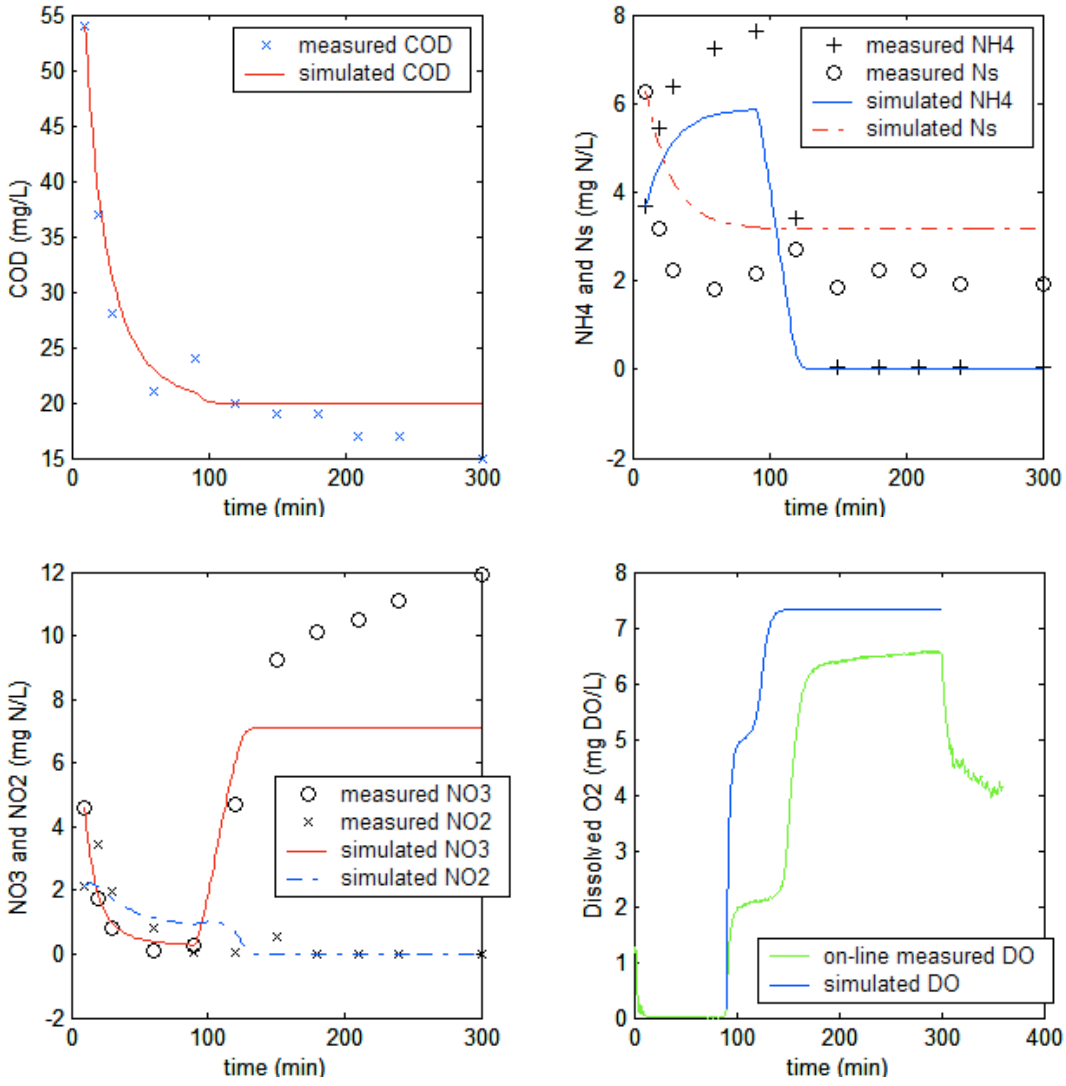


Figure 1-7. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of February 26, 2004

## 1.7. Validation 2

For the second set of validations with different values of the transfer coefficients before and after Christmas on the corresponding validation data, the main conclusion is that there is not a major global improvement (the sum of the absolute values of the errors remain close) except possibly for the last two sets of data.

### 1.7.1. Validation set 1

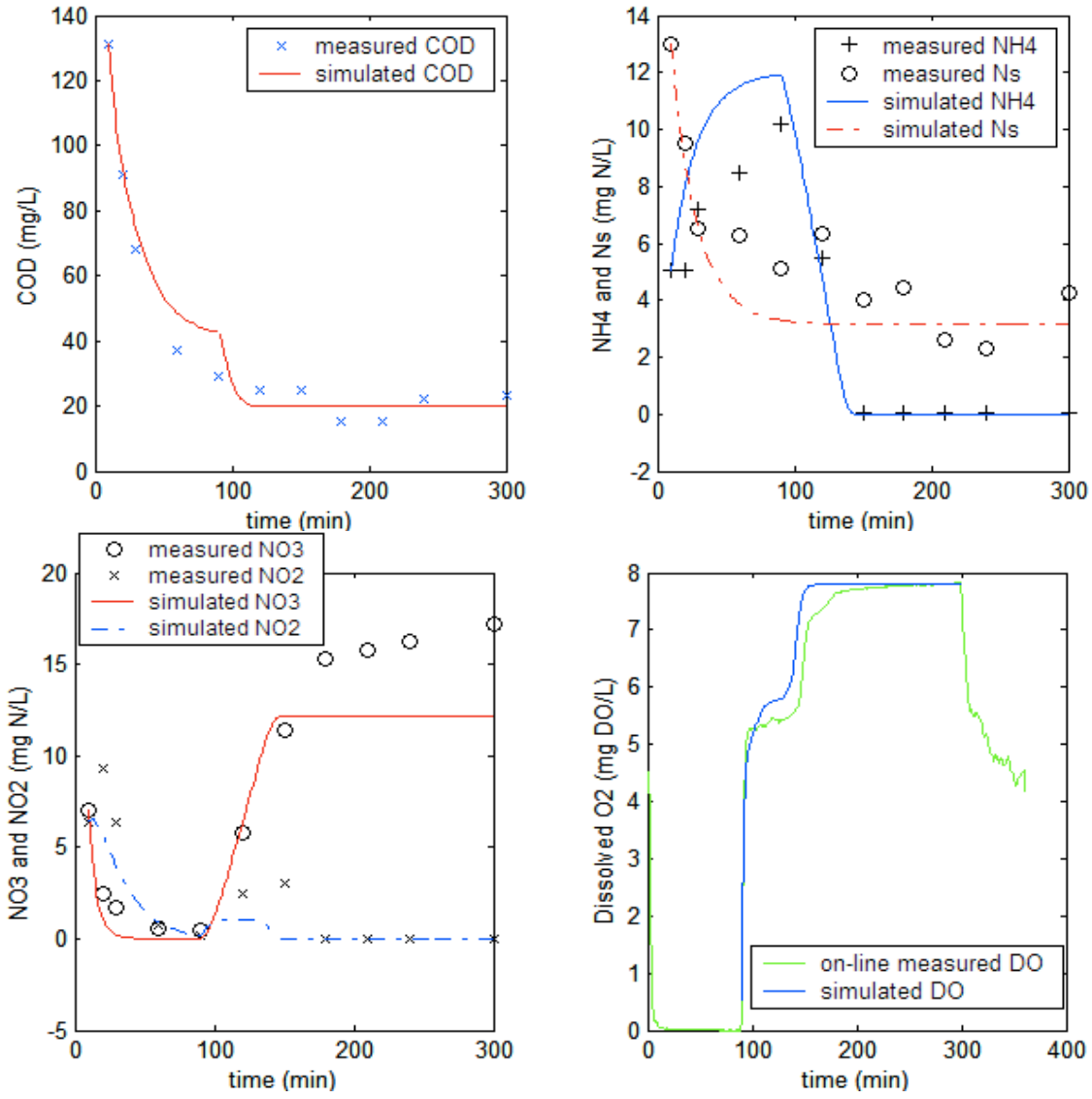


Figure 1-8. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$

Table 1-16. EM2-a error for the validation of November 20, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | *Absolute Error Average* |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | 2.622 | 0.825 | -0.879 | -1.666 | -0.944 | 0.200 | 1.189 |
| | □° (%) | 5.996 | 21.728 | -15.017 | -19.516 | -36.423 | 2.856 | 16.893 |

### 1.7.2. Validation set 2

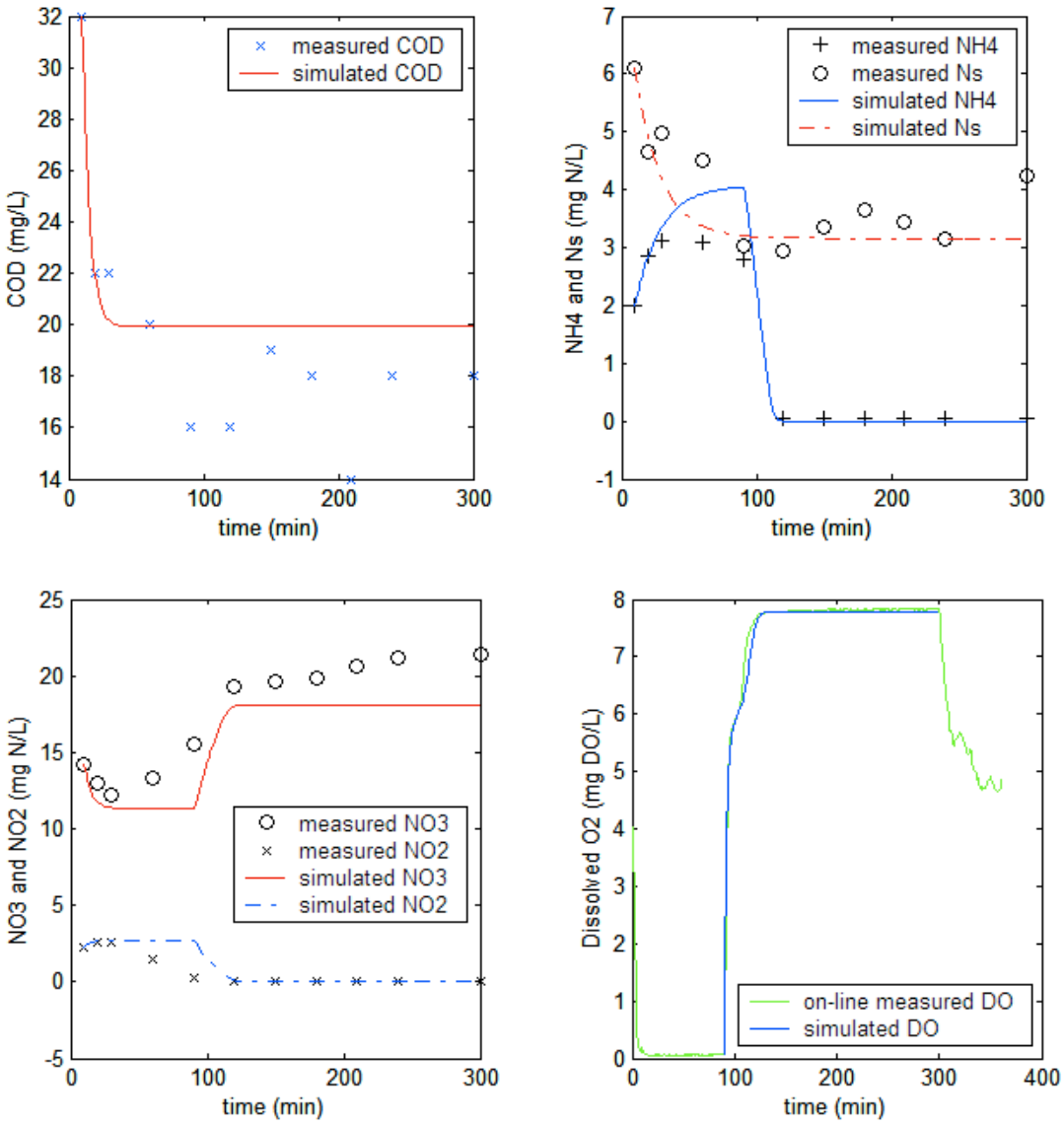


Figure 1-9. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of November 26, 2003

Table 1-17. EM2-a error for the straight-validation of November 26, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | *Absolute Error Average* |
|---|---|---|---|---|---|---|---|---|
| Error | Δ (mg/L) | 1.662 | 0.183 | -0.301 | -1.965 | 0.362 | -0.041 | 0.752 |
| | Δ° (%) | 8.504 | 14.171 | -7.518 | -11.363 | 43.368 | -0.544 | 14.245 |

### 1.7.3. Validation set 3

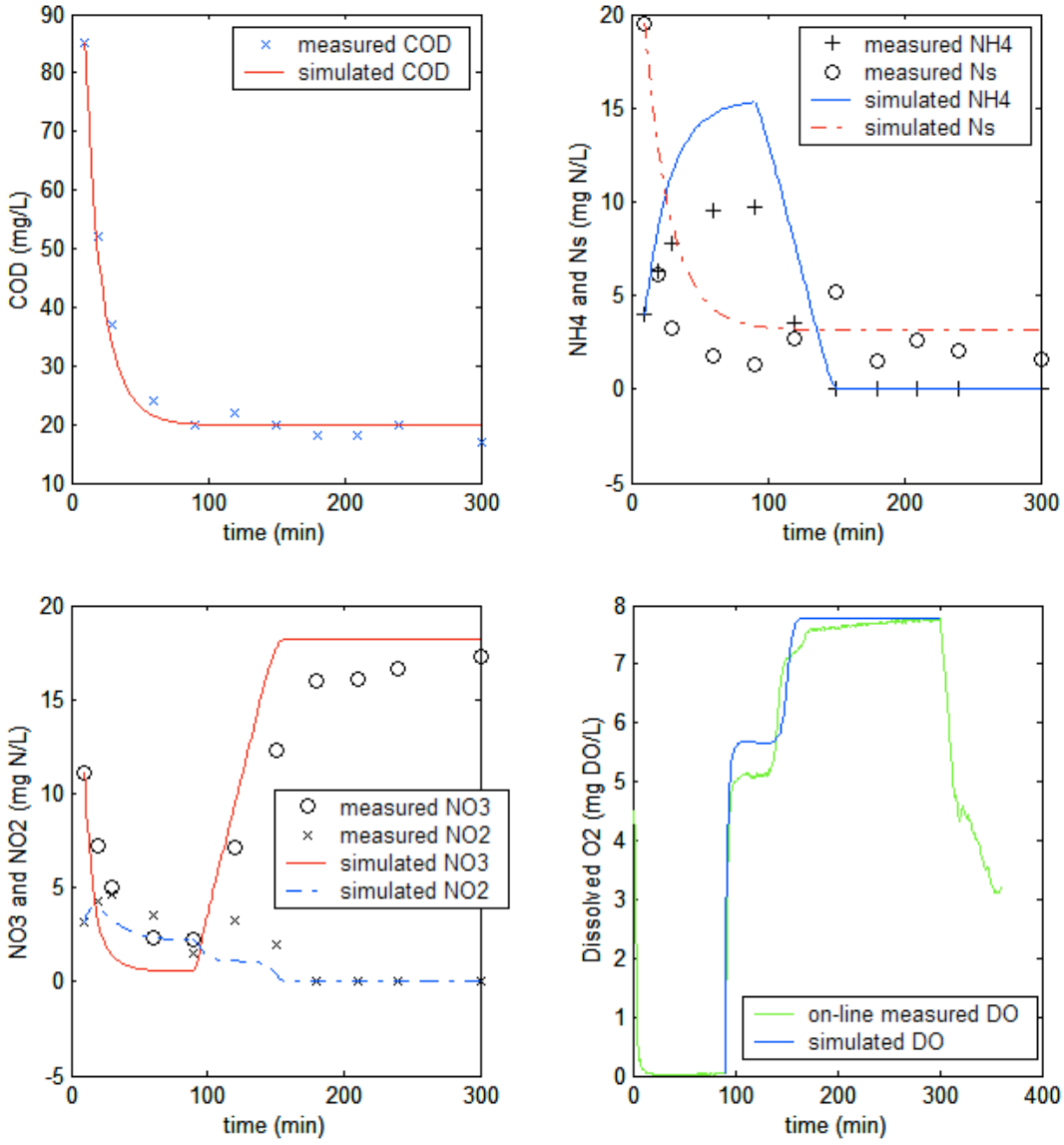


Figure 1-10. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of December 4, 2003

Table 1-18. EM2-a error for the validation of December 4, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | *Absolute Error Average* |
|---|---|---|---|---|---|---|---|---|
| Error | Δ (mg/L) | -0.482 | 1.887 | 1.841 | 0.323 | -0.531 | 0.200 | 0.877 |
| | Δ° (%) | -1.592 | 50.517 | 42.527 | 3.135 | -26.124 | 2.896 | 21.132 |

### 1.7.4. Validation set 4

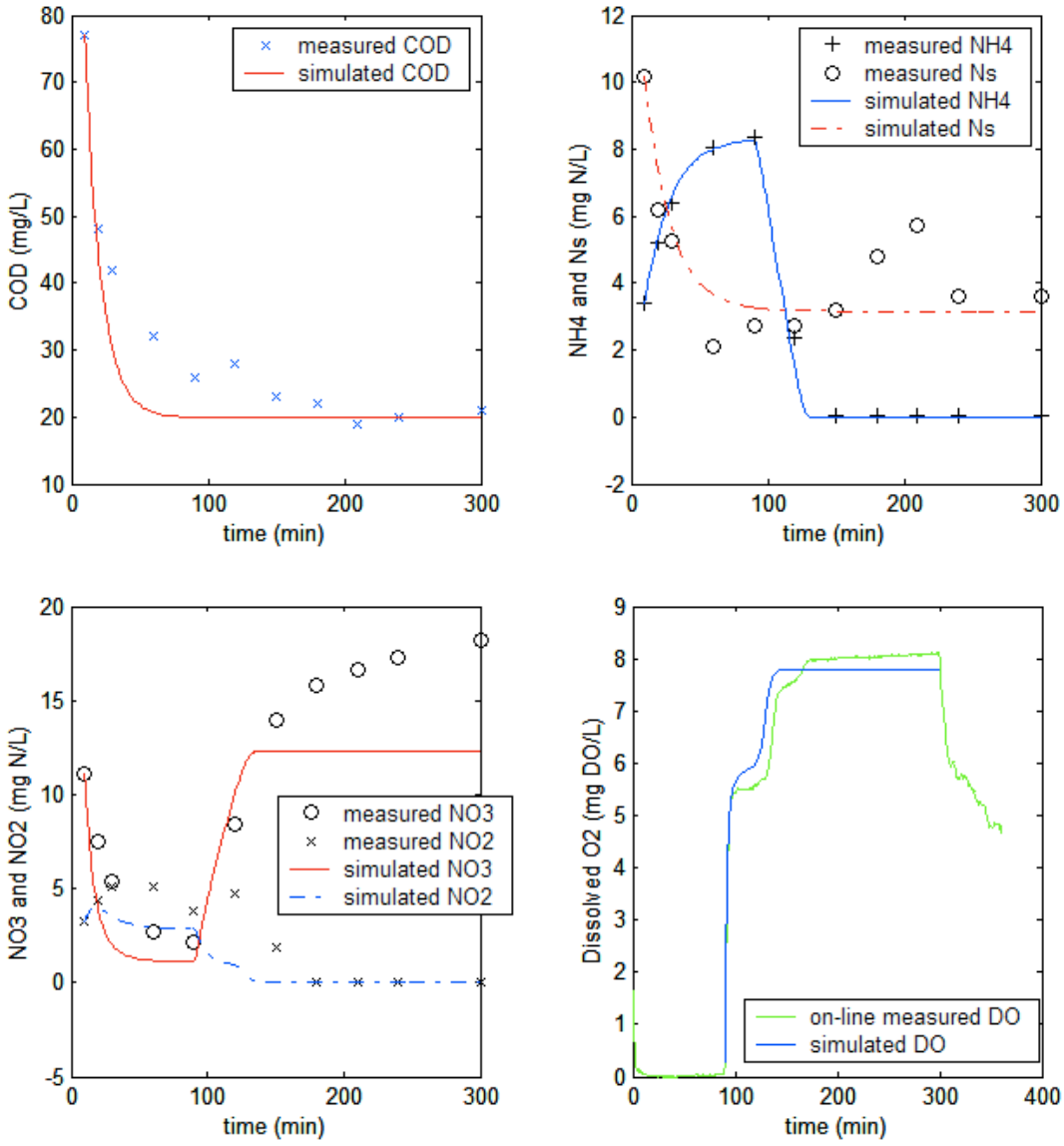


Figure 1-11. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of December 10, 2003

Table 1-19. EM2-a error for the validation of December 10, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | -4.286 | -0.080 | -0.106 | -2.555 | -0.983 | 0.009 | 1.337 |
| | □° (%) | -13.170 | -2.598 | -2.326 | -23.610 | -38.267 | 0.122 | 13.349 |

### 1.7.5. Validation set 5

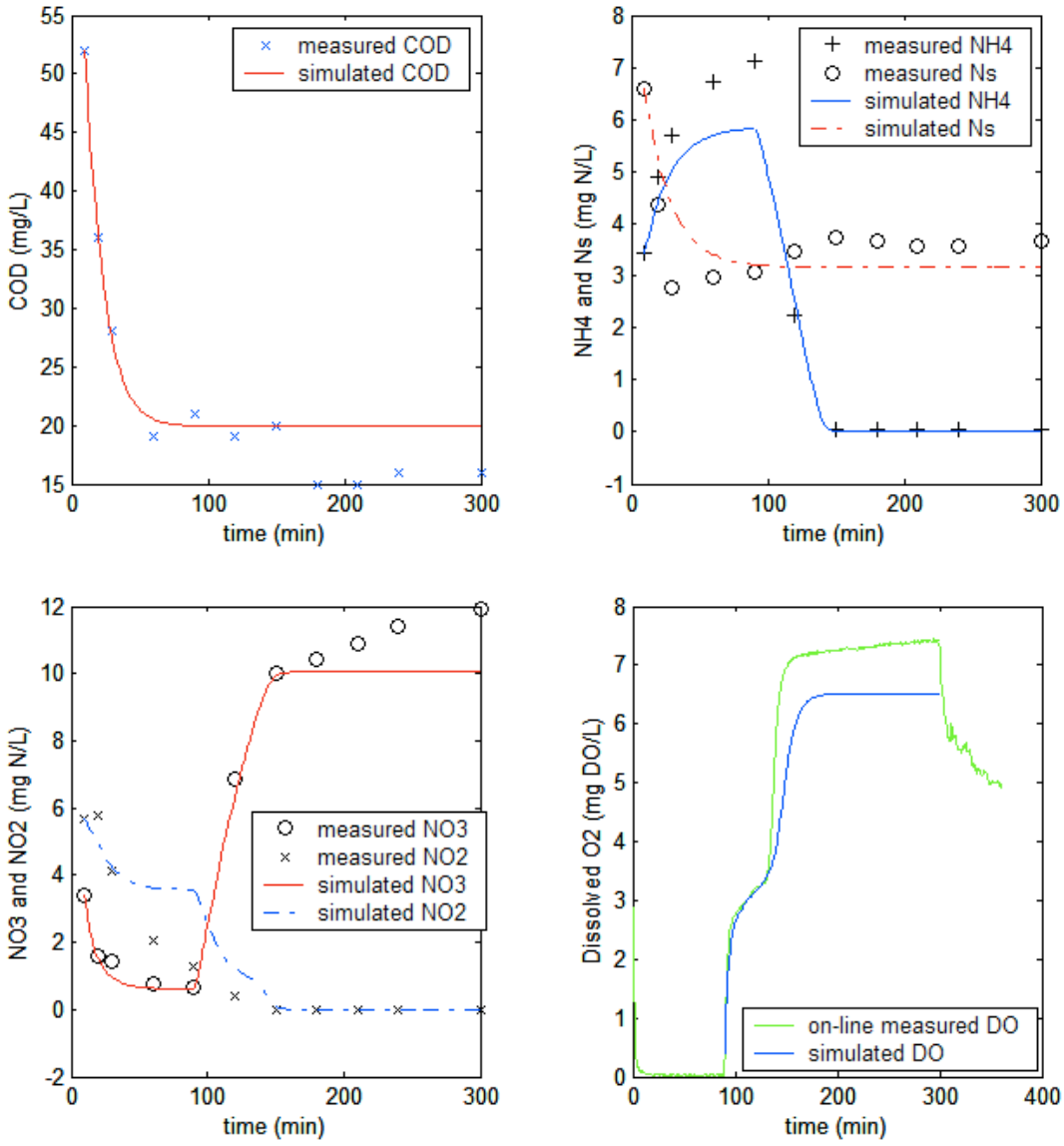


Figure 1-12. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of January 27, 2004

Table 1-20. EM2-a error for the validation of January 27, 2004

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | 1.636 | -0.310 | 0.031 | -0.523 | 0.368 | -0.762 | 0.605 |
| | □° (%) | 7.000 | -11.236 | 0.832 | -8.309 | 20.938 | -12.177 | 10.082 |

### 1.7.6. Validation set 6

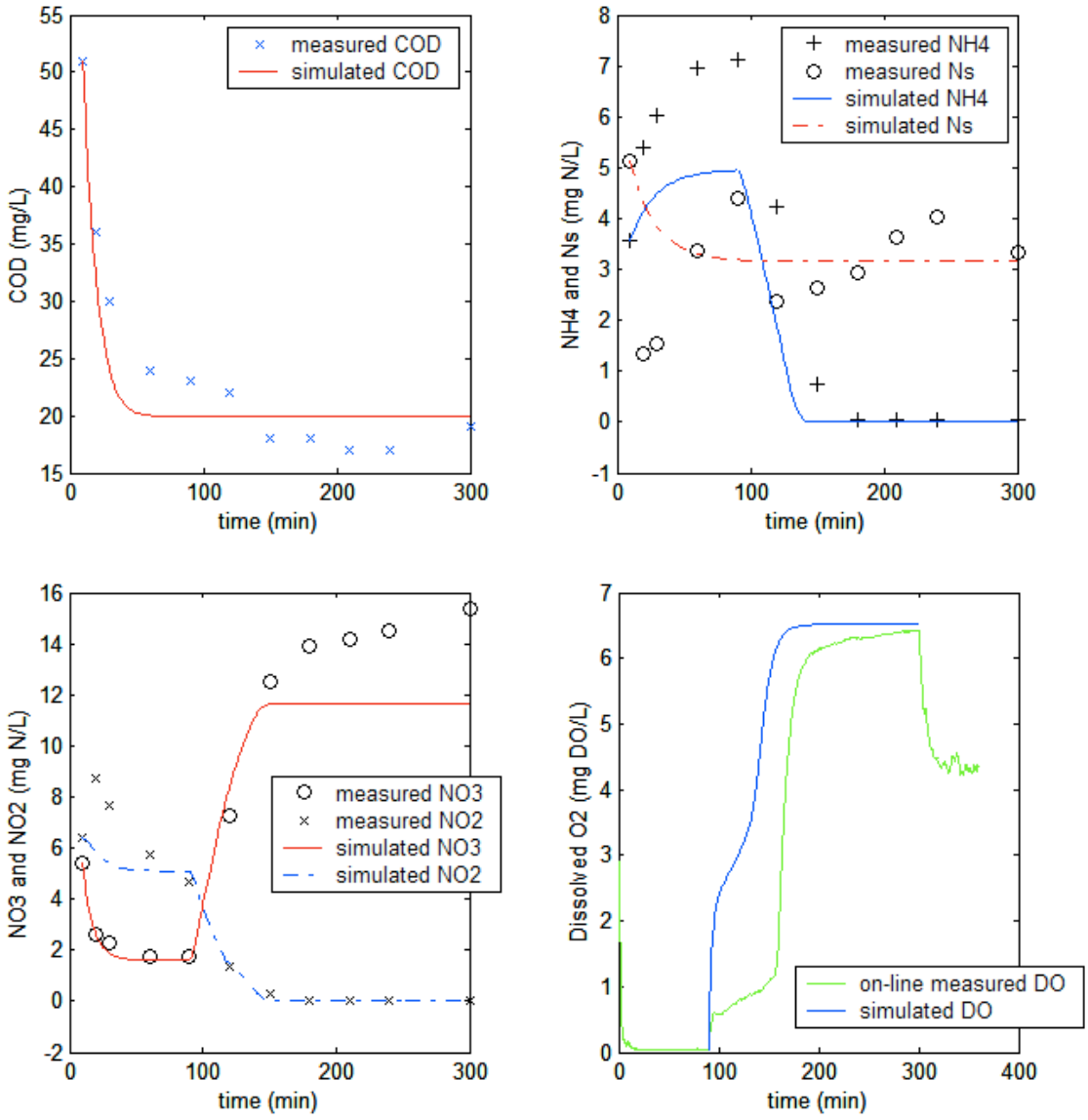


Figure 1-13. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of January 29, 2004

Table 1-21. EM2-a error for the validation of January 29, 2004

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | -0.821 | -0.944 | 0.368 | -1.073 | -0.507 | 1.264 | 0.830 |
| | □° (%) | -3.283 | -30.324 | 11.671 | -12.905 | -15.977 | 29.683 | 17.307 |

### 1.7.7. Validation set 7

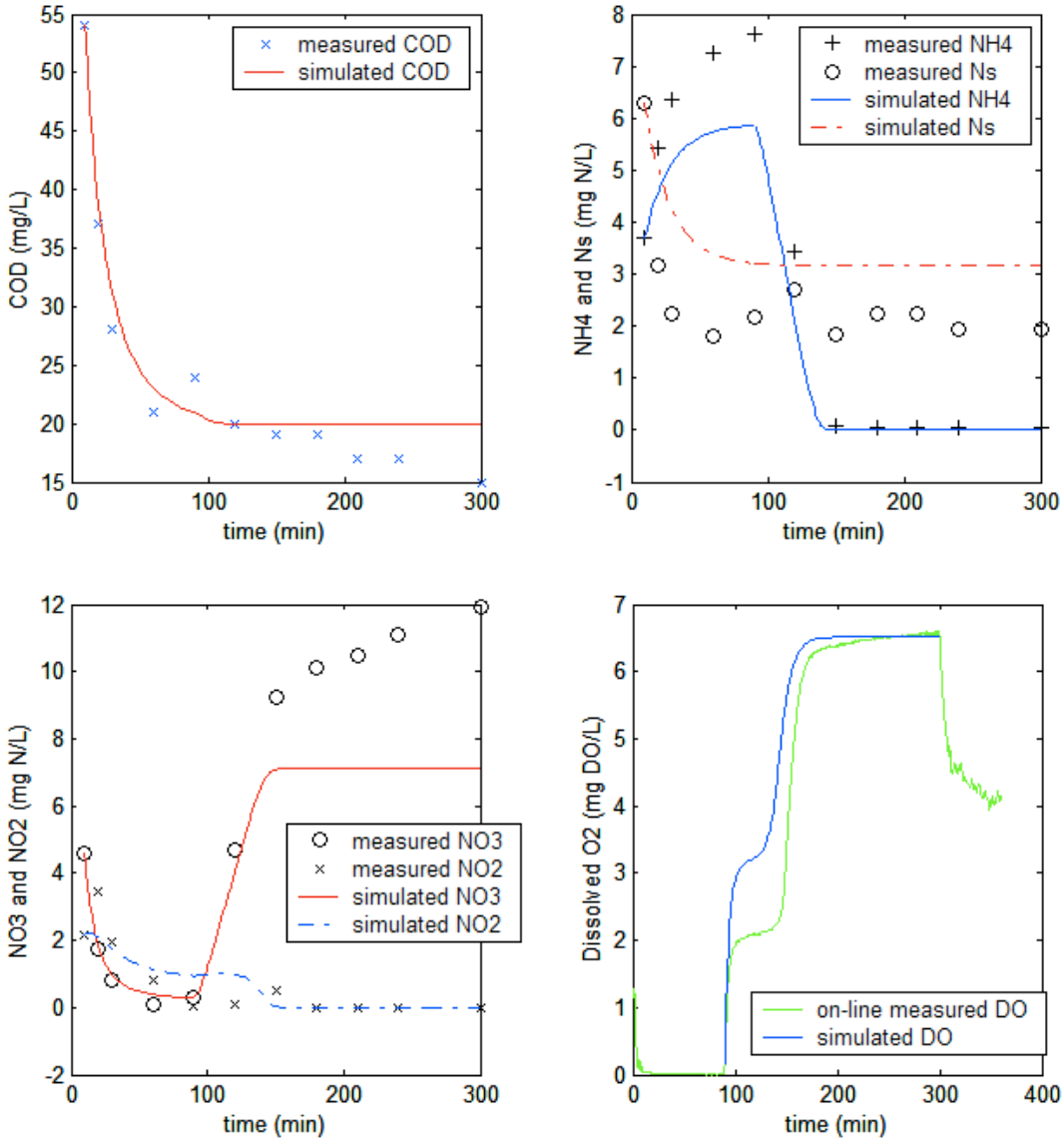


Figure 1-14. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO3}$, $S_{NO2}$ and $S_O$ of February 26, 2004

Table 1-22. EM2-a error for the validation of February 26, 2004

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO3}$ | $S_{NO2}$ | $S_O$ | Absolute Error Average |
|---|---|---|---|---|---|---|---|---|
| Error | □ (mg/L) | 1.485 | -0.630 | 1.138 | -1.586 | -0.001 | 0.511 | 0.892 |
| | □° (%) | 6.027 | -20.336 | 43.804 | -26.787 | -0.138 | 10.090 | 17.864 |

## 2. EM2-b: Denitrification/ Nitrification model of the LBE process

The LBE data and experimental evidence show that one-step denitrification and nitrification [HEN 87, VAN 99, DOC 01] are applicable here. Let us denote $S_C$, $S_{NH}$, $S_{NO}$, $S_O$, $X_h$ and $X_a$, the biodegradable substrate concentration (carbon, mg COD/L), the ammonia nitrogen concentration (mg N/L), the nitrate and nitrite nitrogen concentration (mg N/L), the concentration of the dissolved oxygen (DO) in the water (mg/L) and the concentration of the digester biomasses (heterotrophs and autotrophs), respectively.

### *2.1. Absorption*

An absorption phenomenon is apparently taking place initially with CODs in the LBE reactor. To verify the presence of this phenomenon, the LBE has performed 4 batch tests by taking some sludge outside the reactor and putting 4 different concentrations of CODs in the beginning. A same sludge volume at the same concentration was considered in the four cases. The water does not contain any nitrate or nitrite. The decrease of COD with time is then due to absorption. The results of these experiments are illustrated in the following table and graphs.

Table 2-1: COD absorption test data

| | CODs (mg/L) | | | | COD eliminated % | | | TSS (mg/L) | COD initial/ TSS |
|---|---|---|---|---|---|---|---|---|---|
| | Initial | 2 min | 10 min | 30 min | 2 min | 10 min | 30 min | | |
| Batch 1 | 400 | 341.35 | 278.9 | 225.3 | 85.34% | 69.73% | 56.33% | 8.54 | 46.84 |
| Batch 2 | 700 | 582.47 | 474.09 | 388.25 | 83.21% | 67.73% | 55.46% | 8.5 | 82.35 |
| Batch 3 | 1200 | 987.44 | 772.57 | 514.26 | 82.29% | 64.38% | 42.86% | 8.39 | 143.03 |
| Batch 4 | 2000 | 1624.6 | 1274.12 | 1145.91 | 81.23% | 63.71% | 57.30% | 8.54 | 234.19 |

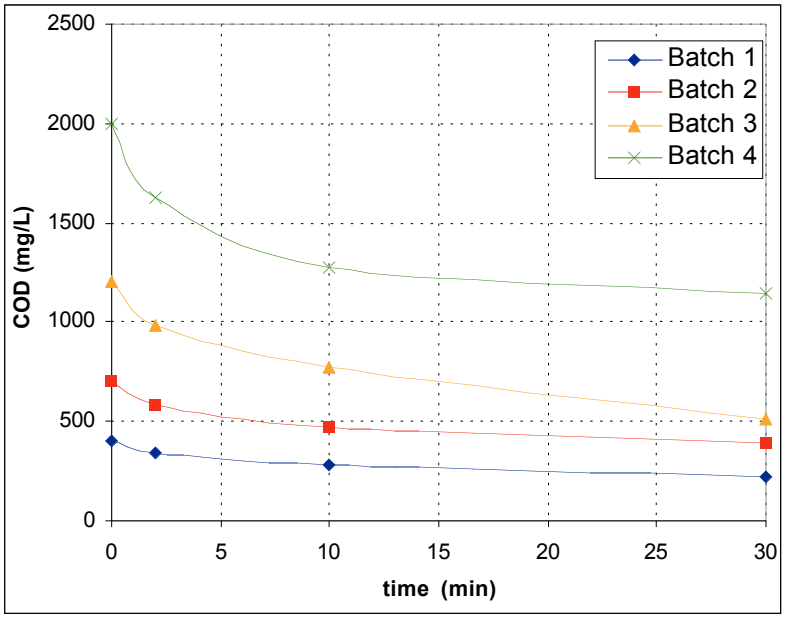


Figure 2-1. COD absorption tests

Let us note that the dynamics of this phenomenon is relatively rapid and there is a convergent point at about 50% of the initial concentration, where no more absorption occurs. In this case we

can assume that beyond this point, equilibrium is reached between the absorbed substrate and the remaining one in the liquid medium. Note also that the filling phase needs about 10 minutes and this time is close to that needed to reach the equilibrium point. Therefore we can fit the model to the measured values of substrate after the filling phase. Moreover the measured values of substrate correspond to the ones contained in the water that will be rejected. Hence it is sufficient if we are able to "control" these values so as to meet the environmental pollution constraints.

## 2.2. ANOXIC PHASE: Activated Sludge Model No. 1 in Denitrification

During the anoxic phase, one reaction involving the nitrate (+nitrite) degradation can be considered, as follows:

$$\frac{1}{Y_h} S_C + \frac{1 - Y_h}{2.86 Y_h} S_{NO} \xrightarrow{r_{hN}} X_h + N_2 \tag{77}$$

where $r_{hN}$ is the denitrification rate, $r_{hN} = \mu^{\circ}_{hN} X_h$. According to the scientific literature, the specific biomass growth rate $\mu^{\circ}_{hN}$ is usually related to the following kinetic expression:

$$\mu^{\circ}_{hN} = \mu_{hN\max} \left[ \frac{S_C}{K_{C1} + S_C} \right] \left[ \frac{S_{NO}}{K_{NO} + S_{NO}} \right] \left[ \frac{K_{Oh}}{K_{Oh} + S_O} \right] \tag{78}$$

In the general case of anoxic phase, the dissolved oxygen concentration is low enough to consider that the last term in the expression above is equal to 1, i.e. $S_O << K_{Oh}$. Therefore the previous expression can be simplified into the following one:

$$\mu_{hN} = \mu_{hN\max} \left[ \frac{S_C}{K_{C1} + S_C} \right] \left[ \frac{S_{NO}}{K_{NO} + S_{NO}} \right] \tag{79}$$

The ammonification follows the reaction:

$$S_N \xrightarrow{r_N} S_{NH} \tag{80}$$

where $S_N$ = TKN – $S_{NH}$, is the soluble organic nitrogen, and the reaction rate: $r_N = \mu_0 S_N$, with $\mu_0$ constant.

The endogenous respiration in the anoxic phase is related to the following reaction:

$$C_X + S_{NO} \xrightarrow{r_{e1}} \ldots \tag{81}$$

with a reaction rate $r_{e1}$. $C_X$ is the organic carbon produced from the dead biomass.

The biomass mortality is represented by the following scheme of reactions:

$$\begin{cases} X_h \xrightarrow{r_{d1}} X_d \\ X_a \xrightarrow{r_{d2}} X_d \end{cases} \text{ and } X_d \xrightarrow{r_{dX}} C_X \tag{82}$$

where $X_d$ is the dead biomass. The organic carbon $C_X$ then hydrolyzes into new organic carbon, such as:

$$C_X \xrightarrow{r_{Cx}} S_C \tag{83}$$

The dynamical model can be related to the following equations:

$$\frac{dS_C}{dt} = -k_1 \mu_{hN} X_h + k_{Cx} r_{Cx} \quad (84)$$

$$\frac{dS_{NO}}{dt} = -k_2 \mu_{hN} X_h - k_{e1} r_{e1} \quad (85)$$

$$\frac{dS_{NH}}{dt} = k_3 r_N \quad (86)$$

$$\frac{dS_N}{dt} = -r_N \quad (87)$$

In the above equations, the yield coefficients $k_1$ and $k_2$ are related to the standard IWA notations as follows:

$$k_1 = \frac{1}{Y_{hN}},\ k_2 = \frac{1-Y_{hN}}{2.86 Y_{hN}},\ k_3 = \frac{1-Y_{h1}}{1.17 Y_{h1}} \quad (88)$$

We have also the following mass balance equations for the bacteria and $C_X$ :

$$\frac{dX_h}{dt} = \mu_{hN} X_h - r_{d1} \text{ with } r_{d1} = k_{d1} X_h \quad (89)$$

$$\frac{dX_a}{dt} = -r_{d2} \text{ with } r_{d2} = k_{d2} X_h \quad (89)$$

$$\frac{dX_d}{dt} = r_{d1} + r_{d2} - k_{dX} r_{dX} \quad (90)$$

$$\frac{dC_X}{dt} = r_{dX} - r_{Cx} - k_{e2} r_{e1} \quad (91)$$

As the EM2-a model, the EM2-b first model contains some parameters that are not directly identifiable. Therefore observations and assumptions based on the knowledge and the literature will provide some model simplifications.

Some carbon is also remaining at the end of reactor operation in the LBE reactor. This corresponds to the organic carbon produced from the dead biomass. As it is not measurable, we assume that there exists a "non-biodegradable" carbon in the model, denoted $S_{C\min}$. With this assumption, the term containing "$r_{Cx}$" can be removed from the model, as it is already taken into account in the non-biodegradable carbon. Therefore, the equation related to the C-degradation can be rewritten as follows:

$$\frac{dS_C}{dt} = -k_1 \mu_{hN} X_h \quad (92)$$

where the reaction is described by $r_{hN} = \mu_{hN} X_h$ with

$$\mu_{hN} = \mu_{hN\max} \left[ \frac{S_C - S_{C\min}}{K_{C1} + S_C - S_{C\min}} \right] \left[ \frac{S_{NO}}{K_{NO} + S_{NO}} \right] \quad (93)$$

The same phenomenon exists also for the soluble organic nitrogen, $S_N$. Therefore we can also assume that there exists a non-degradable $S_N$, denoted $S_{N\min}$, such as the ammonification rate can be expressed as follows :

$$r_N = \rho_0 (S_N - S_{N\min}) \tag{94}$$

Since the $NO_3$ consumption by the endogenous respiration is relatively weak, let us also assume that we can neglect the endogenous term in equation (85), what leads to the following equation:

$$\frac{dS_{NO}}{dt} = -k_2 \rho_{hN} X_h \tag{95}$$

For the biomass decay, we assume that the terms containing "$r_{d1}$" and "$r_{d2}$" are very small so that the biomass dynamics alone is sufficient to describe the biomass growth. In the anoxic phase, the biomass growth follows then only the expressions:

$$\frac{dX_h}{dt} = \rho_{hN} X_h \tag{96}$$

$$\frac{dX_a}{dt} = 0 \tag{97}$$

After some sensitivity analyses (see Appendix 3), the parameters to be identified in this phase are $Y_{hN}$ and $k_N$, related to the yield coefficients, and $\mu_{hN\max}$, $K_{C1}$, $K_{NO}$ and $\mu_0$, related to the kinetics parameters.

### 2.2.1. Data selection

Like in the EM2-a model, the data are treated and analyzed for each phase so as to distribute them into a calibration dataset and into a validation dataset. As before, the proportion of data for the calibration related to those for the validation is 2 to 3, i.e. two third of the data used for parameter calibration. More details of identification operations can be found in the file "EM2b_identification.xls".

### 2.2.2. Yield coefficients

For identifying the coefficients $Y_{hN}$ and $k_N$, two sub-models have been written :

$$\frac{d}{dt}\begin{bmatrix} S_C \\ S_{NO} \end{bmatrix} = \begin{bmatrix} -\frac{1}{Y_{hN}} \\ -\frac{1 - Y_{hN}}{2.86 Y_{hN}} \end{bmatrix} \rho_{hN} X_h \tag{98}$$

and

$$\frac{d}{dt}\begin{bmatrix} S_{NH} \\ S_N \end{bmatrix} = \begin{bmatrix} k_3 \\ -1 \end{bmatrix} r_N \tag{99}$$

As mentioned previously, these equations can be rewritten in the following format that is convenient for applying linear regression techniques :

$$\frac{2.86}{1-Y_h}\frac{dS_{NO}}{dt}+\frac{dS_C}{dt}=0 \quad (100)$$

and

$$\frac{dS_{NH}}{dt}+k_3\frac{dS_N}{dt}=0 \quad (101)$$

The identification procedure applied to the LBE/INRA data in the anoxic phase results in Table 2.2. Note that the confidence intervals have been computed by using the method presented in **Appendix 2**.

Table 2-2. EM2b yield coefficients in the anoxic phase

| Yield coefficient | Unity | Value | Confidence Interval |
|---|---|---|---|
| $Y_{hN}$ | mg VSS/mg COD | 0.828 | 0.069 |
| $k_3$ | mg N-NH/mg N | 0.905 | 0.014 |

### 2.2.3. Kinetics parameters

The kinetics parameters to be identified are $\mu_{hN\max}$, $K_{C1}$, $K_{NO}$ and $\mu_0$. They are identified by following the same procedure as before based on the following model prediction equations :

$$\frac{d}{dt}\begin{bmatrix}\hat{S}_C\\ \hat{S}_{NO}\\ \hat{X}_h\end{bmatrix}=\begin{bmatrix}-1/Y_h\\ -(1-Y_h)/2.86\,Y_h\\ 1\end{bmatrix}\mu_{hN\max}\frac{\hat{S}_C-S_{C\min}}{K_{C1}+\hat{S}_C-S_{C\min}}\frac{\hat{S}_{NO}}{K_{NO}+\hat{S}_{NO}}\hat{X}_h \quad (102)$$

$$\frac{d}{dt}\hat{S}_N=-\mu_0\hat{S}_N \quad (103)$$

Using the Matlab function "lsqnonlin", the identification procedure applied to the LBE/INRA data in the anoxic phase gives the results summarized in Table 2-3.

Table 2-3. EM2bkinetic parameters in the anoxic phase

| Kinetics parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $\mu_{hN\max}$ | $min^{-1}$ | 0.016 | 0.0046 |
| $K_{C1}$ | mg COD/L | 144.45 | 4.16 |
| $K_{NO}$ | mg N/L | 20.47 | 0.85 |
| $\mu_0$ | $min^{-1}$ | 0.0067 | 0.0023 |

## 2.3. AEROBIC PHASE: Activated Sludge Model No. 1 in Nitrification

The C-removal process in the aerobic phase is described by the following reaction

$$\frac{1}{Y_h}S_C+\frac{1-Y_h}{Y_h}S_O \xrightarrow{\mu_h} X_3+CO_2 \quad (104)$$

where the reaction rate, by taking into account the non-biodegradable carbon, is given by $r_h = \rho_h X_h$ with:

$$\rho_h = \rho_{h\max} \frac{S_C - S_{C\min}}{K_{Ch} + S_C - S_{C\min}} \frac{S_O}{K_{Oh} + S_O} \tag{105}$$

and as presented in the last meetings and the first annual report, the nitrification process that can be found in [HEN 87, VAN 99] is associated to:

$$\frac{1}{Y_a} S_{NH} + \frac{4.57 - Y_a}{Y_a} S_O \xrightarrow{r_a} X_4 + \frac{1}{Y_a} S_{NO} \tag{106}$$

where $r_a$ is the nitrification rate, with $r_a = \rho_a X_a$ and

$$\rho_a = \rho_{a\max} \frac{S_{NH}}{K_{NHa} + S_{NH}} \frac{S_O}{K_{Oa} + S_O} \tag{107}$$

Experimental evidence leads us to rewrite the stoichiometric parameters in the nitrification reaction as follows :

$$\frac{1}{Y_a} S_{NH} + \frac{\eta_1}{Y_a} S_O \xrightarrow{r_a} X_4 + \frac{\eta_2}{Y_a} S_{NO} \tag{108}$$

where $\eta_1$ and $\eta_2$ are coefficients related to dissolved oxygen and nitrate/nitrite-nitrogen concentrations, respectively.

Also, the ammonification takes place according to:

$$S_N \xrightarrow{r_N} S_{NH} \tag{109}$$

where the ammonification rate follows the following form (including the non-degradable $S_N$, denoted $S_{N\min}$):

$$r_N = \mu_0 (S_N - S_{N\min}) \text{ ; with } \mu_0 \text{ constant} \tag{110}$$

The endogeneous respiration in the aerobic phase is associated to:

$$C_X + S_O \xrightarrow{r_{e2}} \ldots \tag{111}$$

with $r_{e2}$, its reaction rate.

The biomass mortality is associated to the following reactions:

$$\begin{cases} X_h \xrightarrow{r_{d1}} X_d \\ X_a \xrightarrow{r_{d2}} X_d \end{cases} \text{ and } X_d \xrightarrow{r_{dX}} C_X \tag{112}$$

As previously, the terms corresponding to the biomass decay are assumed to be included in the biomass growth. Therefore we do not put these terms in the model equations.

The organic carbon $C_X$ will also hydrolyse into new organic carbon:

$$C_X \xrightarrow{r_{Cx}} S_C \tag{113}$$

which is already included in the term of non-biodegradable carbon.

Thus, the dynamical model can be described by the following equations:

$$\frac{dX_h}{dt} = \mu_h X_h \tag{114}$$

$$\frac{dX_a}{dt} = \mu_a X_a \tag{115}$$

$$\frac{dS_C}{dt} = -k_4 \mu_h X_h \tag{116}$$

$$\frac{dS_O}{dt} = -k_5 \mu_h X_h - k_6 \mu_a X_a - r_{e2} + k_L a\,(S_{Os} - S_O) \tag{117}$$

$$\frac{dS_{NO}}{dt} = k_7 \mu_a X_a \tag{118}$$

$$\frac{dS_{NH}}{dt} = -k_8 \mu_a X_a + k_{3b}\, r_N \tag{119}$$

$$\frac{dS_N}{dt} = -r_N \tag{120}$$

If we assume that the term $r_{e2}$, corresponding to the aerobic endogenous respiration, is constant, it can be considered as a gap to the DO saturation constant in the liquid medium, that is equal to ($r_{e2}/k_La$). Consequently, we can simplify the model by removing the term $r_{e2}$ and putting $S_{O\max}$ instead of $S_{Os}$ that represents the maximal DO in the liquid medium, where:

$$S_{O\max} = S_{Os} - \frac{r_{e2}}{k_L a} \tag{121}$$

This assumption will allow us to simplify the equation (135) as:

$$\frac{dS_O}{dt} = -k_5 \mu_h X_h - k_6 \mu_a X_a + k_L a\,(S_{O\max} - S_O) \tag{122}$$

This equation is simpler then the previous one as the value of $S_{O\max}$ can be directly deduced from the given data.

The yield coefficients $k_i$ ($i$ = 4 to 8) are elated to the IWA notations via the following expressions:

$$k_4 = \frac{1}{Y_h},\ k_5 = \frac{1 - Y_h}{Y_h},\ k_6 = \frac{4.57 - Y_a}{Y_a} = \frac{\mu_1}{Y_a},\ k_7 = \frac{\mu_2}{Y_a},\ k_8 = \frac{1}{Y_a} \tag{123}$$

Thus, the parameters to be identified are: $Y_h$, $Y_a$ and $k_{3b}$ (the yield coefficients) with the associated coefficients $\mu_1$ and $\mu_2$, also $\mu_{h\max}$, $\mu_{a\max}$, $K_{Ch}$, $K_{Oh}$, $K_{NHa}$, $K_{Oa}$ and $\mu_0$ (the kinetics parameters).

### 2.3.1. Data selection

As the aerobic phase is independent of the anoxic one, the data used for the calibration in the aerobic phase are not necessarily considered in the same dataset than the one used for the anoxic phase. A set of data is selected according to the same criteria than before.

### 2.3.2. Gas transfer parameters

The values of $k_La$ are provided directly by the partners for each experiment. The techniques they used for $k_La$ identification is based on hydrodynamic tests (see the first annual report of EOLI).

The parameter values are given to the Table 2-4

Table 2-4. EM2-b gas transfer parameters

| Parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $k_La$ | $min^{-1}$ | 0.3 | 0.031 |
| $S_{Omax}$ | mg DO/L | 7.86 | 0.59 |

### 2.3.3. Yield coefficients

The identification involves the following yield coefficients: $Y_h$, $Y_a$, $\eta_1$, $\eta_2$ and $k_{3b}$. Some experiment evidence has shown that the value of $k_{3b}$ is equal to that of $k_3$ in the anoxic phase. Therefore, four parameters ($Y_h$, $Y_a$, $\eta_1$, $\eta_2$) remain to be identified.

A sub-model corresponding to the state variables $S_C$, $S_{NH}$, $S_{NO}$ and $S_O$, can be written in the following form:

$$\frac{d}{dt}\begin{bmatrix} S_C \\ S_{NH} \\ S_{NO} \\ S_O \end{bmatrix} = \begin{bmatrix} -\frac{1}{Y_h} & 0 & 0 \\ 0 & -\frac{1}{Y_a} & k_3 \\ 0 & \frac{\eta_2}{Y_a} & 0 \\ \frac{1-Y_h}{Y_h} & \frac{\eta_1}{Y_a} & 0 \end{bmatrix} \begin{bmatrix} \mu_h X_h \\ \mu_a X_a \\ r_N \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ 0 \\ k_L a(S_{O\max} - S_O) \end{bmatrix} \tag{124}$$

which leads as before to the following set of equations that are convenient for linear regression computations :

$$\begin{cases} \frac{1}{\eta_2}\frac{dS_{NO}}{dt} - k_3\frac{dS_N}{dt} = \frac{dS_{NH}}{dt} \\ (1-Y_h)\frac{dS_C}{dt} - \frac{\eta_1}{\eta_2}\frac{dS_{NO}}{dt} = \frac{dS_O}{dt} - k_L a(S_{O\max} - S_O) \end{cases} \tag{125}$$

From the regressions above, all the parameters are structurally identifiable, except $Y_a$. Nevertheless values for $Y_a$ can be found in the literature. Therefore, using the LBE calibration data, the obtained yield coefficient values are given in Table 2-5.

Table 2-5. EM2-b yield coefficients in the aerobic phase

| Yield coefficient | Unity | Value | Confidence Interval |
|---|---|---|---|
| $Y_h$ | mg VSS/mg COD | 0.81 | 0.17 |
| $Y_a$ | mg VSS/mg N | 1.705 | $2 \times 10^{-5}$ |
| $\eta_1$ | - | 11.62 | 3.422 |
| $\eta_2$ | - | 0.35 | 0.076 |
| $k_{3b} = k_3$ | mg N-NH/mg N | 0.905 | 0.014 |

### 2.3.4. Kinetics parameters

The aerobic phase involves the identification of 6 kinetics parameters: $\mu_{h\max}$, $K_{Ch}$, $K_{Oh}$, $\mu_{a\max}$, $K_{NHa}$ and $K_{Oa}$. It has been noticed that the ammonification rate constant $\mu_0$ is invariant in both phases. The parameter identification is based on the following prediction equations :

$$\frac{d}{dt}\begin{bmatrix}\hat{S}_C\\ \hat{S}_{NH}\\ \hat{S}_{NO}\\ \hat{S}_O\\ \hat{X}_h\\ \hat{X}_a\end{bmatrix} = \begin{bmatrix}-\frac{1}{Y_h} & 0 & 0\\ 0 & -\frac{1}{Y_a} & k_3\\ 0 & \frac{\eta_2}{Y_a} & 0\\ -\frac{1-Y_h}{Y_h} & -\frac{\eta_1}{Y_a} & 0\\ 1 & 0 & 0\\ 0 & 1 & 0\end{bmatrix}\begin{bmatrix}\hat{\mu}_h\hat{X}_h\\ \hat{\mu}_a\hat{X}_a\\ \hat{r}_N\end{bmatrix} + \begin{bmatrix}0\\ 0\\ 0\\ k_L a\left(S_{O\max}-\hat{S}_O\right)\\ 0\\ 0\end{bmatrix} \tag{126}$$

with:

$$\hat{\mu}_h = \mu_{h\max}\frac{\hat{S}_C - S_{C\min}}{K_{Ch}+\hat{S}_C - S_{C\min}}\frac{\hat{S}_O}{K_{Oh}+\hat{S}_O} \tag{127}$$

$$\hat{\mu}_a = \mu_{a\max}\frac{\hat{S}_{NH}}{K_{NHa}+\hat{S}_{NH}}\frac{\hat{S}_O}{K_{Oa}+\hat{S}_O} \tag{128}$$

Table 2-6. EM2-b kinetics parameters in the aerobic phase

| Kinetics parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $\mu_{h\,max}$ | $min^{-1}$ | 0.017 | 0.0019 |
| $K_{Ch}$ | mg COD/L | 133.35 | 5.71 |
| $K_{Oh}$ | mg DO/L | 39.68 | 3.61 |
| $\mu_{a\,max}$ | $min^{-1}$ | 0.021 | 0.0042 |
| $K_{Nha}$ | mg N/L | 31.91 | 5.17 |
| $K_{Oa}$ | mg DO/L | 60.72 | 5.43 |
| $\mu_0$ | $min^{-1}$ | 0.0067 | 0.0023 |

The result of the identification procedure are given in Table 2-6. Note also that the identification of the kinetics parameters implies that we had already identified the gas transfer parameters, such as $k_La$ and $S_{Omax}$ (associated to $S_{Os}$).

## *2.4. Non-biodegradable substrates*

Table 2-6. EM2-b non-biodegradable substrates parameters

| Parameter | Unity | Value | Confidence Interval |
|---|---|---|---|
| $S_{C\,min}$ | mg COD/L | 30.42 | 7.42 |
| $S_{N\,min}$ | mg N/L | 4.38 | 0.88 |

## 2.5. EM2-b model validation

### 2.5.1. Validation 1

The first validation is related to the experimental data of October 27, 2003. Note that the first value of $S_C$ seems to be very high (i.e. above 500 mg/L) comparing with the average value in all other data (i.e. about 200 mg/L). For the simulation, we consider the second value as the initial value of $S_C$. The comparisons between the measurement values and the simulation ones are illustrated in the following tables and figures.

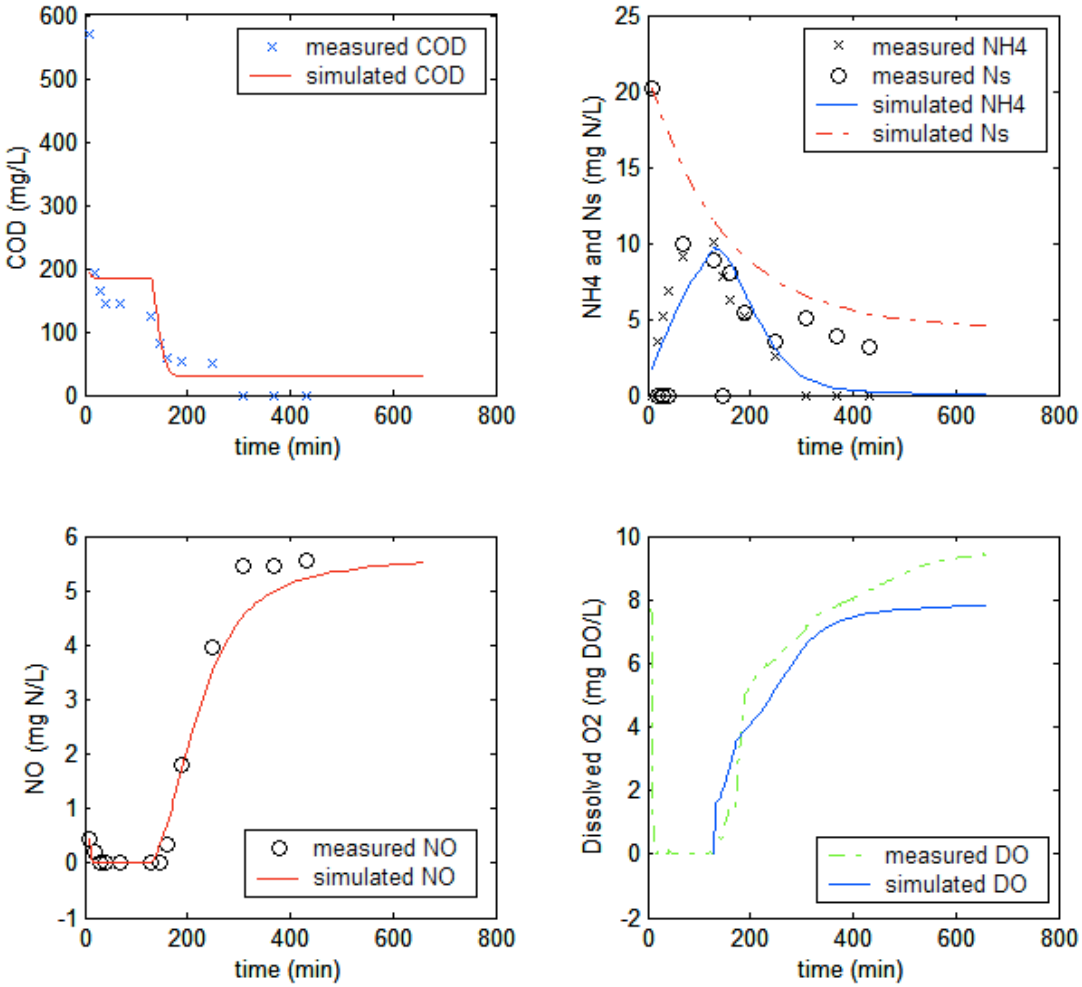


Figure 2-1. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO}$ and $S_O$ of October 27, 2003

Table 2-8. EM2-b error for the data validation of October 27, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO}$ | $S_O$ |
|---|---|---|---|---|---|---|
| Error | Δ (mg/L) | -25.393 | 0.104 | 2.558 | -0.130 | -0.799 |
| | Δ° (%) | -16.044 | 2.398 | 33.893 | -7.305 | -10.993 |

### 2.5.2. Validation 2

The second validation is related to the experimental data of October 29, 2003. The comparisons between the measurement values and the simulation ones are illustrated in the following tables and figures.

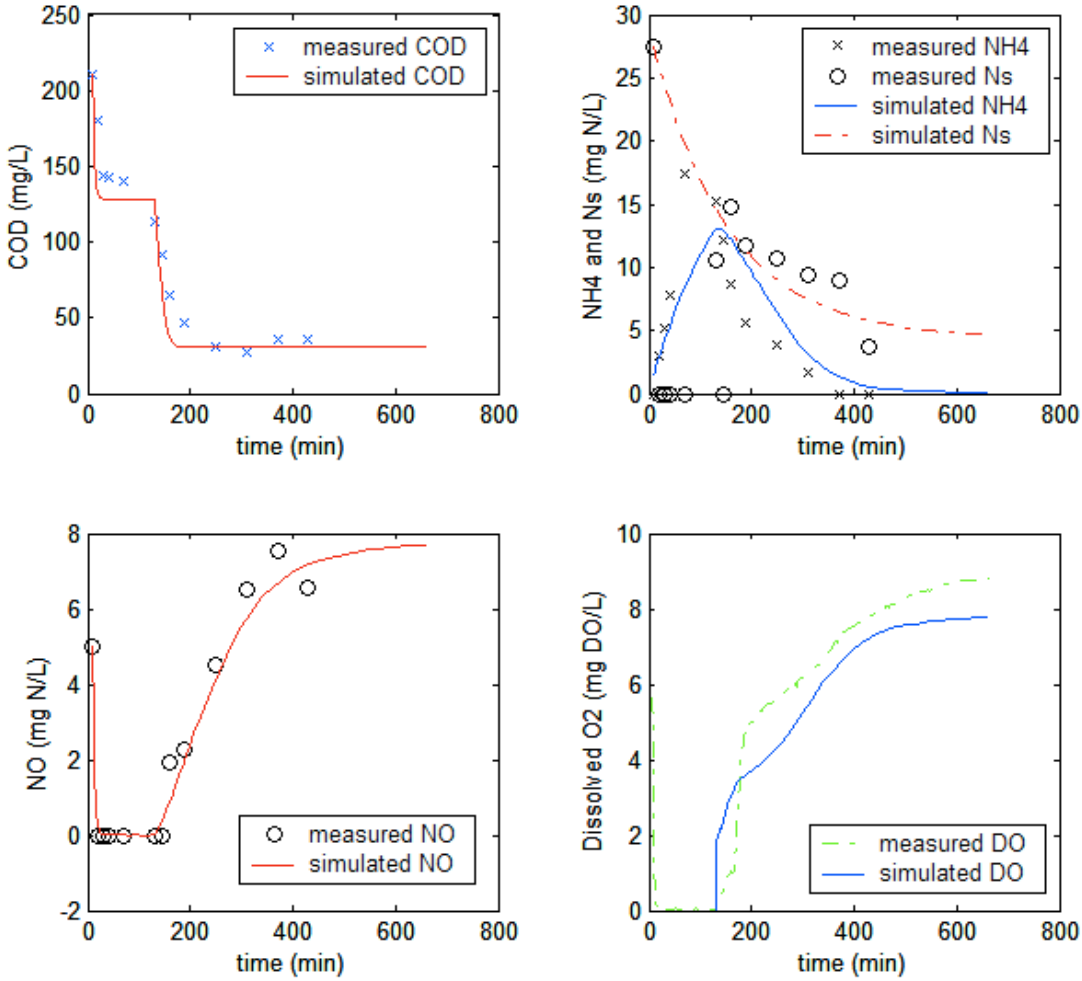


Figure 2-3. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO}$ and $S_O$ of October 29, 2003

Table 2-10. EM2-b error for the data validation of October 29, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO}$ | $S_O$ |
|---|---|---|---|---|---|---|
| Error | Δ (mg/L) | -11.781 | 0.093 | -0.276 | -0.157 | -0.661 |
| | Δ° (%) | -12.107 | 1.489 | -2.277 | -5.936 | -9.793 |

### 2.5.3. Validation 3

The following validation is related to the data of October 31, 2003. The comparisons between the measurement values and the simulation ones are illustrated in the following figures. As in the beginning the values of measured $S_{NO}$ is equal to zero, the denitrification does not take place for the model.

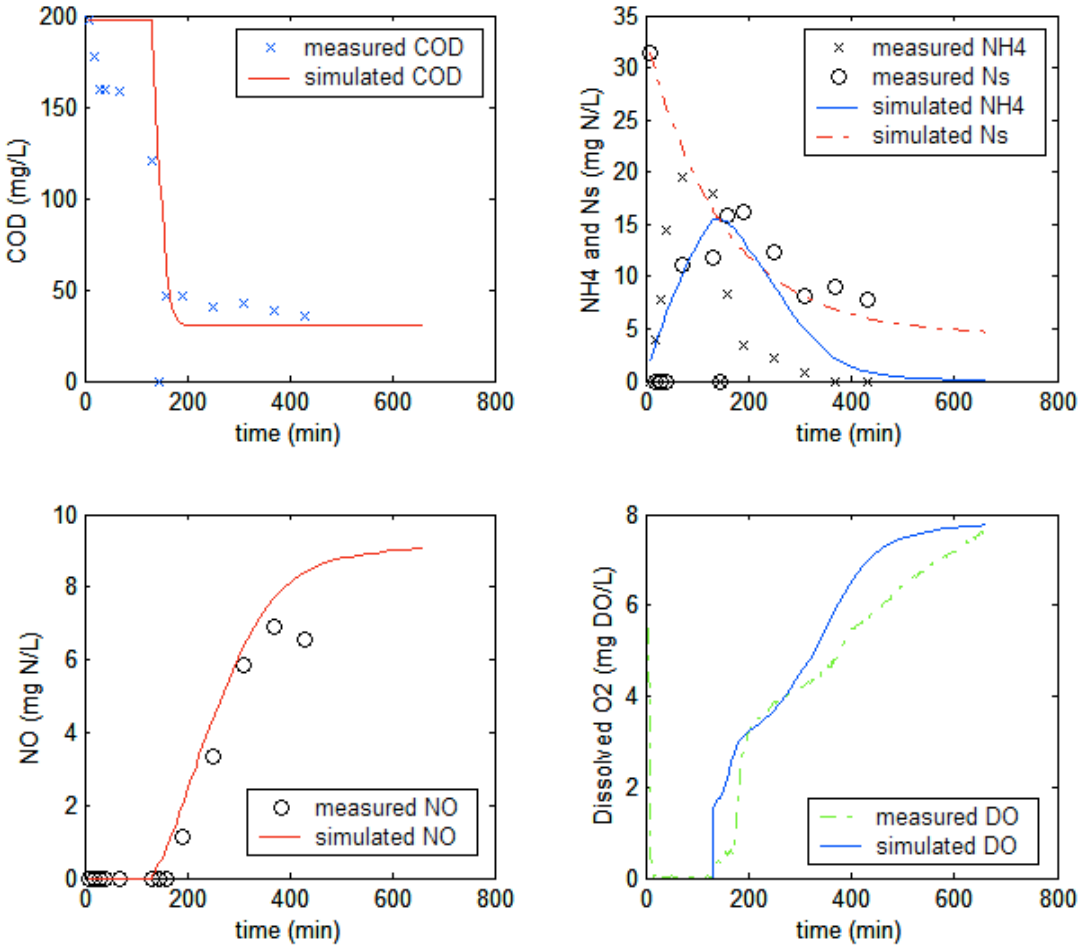


Figure 2-4. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO}$ and $S_O$ of October 31, 2003

Table 2-12. EM2-b error for the data validation of October 31, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO}$ | $S_O$ |
|---|---|---|---|---|---|---|
| Error | □ (mg/L) | 14.931 | 0.795 | 0.443 | 0.468 | 0.722 |
| | □° (%) | 14.652 | 12.175 | 3.227 | 25.584 | 14.447 |

### 2.5.4. Validation 4

This validation is related to the data of November 4, 2003.

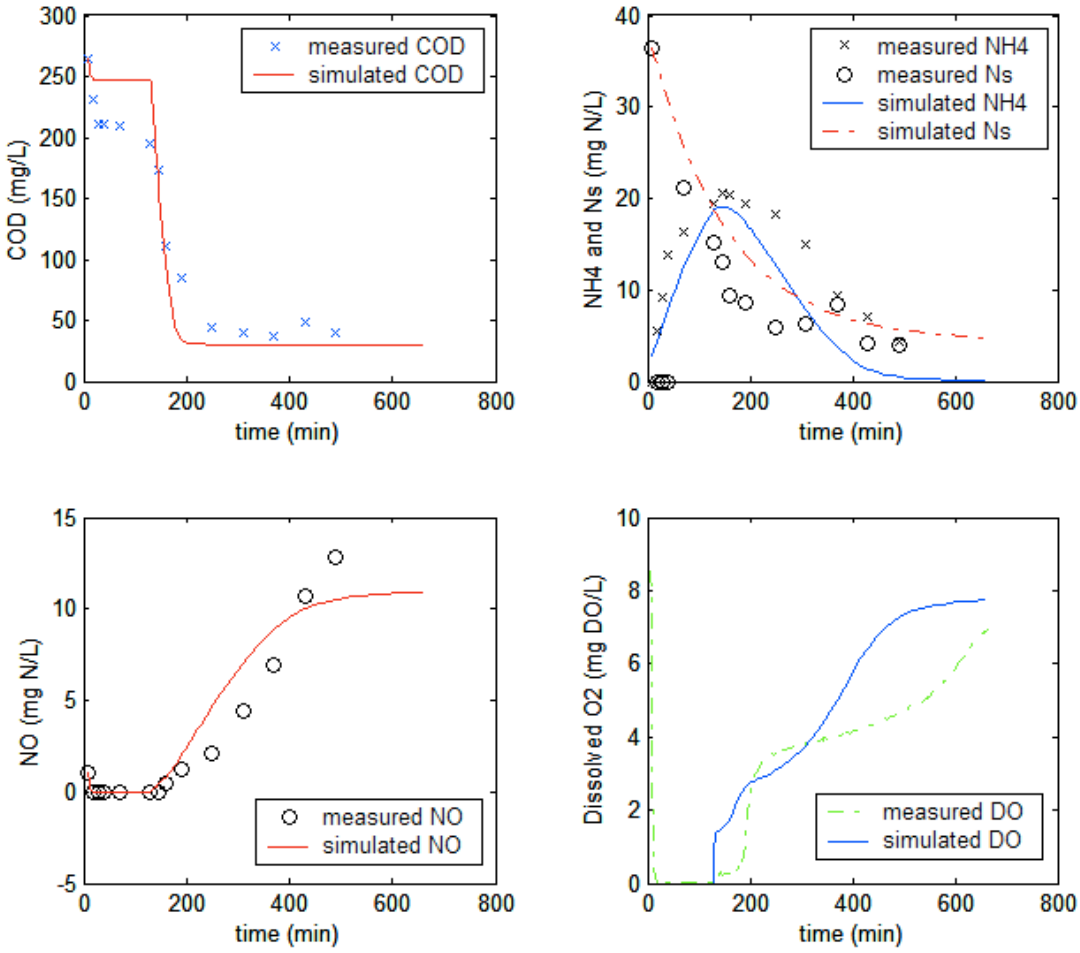


Figure 2-5. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO}$ and $S_O$ of November 4, 2003

Table 2-14. EM2-b error for the data validation of November 4, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO}$ | $S_O$ |
|---|---|---|---|---|---|---|
| Error | □ (mg/L) | 3.791 | -3.164 | 3.131 | 0.391 | 1.258 |
| | □° (%) | 2.796 | -24.778 | 25.978 | 13.781 | 31.338 |

### 2.5.5. Validation 5

This validation is related to the data of November 6, 2003. We can note that the experimental values of $S_N$ in the end of the cycle seem too low comparing with the other experiments. It can be due to some measurement error.

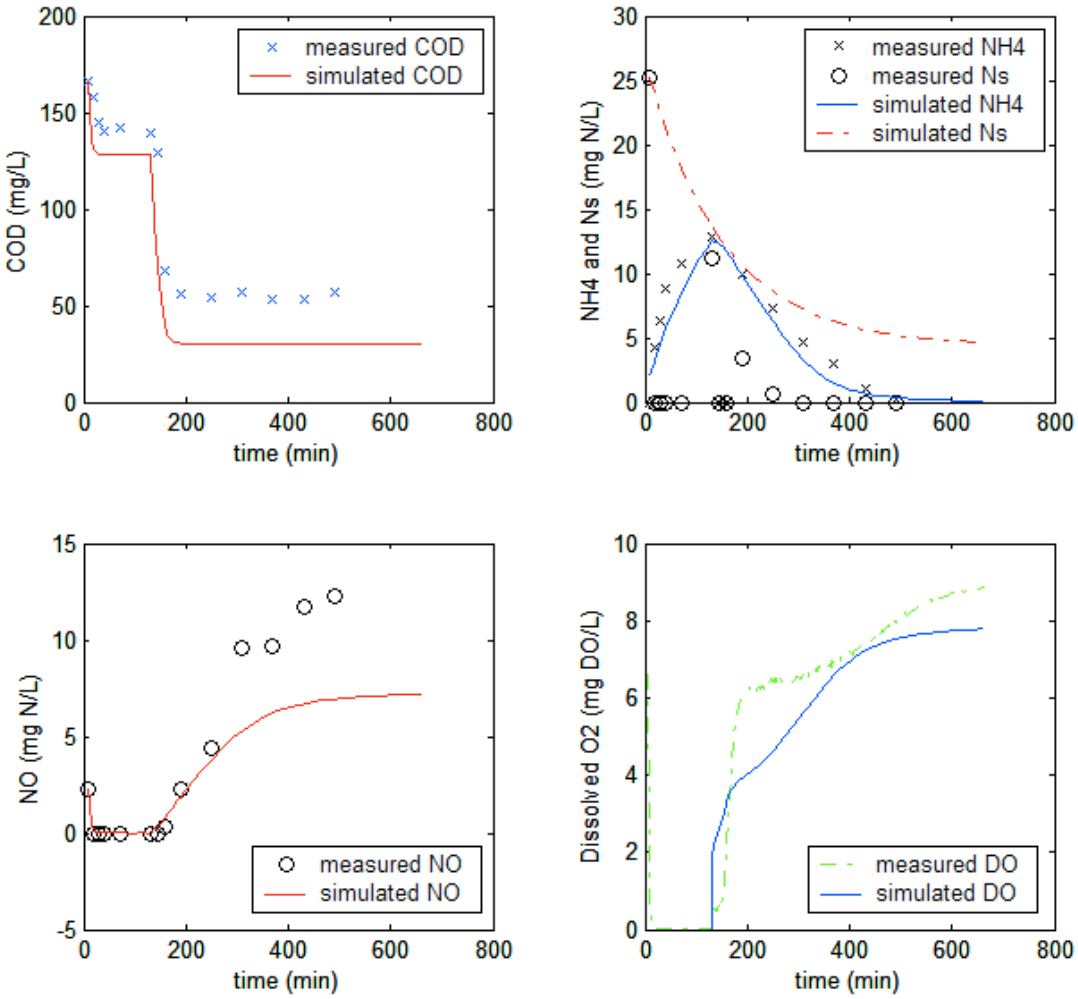


Figure 2-6. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO}$ and $S_O$ of November 6, 2003

Table 2-16. EM2-b error for the data validation of November 6, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO}$ | $S_O$ |
|---|---|---|---|---|---|---|
| Error | □ (mg/L) | -22.611 | -0.925 | 4.402 | -1.293 | -0.738 |
| | □° (%) | -22.293 | -16.041 | 43.519 | -34.478 | -10.652 |

### 2.5.6. Validation 6

This validation is related to the data of November 12, 2003.

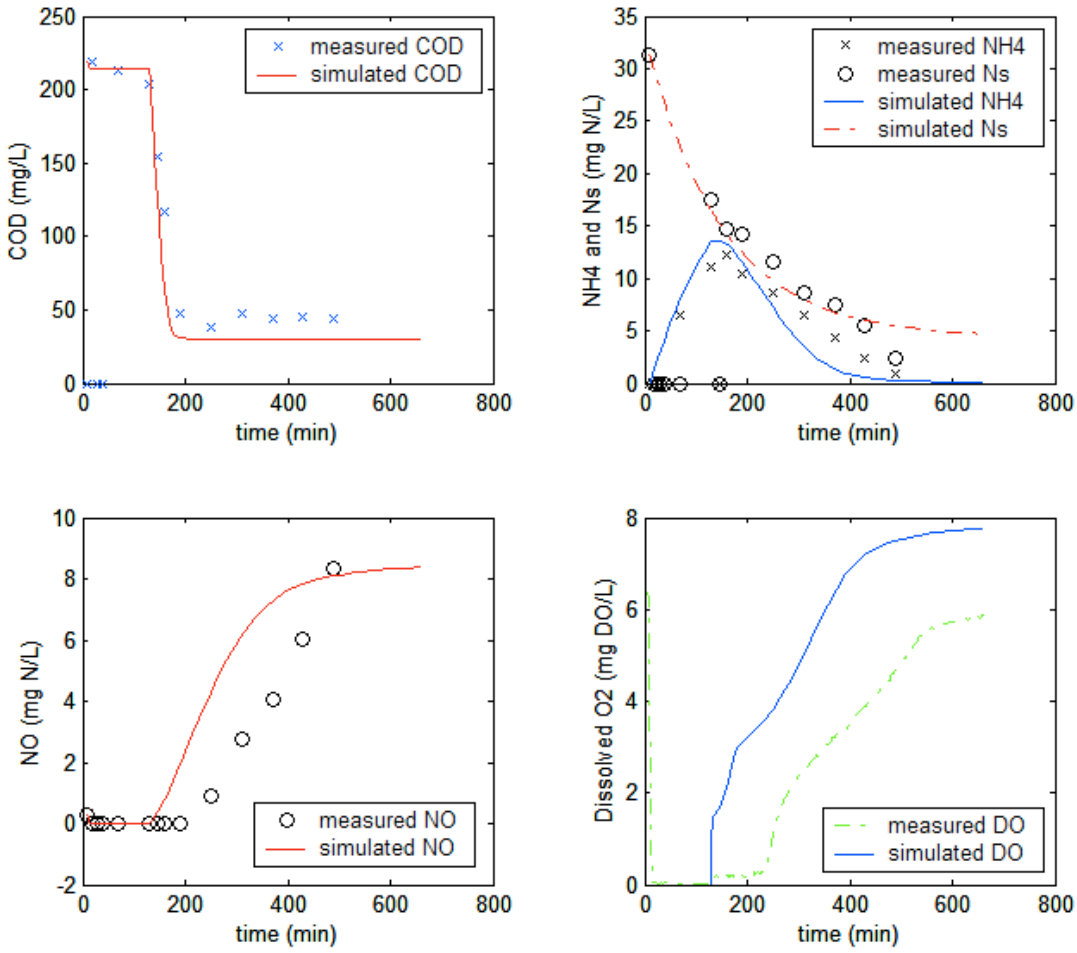


Figure 2-7. Validation of $S_C$, $S_{NH}$, $S_N$, $S_{NO}$ and $S_O$ of November 12, 2003

Table 2-18. EM2-b error for the data validation of November 12, 2003

| Variable | | $S_C$ | $S_{NH}$ | $S_N$ | $S_{NO}$ | $S_O$ |
|---|---|---|---|---|---|---|
| Error | Δ (mg/L) | -13.844 | -0.351 | -0.288 | 1.040 | 2.579 |
| | Δ° (%) | -12.978 | -5.587 | -2.291 | 65.004 | 79.044 |

### *2.6. Conclusions of the EM2-b validation*

There is an outlier for the experiment of October 27, 2003 : the first value of $S_C$ is clearly too high (> 500 mg COD/L) compared to the other $S_C$ values in all experiments.

The experiment of November 6, 2003 exhibits larger $S_N$ measurement errors than those of the other experiments.

In the experiment of November 12, 2003, a decrease is noticed in the aeration capacity of the aeration system, which involves lower DO and $k_La$ values than average values observed in the other experiments.

The large errors in the EM2-b model validation are in particular due to the data inaccuracy, especially for the nitrate/nitrite quantities in the anoxic phase that are very low. Those quantities are small related to the device measurement accuracy. In that case, the simulator does not detect the denitrifying activity in the anoxic phase.

## References

[BAR 83] Barnes, D. and PJ Bliss, *Biological control of nitrogen in wastewater treatment*, E. and FN Spon Inc, London. Carlson, DE 1971, 1983.

[BAS 90] Bastin G. and Dochain D., *On-line Estimation and Adaptive Control of Bioreactors*, Elsevier, Amsterdam, 1990.

[BOU 96] Bourrel S., "Estimation et commande d'un procédé à paramètres répartis utilisé pour le traitement biologique de l'eau à potabiliser", *PhD thesis*, LAAS, Toulouse, France, 1996.

[DOC 01] Dochain D. and Vanrolleghem P.A., *Dynamical Modelling and Estimation in Wastewater Treatment Processes*, IWA Publishing, London, 2001.

[HEN 87] Henze, M., Grady, C.P.L., Gujer, W., Marais, G.v.R and Matsuo, T., "Activated Sludge Model No.1", *IAWPRC Scientific and Technical reports*, No.1, IAWPRC, London, 1987.

[PET 00] Petersen B., "Calibration, identifiability and optimal experimental design of Activated Sludge Models", *PhD thesis*, Universiteit Gent, Belgium, 2000.

[VAN 99] Vanrolleghem P.A., Spanjers H., Petersen B., Ginestet P. and Tacács I., "Estimating (combinations of) Activated Sladge Model No. 1 parameters and compenents by respirometry", *Water Science Technology*, 39(1):195-215, 1999.

**Efficient Operation of Urban Wastewater Treatment Plants**
**(EOLI)**

**Work Package 2**

# APPENDICES

## WP2 – Model Selection and Parameter Identification

***EM2 Associated to C/N Removal Processes***

**November 2002 - May 2004**

# APPENDIX 1. Methods used for the measurements (POLIMI data)

The methods followed for the analysis performed are described in this table:

| parameter | Analytical method | Principle |
|---|---|---|
| NO2-N | photometric determination (cuvette-test Dr. Lange LCK341). | 50 mL of mixed liquor were filtered with a 0.45 mm membrane (cellulose nitrate) and collected in plastic vials. They were immediately analysed. To determine the NO2-N, 2 ml of the filtrate were placed in a vial, according to the concentration range of the sample (0.015-0.6 mgN/L).<br>Expanded uncertainty (95%): ± 5%<br>Detection limit: 0.02 mg/L |
| NO3-N | photometric determination (cuvette-test Dr. Lange LCK339). | 50 mL of mixed liquor were filtered with a 0.45 mm membrane (cellulose nitrate) and collected in plastic vials. They were immediately analysed. To determine the NO3-N, 1 ml of the filtrate were placed in a vial, according to the concentration range of the sample (0.2-13.5 mgN/L).<br>Expanded uncertainty (95%): ± 5%<br>Detection limit: 0.2 mg/L |
| NH4-N | photometric determination (cuvette-test Dr. Lange LCK303 and LCK 304). | 50 mL of mixed liquor were filtered with a 0.45 mm membrane (cellulose nitrate) and collected in plastic vials. They were immediately analysed. To determine the NH4-N, 0.2 ml or 5 ml of the filtrate were placed in a vial according to the concentration range of the sample (2 to 47 or 0.015 to 2 mgN/L).<br>Expanded uncertainty (95%): ± 10% (vials of 0.015 to 2 mgN/L), and ± 5% for vials of 2 to 47 mgN/L.<br>Detection limit: 0.02 mgN/L (vials of 0.015 to 2 mgN/L), 2 mg/L (vials of 2 to 47mg/L). |
| N total | Reactor digestion and photometric determination (cuvette-test Dr. Lange LCK238 and LCK 338). | 50 mL of mixed liquor were filtered with a 0.45 mm membrane (cellulose nitrate) and collected in plastic vials. They were immediately analysed or they were preserved adding sulphuric acid (pH <2) and refrigerated at 4 ºC before the analysis. To determine the N total, 0.5 ml of the filtrate were placed in a vial according to the concentration range of the sample (5 to 40 or 20 to 100 mg/L).<br>Expanded uncertainty (95%): ± 10% ( for both vials).<br>Detection limit: 5 mg/L (vials of 5 to 40 mgN/L), 20 mg/L (vials of 20 to 100mgN/L). |
| COD | Reactor digestion and photometric determination (cuvette-test Dr. | 50 mL of mixed liquor were filtered with a 0.45 mm membrane (cellulose nitrate) and collected in plastic vials. They were immediately analysed or they were preserved adding sulphuric acid (pH <2) and |

| | | |
|---|---|---|
| | Lange LCK114 and LCK 314). | refrigerated at 4 ºC before the analysis. To determine the COD, 2 ml of the filtrate were placed in a vial according to the concentration range of the sample (15 to 150 or 150 to 1000 mg/L). When necessary, a raw sample was analysed too.<br>Expanded uncertainty (95%): ± 10% (vials of 15 to 150 mg/L), and ± 5% for vials of 150 to 1000 mg/L.<br>Detection limit: 15 mg/L (vials of 15 to 150 mg/L), 5 mg/L (vials of 150 to 1000mg/L). |
| TOC | Instrumental analyzer Shimadzu TOC 5050A. | 50 mL of mixed liquor were filtered with a 0.45 □m membrane (cellulose nitrate) and collected in plastic vials. They were preserved adding sulfuric acid (pH <2) and refrigerated at 4 ºC before the analysis.<br>Total carbon is converted to $CO_2$ by combustion in the presence of an oxidation catalyst. $CO_2$ is detected in a non-dispersive infrared gas analyser (NDIR).<br>Inorganic carbon is converted to $CO_2$ by acidification with phosphoric acid. $CO_2$ is detected in a non-dispersive infrared gas analyser (NDIR).<br>TOC carbon is obtained by subtracting the IC concentration from the TC concentration. About 0.5 ml of raw samples or filtered samples were injected in the instrument.<br>Expanded uncertainty (95%): ± 5%.Detection limit: 1 mg/L. |
| SVI | Imhoff cone | One litre of mixed liquor is withdrawn at the end of the aerobic phase and it settles for 30 minutes inside an Imhoff cone.<br>At the end of the settling the volume of sludge settled in the graduated container is read and SVI is calculated dividing this volume for the TSS concentration of the mixed liquor. SVI is expressed in ml/g. |
| TSS | | 20 ml of the sample are filtered with a GFC filter.<br>Then the filter is kept at 105°C for 24 h.<br>When the filter reaches again the ambient temperature (in a drier), it is weighted and it's calculated the concentration of TSS. |
| VSS | | The filter used before to measure TSS is kept at 540°C for 2 h.<br>When the filter reaches again the ambient temperature (in a drier), it is weighted and it's calculated the concentration of TSS. |

# APPENDIX 2. Confidence Intervals

To compute the confidence interval of a set of data, the following information have to be provided:

### Confidence interval CI

$\alpha$ is the significance level used to compute the confidence level. The confidence level is equal to 100 $\cdot$ (1–$\alpha$) %. In the usual terms we assume $\alpha$ equals 0.05, which indicates a 95% confidence level.

In our case we consider also $\alpha$ = 0.05. Once $\alpha$ is defined, we need to calculate the area under the standard normal curve that is equal to (1 - $\alpha$), or 95%, here. This value is ± 1.96. The confidence interval, CI, is therefore:

$$CI = \pm 1.96 \left( \frac{\sigma}{\sqrt{n}} \right)$$

For a set of data with the mean $\bar{x}$, its confidence interval with 95 percent of confidence level implies that 95% of the variables x are statistically within the following range :

$$\bar{x} \pm 1.96 \left( \frac{\sigma}{\sqrt{n}} \right)$$

with $$\bar{x} = \frac{1}{n} \sum_{n} x_i$$

### Standard deviation $\sigma$

The standard deviation, denoted $\sigma$, is a measure of how widely values are dispersed from the average value (the mean). It is given by the following expression:

$$\sigma = \sqrt{\frac{n \sum x^2 - \left( \sum x \right)^2}{n(n-1)}}$$

where $n$ is the sample size, and $x$ is the sample values.

### Sample size *n*

The sample size n is the number of data that is treated.