Estimation of bio-kinetic parameters of nitrification processes from an batch test:

December 31, 2016

Experiment	$NO_3^-(mg/L)$	$NH_3(mg/L)$	$DO(mg/L)$	$VSS(mg/L)$
No Spike	0	0	UK*	730
NO_2^- Spike	50	0	UK	695
NH_3 Spike	0	50	UK	645
NO_2^- and NH_3	50	50	UK	660

Table 1: Initial condition for the declining DO test aimed at estimating AOB and NOB biokinetics. *- UK: The initial condition for DO is treated as a parameter to be estimated by the model

Process	Reaction Expression
Ammonia oxidation (AO)	$21.9O_2 + \frac{21.9}{3.43}NH_3 \rightarrow \frac{21.9}{3.43}NO_2^-$
Nitrite oxidation (NO)	$11.7O_2 + \frac{11.7}{1.14}NO_2^- \rightarrow \frac{11.7}{1.14}NO_3^-$
Ordinary heterotrophic growth (OHO)	$BOD + O_2 \rightarrow CO_2$

Table 2: Reactions considered in the nitrification bio-kinetics parameter estimation example

This case represent interpretation of an actual experiment to determine the rates of microbial activities during ammonia and nitrite oxidation. Four experiments were conducted using the same sludge sample. The variation of dissolved oxygen with respect to time was measured for each of the four experiments. The initial conditions for each of the experiments is shown in Table 1 and the observed variation of DO for the four cases are shown in Figure 1.

The processes considered in the model are shown in table 2. The only constituents that will be explicitly considered in the model include DO, NH_3, NO_2^-, and VSS. VSS is used as a surrogate for biomass (i.e. it is assumed to be proportional to AOB, NOB and OHO) and it is also assumed to stay unchanged throughout each experiment. the Petersen matrix is shown in table 3.

Process	Rate Expression	O_2	NH_3	NO_2^-	VSS
AO	$VSS\mu_{AOB}\frac{[O_2]}{(k_{OA}+[O_2]}\frac{[NH_3]}{[NH_3]+k_{NH3}}$	-21.9	$-\frac{21.9}{3.43}$	$\frac{21.9}{3.43}$	
NO	$VSS\mu_{NOB}\frac{[O_2]}{k_{ON}+[O_2]}\frac{[NO_2^-]}{[NO_2^-]+k_{NO2}}$	-11.7		$-\frac{11.7}{1.14}$	
OHO	$VSS\mu_{OHO}\frac{[O_2]}{k_{OH}+[O_2]}$	$-\frac{1-0.52}{0.52}$			

Table 3: Petersen matrix for the nitrification bio-kinetics parameter estimation example

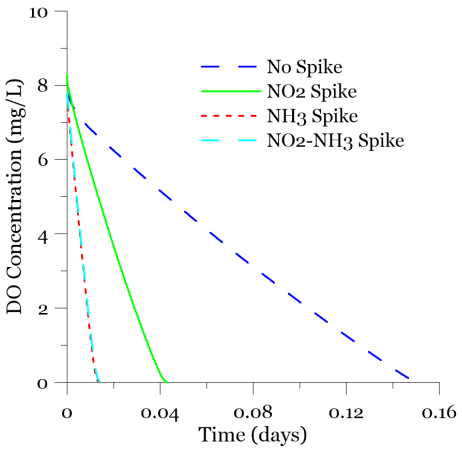

Figure 1: Temporal variation of DO for the four different experiments used to estimate nitrification bio-kinetics parameters

Table 4 shows the prior 95% ranges and the prior distributions of each of the parameters. In this particular case due to lack of information about NH_3 and NO_2^- concentration variation with time if k_{NH3}, and k_{NO2} are considered unknown, there is a risk of problem becoming over-parametrized and therefore, we here assume the values of these two parameters to be fixed.

Steps to set-up the model:

To construct the model in GIFMod follow the following steps:

1. **Add a pond:** We will simulate the reactor using a **Pond** block.

Parameter	2.5%	97.5%	Distribution
μ_{AOB}	0.005	0.5	lognormal
k_{OA}	0.05	2.0	lognormal
μ_{NOB}	0.005	0.5	lognormal
k_{ON}	0.05	2.0	lognormal
k_{NH3}		FIXED = 0.5	
k_{NO2}		FIXED = 0.5	
μ_{OHO}	0.0001	0.1	lognormal
k_{OH}	0.00125	10	lognormal

Table 4: Prior range of parameters used in nitrification bio-kinetics example

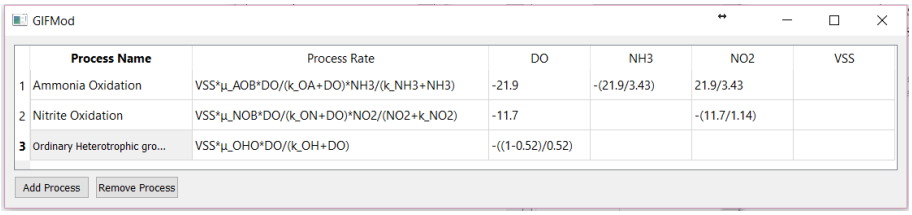

Figure 2: Reaction network for the nitrification parameter estimation example

Other media types can also be used. Add a pond by clicking on the pond icon on the top tool bar. Set the following properties for the pond:
- **Area:** $1m^2$
- **Initial water depth:** 1m

2. **Add the constituents:** Add constituents (DO, NH_3, NO_2^-, VSS) by right-clicking on **Water quality**→**Constituents**.

3. **Adding experiments:** The goal of this example is to infer the values of reaction parameters using four experiments in a holistic way. This means that the best parameter set that can collectively explain the results from the four experiments in sought for. There are two ways to consider four experiments in the model. The first way is to define four independent ponds with different initial conditions and the second way is to use **Experiments**. Here we will use the second approach.

   To add experiments click on the **Add new experiment** button three times to add three new experiments.

4. **Setting the duration of the simulation:** The duration of the experiments are all below 0.2 days. First from the experiment menu on the top tool bar select **All experiments**. This forces the program to apply any changes in the properties to all the experiments. To set the simulation duration to 0.2 from **Settings**→**Project settings** and from the **Properties** window right-click on the label for **Simulation end time** and click on **Enter number** from the drop-down menu that appears. Enter 0.2 in the dialog box that appears.

5. **Adding reaction parameters:** Add the eight reaction parame-

Experiment	$DO(mg/L)$	$NH_3(mg/L)$	$NO_2^-(mg/L)$	VSS (mg/L)
1	7.78	0	0	730
2	7.76	50	0	645
3	8.02	0	50	695
4	7.8	50	50	660

Table 5: Initial conditions for the four experiments used for estimation of bio-kinetics and stoichiometric parameters of nitrification

ters by right-clicking on **Water quality→Reactions→Reaction parameters** according to table 4. For the two fixed parameters k_{NH3} and k_{NO2}, enter a value of 0.5. **Add reaction network:** Right click on reaction **Water quality→Reactions→Reaction network**. Enter the processes according to the Petersen matrix shown in table 3. The finished reaction network window should look like figure 2.

6. **Setting initial conditions:** From the **Experiments** drop-down menu on the top tool bar, select **Experiment1**. Click on the pond block and then from the **Properties** window choose **Constituent initial conditions**. Enter the initial conditions for experiment 1 according to Table 5.

   The initial condition window for the first experiment should look like Figure 3.

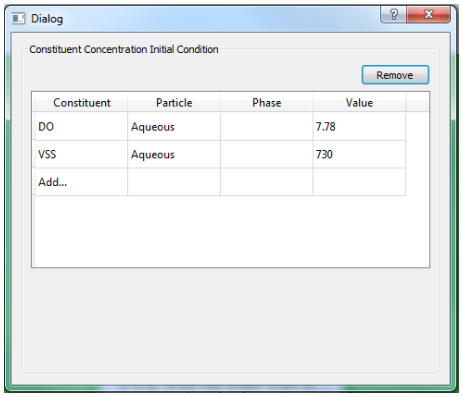

Figure 3: Initial conditions for the nitrification inverse modeling example

Change the experiment to experiment2 from the **Experiments** drop

down menu and similarly set the initial condition according to the second row of table 5.

Similarly assign the initial conditions for experiment 3 and 4.

7. **Setting up parameters to be estimated:** Add a parameter representing μ_{AOB} by right-clicking of **Inverse modeling→Parameters** and clicking on **Add parameters** from the drop-down menu. Assign the following parameter to the newly added parameter:
   - **Name:** μ_{AOB}
   - **Maximum value:** *0.5*
   - **Minimum value:** *0.005*
   - **Distribution:** *Log-Normal*

   Repeat for the other parameters to be estimated including k_{OA}, μ_{NOB}, k_{ON}, μ_{OHO}, and k_{OH} and assign the ranges and the distribution according to table 4. As for the **Value** of the parameters respectively use $\mu_{AOB} = 0.05$, $k_{OA} = 0.31$, $\mu_{NOB} = 0.05$, $k_{ON} = 0.31$, $\mu_{OHO} = 0.003162$, $k_{OH} = 0.111$. These values are used when the model is run in forward mode.
   Please note that the name of the parameters do not have to be identical to their corresponding reaction parameters.

8. **Assigning the parameters to the corresponding model properties:** The parameters defined in the previous step should not be assigned to their corresponding properties in the model. Choose the reaction parameter μ_{AOB} from **Water quality→Reactions→Reaction parameters**, and the right click on the label of **Value** property and from the drop-down menu select **Parameters→**μ_{AOB} figure 4. Repeat for the other parameters to be estimated including k_{OA}, μ_{NOB}, k_{ON}, μ_{OHO}, and k_{OH}.

9. **Setting observations:** Here we specify the properties of the observed data used to perform the parameter estimation.
   Right-click on **Project explorer→Inverse modeling→Observations** and click on **Add Observation**.
   Set the following properties for the first observation:
   <u>observation 1:</u>
   - **Name:** *DO_no_spike*
   - **Standard deviation ID:** *std*
   - **Block/Connector:** *Block*
   - **Error Distribution:** *Normal*

- **Location:** *Pond (1)*
- **Experiment:** *experiment1*
- **Observed data:** *Obs_nospike.txt*

Quantity *DO:Aqueous*

Add three more observation and set the properties as follows:

observation 2:
- **Name:** *DO_NH3_spike*
- **Standard deviation ID:** *std*
- **Block/Connector:** *Block*
- **Error Distribution:** *Normal*
- **Location:** *Pond (1)*
- **Experiment:** *experiment2*
- **Observed data:** *Obs_NH3.txt*

Quantity *DO:Aqueous*

observation 3:
- **Name:** *DO_NO2_spike*
- **Standard deviation ID:** *std*
- **Block/Connector:** *Block*
- **Error Distribution:** *Normal*
- **Location:** *Pond (1)*
- **Experiment:** *experiment3*
- **Observed data:** *Obs_NO2.txt*

Quantity *DO:Aqueous*

observation 4:
- **Name:** *DO_both*
- **Standard deviation ID:** *std*
- **Block/Connector:** *Block*
- **Error Distribution:** *Normal*
- **Location:** *Pond (1)*
- **Experiment:** *experiment3*
- **Observed data:** *Obs_both.txt*

Quantity *DO:Aqueous*

Note: Entering the same **Standard deviation ID** for all the observation forces the program to find a single observation error standard

deviation for all the observation. In this case because the measured quantity for all observations is dissolved oxygen it is expected that the measurement error for all observation to have the same statistical distribution.

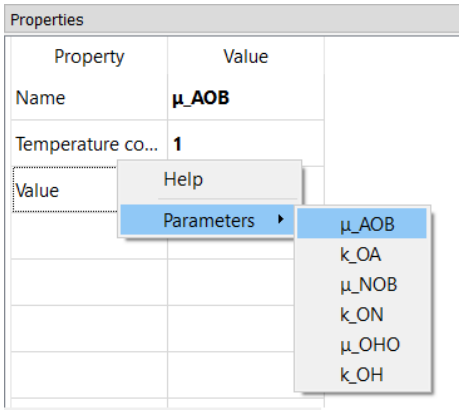

Figure 4: Assigning parameters to model properties

10. **Running in forward mode:** When the model is run in forward mode, the values of the parameters as specified in the **Value** field are used and a single simulation is performed. Click on the forward run icon and wait for the simulation to end. Choose an experiment from the **Experiments** drop-down menu and then right click on the block and choose **Plot water quality results→DO**.

    - Right-click on **Project Explorer→Inverse modeling→ Observations→** *DO_NH3_spike* and then click on **Plot modeled data**. This shows the corresponding model prediction to observations for experiment 2. You can also check the agreement plot.

11. **Change the initial time-step:** The model results that are used to calculate the likelihood are interpolated at time-intervals specified in the **initial time-step field**. Because the experiments in this example are short (0.2 day), the default initial time-step of 0.01 day is not adequate. From the **Project Explorer** choose **Settings→Solver Settings** and then from the **Properties** window find **Initial time step size** and change the value to 0.001 day.

12. **Inverse modeling:**
    - Choose **number of generations** from **Inverse modeling→Genetic Algorithm** and change the value to 100. This makes the number of generations in the Genetic Algorithm to 100. Keep the rest of the parameters unchanged.

    - Choose **number of realizations** from **Inverse modeling→Markov chain Monte Carlo** and change the value to 1000. This makes the number of posterior prediction realizations to 1000. Keep the rest of the parameters unchanged.

    - Click on the inverse modeling icon  on the left side tool bar. Inverse simulation can take up to one hour depending on the number and speed of the CPUs of the computer being used for the simulation. Wait until the deterministic inverse modeling and the MCMC is finished. The progress bars on the **Simulation** window shows the percentage of each stage on inverse modeling being completed (Figures 5 and 6).

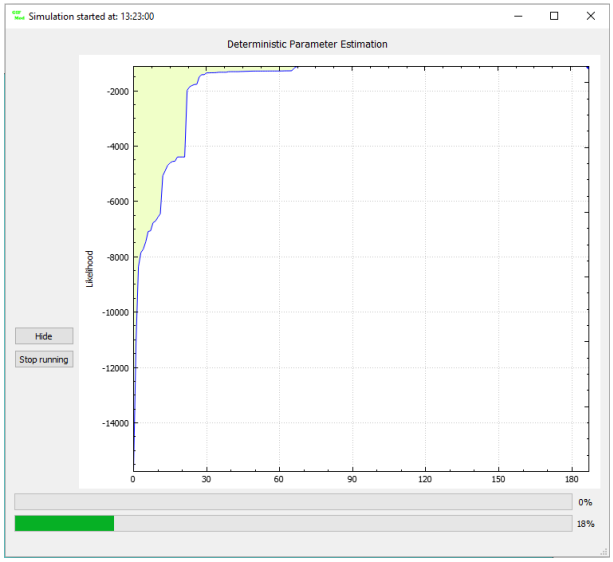

Figure 5: Inverse modeling progress window during deterministic parameter estimation stage

13. **Estimated values of the parameters:** To see the estimated values of the parameters select a parameter from **Project Explorer→Inverse Modeling→Parameters** and look at the **Value** field. The value

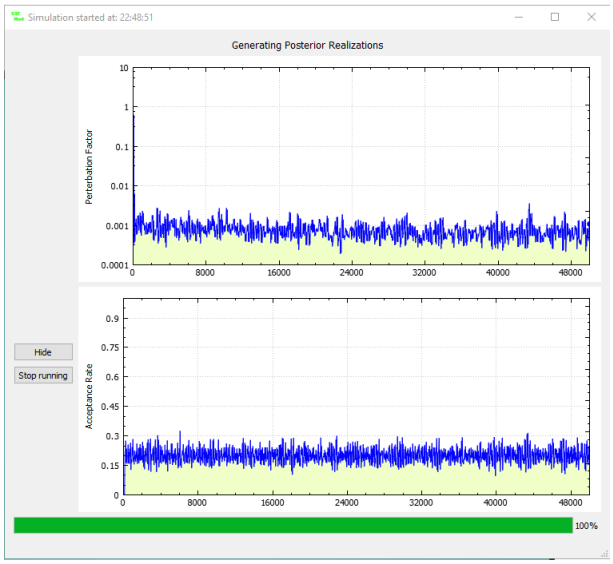

Figure 6: Inverse modeling progress window during probabilistic parameter estimation

should be replaced by the estimated parameter value.

14. **Checking the model vs. observed agreement:** Right-click on **Project Explorer→Inverse Modeling→Observations→***DO_nospike* and the choose **Plot modeled data**. A graph will appear that will show observed data and the model prediction based on the estimated parameters. Do the same for other observation data (Figure 7).

15. **Checking the posterior distributions of the parameters:**
- From **Project Explorer→Inverse Modeling→Parameters** right-click on μ_{NOB} and select **Plot posterior distribution histogram**. A graph will appear that shows the posterior distribution of parameter μ_{NOB} (Figure 8). Similarly inspect the posterior distribution for other parameters. (Figure 9). In this figure the box plot shows the 95% credible interval for the parameter while the solid line shows the median and the dot shows the expected value of the parameter.

- To see the 95% credible intervals for all the parameters right-click on **Project Explorer→Inverse Modeling→Parameters** and select **Plot Percentile data** (Figure 10).

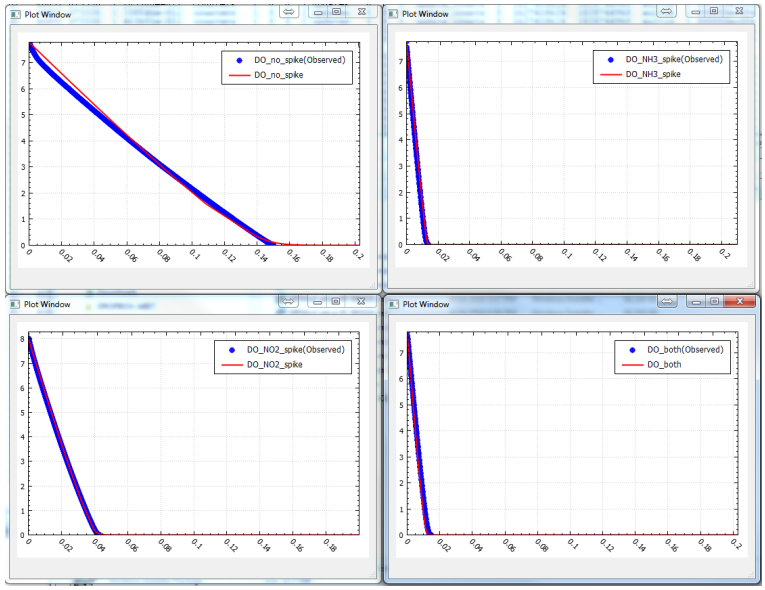

Figure 7: Observed and predicted DO variation in all four experiments

- From **Project Explorer→Inverse Modeling→Parameters** right-click on μ_{NOB} and select **Plot percentiles**.

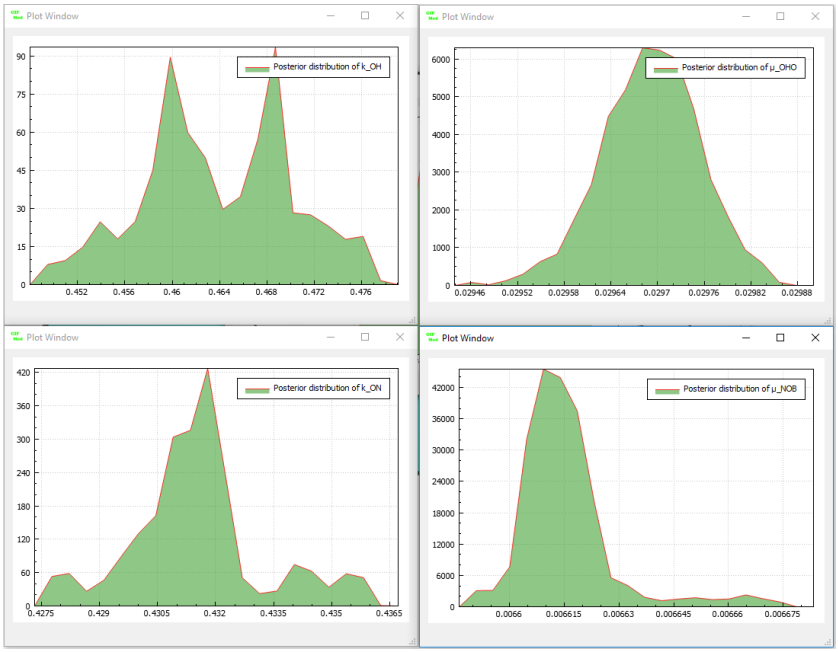

Figure 8: Posterior distribution of k_{OH}, μ_{OHO}, k_{ON}, μ_{NOB}

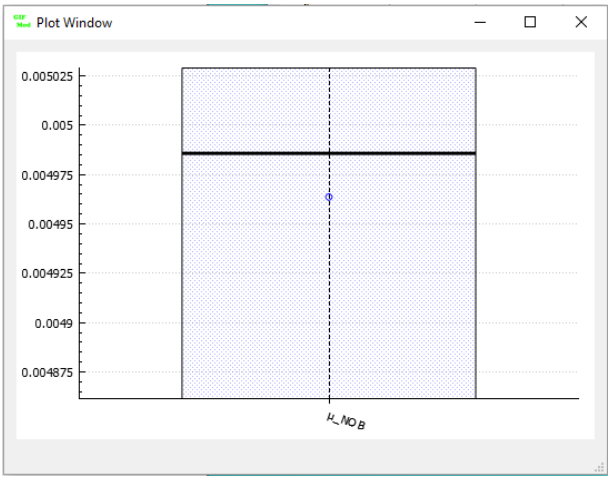

Figure 9: Posterior credible interval for

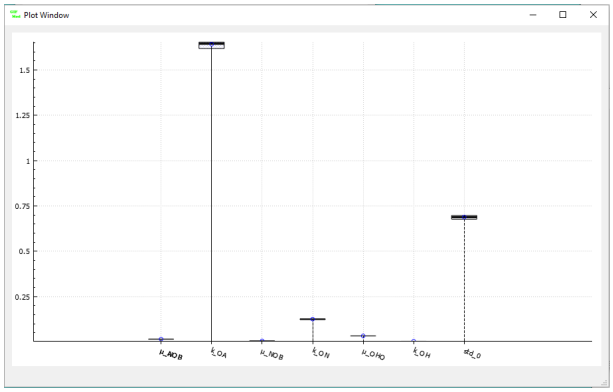

Figure 10: Posterior credible interval for all parameters