Supporting Information

Title:

A Novel Protocol for Model Calibration in Biological Wastewater Treatment

Authors:

Ao Zhu[a,c], Jianhua Guo[a,b,*], Bing-Jie Ni[b], Shuying Wang[a], Qing Yang[a], Yongzhen Peng[a,*]

[a]*Key Laboratory of Beijing for Water Quality Science and Water Environmental Recovery Engineering, Engineering Research Center of Beijing, Beijing University of Technology, Beijing* 100124, *PR China*

[b]Advanced Water Management Centre (AWMC), The University of Queensland, St Lucia, Brisbane, QLD 4072, Australia

[c]Tsinghua Holding Human Settlements Environment Institute, *Beijing* 100083, *PR China*

*Corresponding authors:

Jianhua Guo, Phone: +86-10-67392627; fax: +86-10-67392627; e-mail: gjh@bjut.edu.cn.

Yongzhen Peng, Phone: +86-10-67392627; fax: +86-10-67392627; e-mail: pyz@bjut.edu.cn

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Table S1. Characterizations explanations of the symbols.	
Symbol	Characterization
$\boldsymbol{x}$	State variables of the Ordinary Differential Equations(ODEs)
$\boldsymbol{u}$	Input variables of the ODEs
$\boldsymbol{y}$	Outputs of the ODEs , such as$[COD\ S_{NH4} S_{NO2}\ S_{NO3}]^T$, $\boldsymbol{y}^s$ the simulation ones and $\boldsymbol{y}^o$ the observed measurements
$\boldsymbol{\theta}$	Parameter set of the ODEs
$\boldsymbol{\omega}$	the square noise variance matrix, whose inverse form $\boldsymbol{\omega}^{-1}$ acts as the weights
$E(\boldsymbol{\theta})$	Objective function of the parameter estimation
$\boldsymbol{y}_i$, N_y	the i-th state variable or output, the number of outputs
$\boldsymbol{\theta}_j$, $N_{\boldsymbol{\theta}}$	the j-th parameter in the parameter set, the number of parameters
t_k, N_t	the k-th measuring time, the number of measuring times
$\overline{\boldsymbol{S}}$	the local relative time varying sensitivity matrix at parameter point $\hat{\theta}$
$\overline{\boldsymbol{M}}$	the global relative time varying sensitivity matrix over the bounds-defined parameter space
$\boldsymbol{FIM}$	the local Fisher Information Matrix
$\boldsymbol{C}$	the local covariance matrix derived from the $\boldsymbol{FIM}$
$\overline{\boldsymbol{C}}$	the pseudo-global covariance matrix, derived from $\boldsymbol{C}$ and $E(\boldsymbol{\theta})$
$\boldsymbol{R}$	the pseudo-global correlation matrix, derived from $\overline{\boldsymbol{C}}$

Table S2. Summary of the process rates equations for related processes.

		j	Process	Modified process rate equation
Heterotrophic organisms	1	p1	Hydrolysis	$k_H \frac{X_S / X_H}{K_X + X_S / X_H} X_H$
	2	p2	Aerobic Storage of S_S	$k_{STO} \frac{S_O}{K_{H,O_2} + S_O} \frac{S_S}{K_{H,SS} + S_S} X_H$
	3	p3(a)	Anoxic Storage of S_S NO_3-NO_2	$k_{STO}\eta_{H,NO_3} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_S}{K_{H,SS} + S_S} \frac{S_{NO_3}}{K_{H,NO_3} + S_{NO_3}} X_H$
	4	p3(b)	Anoxic Storage of S_S NO_2-N_2	$k_{STO}\eta_{H,NO_2} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_S}{K_{H,SS} + S_S} \frac{S_{NO_2}}{K_{H,NO_2} + S_{NO_2}} X_H$
	5	p4	Aerobic Growth of X_H	$\mu_H \frac{S_O}{K_{H,O_2} + S_O} \frac{S_{NH_4}}{K_{H,NH_4} + S_{NH_4}} \frac{S_{ALK}}{K_{H,ALK} + S_{ALK}} \frac{X_{STO} / X_H}{K_{H,STO} + X_{STO} / X_H} X_H$
	6	p5(a)	Anoxic Growth of X_H NO_3-NO_2	$\mu_H\eta_{H,NO_3} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_{NH_4}}{K_{H,NH_4} + S_{NH_4}} \frac{S_{ALK}}{K_{H,ALK} + S_{ALK}} \frac{X_{STO} / X_H}{K_{H,STO} + X_{STO} / X_H} \frac{S_{NO_3}}{K_{H,O_2inh} + S_{NO_3}} X_H$
	7	p5(b)	Anoxic Growth of X_H NO_2-N_2	$\mu_H\eta_{H,NO_3} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_{NH_4}}{K_{H,NH_4} + S_{NH_4}} \frac{S_{ALK}}{K_{H,ALK} + S_{ALK}} \frac{X_{STO} / X_H}{K_{H,STO} + X_{STO} / X_H} \frac{S_{NO_2}}{K_{H,O_2inh} + S_{NO_2}} X_H$
	8	p6	Aerobic Endog. Resp. of X_H	$b_{H,O_2} \frac{S_O}{K_{H,O_2} + S_O} X_H$
	9	p7(a)	Anoxic Endog. Resp. of X_H NO_3-NO_2	$b_{H,O_2}\eta_{H,endNO_3} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_{NO_3}}{K_{H,NO_3} + S_{NO_3}} X_H$
	10	p7(b)	Anoxic Endog. Resp. of X_H NO_2-N_2	$b_{H,O_2}\eta_{H,endNO_2} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_{NO_2}}{K_{H,NO_2} + S_{NO_2}} X_H$
	11	p8	Aerobic Endog. Resp. of X_{STO}	$b_{STO,O_2} \frac{S_O}{K_{H,O_2} + S_O} X_{STO}$
	12	p9(a)	Anoxic Endog. Resp. of X_{STO} NO_3-NO_2	$b_{STO,O_2}\eta_{H,endNO_3} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_{NO_3}}{K_{H,NO_3} + S_{NO_3}} X_{STO}$
	13	p9(b)	Anoxic Endog. Resp. of X_{STO} NO_2-N_2	$b_{STO,O_2}\eta_{H,endNO_2} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_{NO_2}}{K_{H,NO_2} + S_{NO_2}} X_{STO}$
AOB	14	p10(a)	Aerobic Growth of X_{AOB}, Nitritation	$\mu_{AOB} \frac{S_O}{K_{AOB,O_2} + S_O} \frac{S_{NH_4}}{K_{AOB,NH_4} + S_{NH_4}} \frac{S_{ALK}}{K_{N,ALK} + S_{ALK}} X_{AOB}$
	15	p11(a)	Aerobic End. Resp. of X_{AOB}	$b_{AOB} \frac{S_O}{K_{H,O_2} + S_O} X_{AOB}$
	16	p12(a)	Anoxic End. Resp. of X_{AOB}	$b_{AOB}\eta_{N,end} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_{NO_3}}{K_{H,NO_3} + S_{NO_3}} X_{AOB}$
NOB	17	p10(b)	Aerobic Growth of X_{NOB}, Nitratation	$\mu_{NOB} \frac{S_O}{K_{NOB,O_2} + S_O} \frac{S_{NH_4}}{K_{H,NH_4} + S_{NH_4}} \frac{S_{NO_2}}{K_{NOB,NO_2} + S_{NO_2}} \frac{S_{ALK}}{K_{N,ALK} + S_{ALK}} X_{NOB}$
	18	p11(b)	Aerobic End. Resp. of X_{NOB}	$b_{NOB} \frac{S_O}{K_{H,O_2} + S_O} X_{NOB}$
	19	p12(b)	Anoxic End. Resp. of X_{NOB}	$b_{NOB}\eta_{N,end} \frac{K_{H,O_2inh}}{K_{H,O_2inh} + S_O} \frac{S_{NO_3}}{K_{H,NO_3} + S_{NO_3}} X_{NOB}$
	20		Aeration	$e^{0.024(T-20)} \cdot K_L a\_20 \cdot (S_{O,SAT} - S_O)$

Table S3. Stoichiometric matrix for the extended processes and selected compounds.

	j	Process	S_O	S_S	S_{NH}	S_{NO2}	S_{NO3}	S_{N2}	S_{ALK}	S_I	X_I	X_H	X_S	X_{STO}	X_{AOB}	X_{NOB}
1	p1	Hydrolysis	0	1-f_{SI}	0	0	0	0	$\frac{i_{N,XS}-f_{SI}\cdot i_{N,SI}-(1-f_{SI})\cdot i_{N,SS}}{14}$	f_{SI}	0	0	-1	0	0	0
2	p2	Aerobic Storage of S_S	$Y_{STO,O_2}-1$	-1	$i_{N,SS}$	0	0	0	$\frac{i_{N,SS}}{14}$	0	0	0	0	Y_{STO,O_2}	0	0
3	p3(a)	Anoxic Storage of S_S NO_3-NO_2	0	-1	$i_{N,SS}$	$\frac{1-Y_{STO,NO_3}}{1.14}$	$-\frac{1-Y_{STO,NO_3}}{1.14}$	0	$\frac{i_{N,SS}}{14}$	0	0	0	0	Y_{STO,NO_3}	0	0
4	p3(b)	Anoxic Storage of S_S NO_2-N_2	0	-1	$i_{N,SS}$	$-\frac{1-Y_{STO,NO_2}}{1.72}$	0	$\frac{1-Y_{STO,NO_2}}{1.72}$	$\frac{i_{N,SS}-(Y_{STO,NO_2}-1)/1.72}{14}$	0	0	0	0	Y_{STO,NO_2}	0	0
5	p4	Aerobic Growth of X_H	$1-1/Y_{H,O_2}$	0	$-i_{N,BM}$	0	0	0	$-\frac{i_{N,BM}}{14}$	0	0	1	0	-1/ Y_{H,O_2}	0	0
6	p5(a)	Anoxic Growth of X_H NO_3-NO_2	0	0	$-i_{N,BM}$	$\frac{1-Y_{H,NO_3}}{1.14\cdot Y_{H,NO_3}}$	$-\frac{1-Y_{H,NO_3}}{1.14\cdot Y_{H,NO_3}}$	0	$-\frac{i_{N,BM}}{14}$	0	0	1	0	-1/ Y_{H,NO_3}	0	0
7	p5(b)	Anoxic Growth of X_H NO_2-N_2	0	0	$-i_{N,BM}$	$-\frac{1-Y_{H,NO_2}}{1.72\cdot Y_{H,NO_2}}$	0	$\frac{1-Y_{H,NO_2}}{1.72\cdot Y_{H,NO_2}}$	$\frac{(Y_{H,NO_2}-1)/(1.72\cdot Y_{H,NO_2})-i_{N,BM}}{14}$	0	0	1	0	-1/ Y_{H,NO_2}	0	0
8	p6	Aerobic Endog. Resp. of X_H	-(1- f_{XI})	0	$-f_{XI}\cdot i_{N,XI}+i_{N,BM}$	0	0	0	$\frac{-f_{XI}\cdot i_{N,XI}+i_{N,BM}}{14}$	0	f_{XI}	-1	0	0	0	0
9	p7(a)	Anoxic Endog. Resp. of X_H NO_3-NO_2	0	0	$-f_{XI}\cdot i_{N,XI}+i_{N,BM}$	$\frac{1-f_{XI}}{1.14}$	$-\frac{1-f_{XI}}{1.14}$	0	$\frac{-f_{XI}\cdot i_{N,XI}+i_{N,BM}}{14}$	0	f_{XI}	-1	0	0	0	0
10	p7(b)	Anoxic Endog. Resp. of X_H NO_2-N_2	0	0	$-f_{XI}\cdot i_{N,XI}+i_{N,BM}$	$-\frac{1-f_{XI}}{1.72}$	0	$\frac{1-f_{XI}}{1.72}$	$\frac{i_{N.BM}-f_{XI}\cdot i_{N,XI}-(f_{XI}-1)/1.72}{14}$	0	f_{XI}	-1	0	0	0	0
11	p8	Aerobic Endog. Resp. of X_{STO}	-1	0	0	0	0	0	0	0	0	0	0	-1	0	0
12	p9(a)	Anoxic Endog. Resp. of X_{STO} NO_3-NO_2	0	0	0	$\frac{1}{1.14}$	$-\frac{1}{1.14}$	0	0	0	0	0	0	-1	0	0
13	p9(b)	Anoxic Endog. Resp. of X_{STO} NO_2-N_2	0	0	0	$-\frac{1}{1.72}$	0	$\frac{1}{1.72}$	$\frac{1}{24.08}$	0	0	0	0	-1	0	0
14	p10(a)	Aerobic Growth of X_{AOB}, Nitritation	$1-\frac{48}{14\cdot Y_{AOB}}$	0	$-\frac{1}{Y_{AOB}}-i_{N,BM}$	$\frac{1}{Y_{AOB}}$	0	0	$-\frac{1}{14}(\frac{2}{Y_{AOB}}+i_{N.BM})$	0	0	0	0	0	1	0
15	p11(a)	Aerobic End. Resp. of X_{AOB}	-(1- f_{XI})	0	$-f_{XI}\cdot i_{N,XI}+i_{N,BM}$	0	0	0	$\frac{-f_{XI}\cdot i_{N,XI}+i_{N,BM}}{14}$	0	f_{XI}	0	0	0	-1	0
16	p12(a)	Anoxic End. Resp. of X_{AOB}	0	0	$-f_{XI}\cdot i_{N,XI}+i_{N,BM}$	0	$-\frac{1-f_{XI}}{2.86}$	$\frac{1-f_{XI}}{2.86}$	$\frac{i_{N.BM}-f_{XI}\cdot i_{N,XI}-(f_{XI}-1)/2.86}{14}$	0	f_{XI}	0	0	0	-1	0
17	p10(b)	Aerobic Growth of X_{NOB}, Nitratation	$1-\frac{16}{14\cdot Y_{AOB}}$	0	$-i_{N,BM}$	$-\frac{1}{Y_{NOB}}$	$\frac{1}{Y_{NOB}}$	0	$-\frac{i_{N,BM}}{14}$	0	0	0	0	0	0	1
18	p11(b)	Aerobic End. Resp. of X_{NOB}	-(1- f_{XI})	0	$-f_{XI}\cdot i_{N,XI}+i_{N,BM}$	0	0	0	$\frac{-f_{XI}\cdot i_{N,XI}+i_{N,BM}}{14}$	0	f_{XI}	0	0	0	0	-1
19	p12(b)	Anoxic End. Resp. of X_{NOB}	0	0	$-f_{XI}\cdot i_{N,XI}+i_{N,BM}$	0	$-\frac{1-f_{XI}}{2.86}$	$\frac{1-f_{XI}}{2.86}$	$\frac{i_{N.BM}-f_{XI}\cdot i_{N,XI}-(f_{XI}-1)/2.86}{14}$	0	f_{XI}	0	0	0	0	-1

Table S4. Kinetic and stoichiometric parameters at 20 ℃.								
Index	Symbol	Characterization	Low	Value	High	θ	Units	references
	$i_{N,SI}$	N content of inert soluble COD S_I	0.005	0.01	0.01		[g N/g COD]	[1]
1	$i_{N,SS}$	N content of readily biodegradable substrate	0.01	0.03	0.05		[g N/g COD]	[1]
2	$i_{N,XI}$	N content of inert particulate COD X_I	0.01	0.04	0.07		[g N/g COD]	[1]
	$i_{N,XS}$	N content of slowly biodegradable substrate	0.01	0.03	0.05		[g N/g COD]	[1]
3	$i_{N,BM}$	N content of biomass X_H, X_{AOB}, X_{NOB}	0.03	0.07	0.11		[g N/g COD]	[1]
	f_{SI}	Production of S_I in hydrolysis	0.00	0.00	0.02		[g COD/g COD]	[2]
4	f_{XI}	Fraction of inert COD generated in biomass lysis	0.1	0.2	0.3		[g COD/g COD]	[1]
5	Y_{H,O_2}	Yield coeff. for heterotrophs in aerobic growth	0.65	0.8	0.95		[g COD/g COD]	[1]
6	Y_{H,NO_3}	Yield coeff. for heterotrophs in anoxic growth (NO_3^--N- NO_2^--N)	0.5	0.65	0.8		[g COD/g COD]	[1]
7	Y_{H,NO_2}	Yield coeff. for heterotrophs in anoxic growth (NO_2^--N- N_2-N)	0.5	0.65	0.8		[g COD/g COD]	[1]
8	Y_{STO,O_2}	Yield coeff. for X_{STO} in aerobic growth	0.2	0.8	1		[g COD/g COD]	[1]
9	Y_{STO,NO_3}	Yield coeff. for X_{STO} in anoxic growth (NO_3^--N- NO_2^--N)	0.2	0.7	1		[g COD/g COD]	[1]
10	Y_{STO,NO_2}	Yield coeff. for X_{STO} in anoxic growth (NO_2^--N- N_2-N)	0.2	0.7	1		[g COD/g COD]	[1]
11	Y_{AOB}	Yield coeff. for X_{AOB}	0.1	0.18	0.3		[g COD/g N]	[3]
12	Y_{NOB}	Yield coeff. for X_{NOB}	0.02	0.06	0.1		[g COD/g N]	[3]
13	k_H	Hydrolysis rate constant	4	9	15	0.04	[d^{-1}]	[1]
14	k_{STO}	Maximum storage rate	4	12	20	0.07	[d^{-1}]	[1]
15	μ_H	Maximum growth rate on substrate of heterotrophs	1	3	6	0.07	[d^{-1}]	[1]
16	μ_{AOB}	Maximum growth rate of X_{AOB}	0.8	0.9	1.1	0.12	[d^{-1}]	[3]
17	μ_{NOB}	Maximum growth rate of X_{NOB}	0.5	0.65	1.0	0.078	[d^{-1}]	[3]
18	b_{H,O_2}	Aerobic end. resp. rate for X_H	0.1	0.3	0.5	0.07	[d^{-1}]	[1]
19	b_{STO,O_2}	Aerobic end. resp. rate for X_{STO}	0.1	0.3	0.5		[d^{-1}]	[1]
20	b_{AOB}	Decay rate of X_{AOB}	0.05	0.15	0.25	0.12	[d^{-1}]	[4]
21	b_{NOB}	Decay rate of X_{NOB}	0.1	0.22	0.34	0.078	[d^{-1}]	[4]
22	η_{H,NO_3}	Reduction factor for denitrification (NO_3^--N- NO_2^--N)	0.1		1		-	[3]
23	η_{H,NO_2}	Reduction factor for denitrification (NO_2^--N- N_2-N)	0.1		1		-	[3]
24	$\eta_{H,end.NO_3}$	Reduction factor for b_H, anoxic condition (NO_3^--N- NO_2^--N)	0.25		1		-	[3]
25	$\eta_{H,end.NO_2}$	Reduction factor for b_H, anoxic condition (NO_2^--N- N_2-N)	0.35		1		-	[3]
26	$\eta_{N,end}$	Reduction factor for b_{AOB} and b_{NOB}, anoxic condition	0.1		1		-	[4]
27	K_X	Hydrolysis saturation constant	0.2	1.0	2		[g X_S g^{-1} X_H]	[1]
28	K_{H,O_2}	Saturation coeff. for oxygen, het. growth	0.05	0.2	0.5		[g O_2 m^{-3}]	[1]
29	$K_{H,O_2,inh}$	Inhibition coeff. for oxygen, het. growth	0.05	0.2	5		[g O_2 m^{-3}]	[1]
30	$K_{H,SS}$	Saturation coeff. for readily biodegradable substrates, het. growth	5	10	20		[g COD m^{-3}]	[1]
31	K_{H,NH_4}	Saturation/inhibition coefficient for ammonium, het. growth	0.001	0.01	0.1		[g N m^{-3}]	[1]
32	K_{H,NO_3}	Saturation/inhibition coefficient for nitrate, het. growth	0.1	0.5	10		[g N m^{-3}]	[1]
33	K_{H,NO_2}	Saturation/inhibition coefficient for nitrite, het. growth	0.1	0.5	10		[g N m^{-3}]	[1]
34	$K_{H,ALK}$	Saturation/inhibition coefficient for alkalinity, het. growth	0.01	0.1	1		[mole HCO_3^- m^{-3}]	[1]
35	$K_{H,STO}$	Saturation coeff. for storage products	0.01	0.1	1		[g COD m^{-3}]	[1]
36	K_{AOB,O_2}	Saturation coefficient for oxygen, AOB	0.2	0.8	5		[g O_2 m^{-3}]	[5]
37	K_{NOB,O_2}	Saturation coefficient for oxygen, NOB	0.2	0.8	5		[g O_2 m^{-3}]	[5]
38	K_{AOB,NH_4}	Saturation coeff. for ammonium, AOB	0.05	0.14	0.5		[g N m^{-3}]	[5]
39	K_{NOB,NO_2}	Saturation coefficient for nitrite, NOB	0.05	0.28	0.5		[g N m^{-3}]	[5]
40	$K_{N,ALK}$	Saturation/inhibition coefficient for alkalinity, aut. growth	0.1	0.5	1		[mole HCO_3^- m^{-3}]	[1]

References:

1. Koch G, Kuhni M, Gujer W, Siegrist H. Calibration and Validation of Activated Sludge Model no. 3 for Swiss Municipal Wastewater. *Water Research* **34**, 3580-3590 (2000).

2. Gujer W, Henze M, Mino T, van Loosdrecht M. Activated sludge model No. 3. *Water Science and Technology* **39**, 183-193 (1999).

3. Kaelin D, Manser R, Rieger L, Eugster J, Rottermann K, Siegrist H. Extension of ASM3 for two-step nitrification and denitrification and its calibration and validation with batch tests and pilot scale data. *Water Research* **43**, 1680-1692 (2009).

4. Manser R, Gujer W, Siegrist H. Decay processes of nitrifying bacteria in biological wastewater treatment systems. *Water Research* **40**, 2416-2426 (2006).

5. Manser R, Gujer W, Siegrist H. Consequences of mass transfer effects on the kinetics of nitrifiers. *Water Research* **39**, 4633-4642 (2005).