



HAL
open science

Simulating biotechnological processes affected by meteorology: Application to algae–bacteria systems

Francesca Casagli, Olivier Bernard

► To cite this version:

Francesca Casagli, Olivier Bernard. Simulating biotechnological processes affected by meteorology: Application to algae–bacteria systems. *Journal of Cleaner Production*, 2022, 377, pp.134190. 10.1016/j.jclepro.2022.134190 . hal-03935662

HAL Id: hal-03935662

<https://inria.hal.science/hal-03935662>

Submitted on 12 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

Simulating biotechnological processes affected by meteorology: application to algae-bacteria systems

14
15
16
17
18
19
20
21
22

Francesca Casagli^a, Olivier Bernard^{a,b*}

^a*BIOCORE, INRIA, Université côte d'Azur, BP 93, 06902 Sophia-Antipolis Cedex, France.*

^b*LOV, Sorbonne University, CNRS, UMR 7093, Station Zoologique, BP 28, 06234 Villefrance-sur-mer, France.*

Abstract

23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41

Most of the existing mathematical models for outdoor biotechnological processes require the measurement of the medium temperature, and therefore, they cannot forecast the process dynamics in the future or perform scenario analysis under different climatology. Fully predictive models are thus required for advanced predictions and optimization of environmental bioprocesses affected by weather fluctuations. This is of major importance for supporting the industries in the bioprocess design, decision making and process management.

42
43
44
45
46
47
48
49
50
51
52
53

Here, we introduce the FLAME modelling framework for forecasting the fate of outdoor bioprocesses. It integrates, on top of a biological model conserving carbon, nitrogen and phosphorus, a heat transfer model and a chemical sub-model for computing the speciation of all the dissociated chemical molecules. The versatile FLAME modelling platform includes different modules with balanced complexities. Alternative biological models can eas-

54
55
56
57
58

*Corresponding author

Email address: `olivier.bernard@inria.fr` (Olivier Bernard^{a,b*})

59
60
61
62
63
64
65

Preprint submitted to Journal of Cleaner Production

May 22, 2022

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

ily be interchanged, in order to promote a dialog for bioremediation model comparisons and improvements.

The approach is illustrated with an algae-bacteria wastewater treatment pond, subjected to the solar flux and to the meteorological events (wind, rain, ...). The fully predictive model was validated over more than one year, therefore representing all the seasons. The temperature prediction turns out to be crucial, especially to appropriately simulate nitrification. The model estimates the dynamics of the different biomasses in the system, providing a diagnosis tool to follow the hidden part of the process dynamics. The proposed framework is a powerful tool for advanced control and optimization of environmental processes, which can guide the scaling up and management of the most innovative bioprocesses.

Keywords: Algae-bacteria, temperature, meteorology, chemical model, modelling framework, wastewater

1
2
3
4
5
6
7
8
9
10 **Nomenclature**
11

12	ADM1	Anaerobic Digestion Model 1
13	ALBA	ALgae-BActeria model
14	AOB	Ammonium Oxidizing Bacteria
15	ASMx	Activated Sludge Model x
16	BSM2	Benchmark Simulation
17		Model no. 2
18	COD	Chemical Oxygen Demand
19	FLAME	Framework for
20		physicaL-biologicAl ModEls
21	HRT	Hydraulic Retention Time
22	HRABP	High Rate
23		Algae Bacteria Pond
24	IWA	International Water Association
25	MPC	Model Predictive Control
26	NOB	Nitrite Oxidizing Bacteria
27	PAR	Phosynthetic Active Radiation
28	PDE	partial differential equations
29	SRT	Solid Retention Time
30	TA	Total Alkalinity
31	TSS	Total Suspended Solids
32	VFA	Volatile Fatty Acids
33	VSS	Volatile Suspended Solids
34	WWTP	WasteWater Treatment plant

1
2
3
4
5
6
7
8
9 **1. Introduction**

10 Modelling environmental biotechnological processes is a challenging task
11
12 which requires long term experimental and mathematical developments (Dochain
13
14 and Vanrolleghem, 2001; Osborne et al., 2014; Mairet and Bernard, 2019).
15
16 So far, most of the modelling efforts have been focused on the identification
17
18 of reliable biological models balancing the mathematical and the underlying
19
20 ecological complexity by appropriately choosing the number of involved
21
22 species and processes. A new generation of models of increasing complexity is
23
24 now appearing (see Table. 1) based on elemental conservation, in the perspective
25
26 of developing more efficient processes for recycling energy, nitrogen and
27
28 phosphorus. These environmental outdoor processes are deeply affected by
29
30 the climate which triggers the medium temperature (Zouboulis and Tolkou,
31
32 2015; Plósz et al., 2009) and thus the biological activities. Including the effect
33
34 of temperature in the associated numerical models did so far not receive
35
36 the requested attention and this paper focuses on this challenge.
37
38
39
40

41 Activated sludge plants are known to be directly influenced by the weather
42
43 (Luo et al., 2020). Operating them in winter is typically more complicated
44
45 than in summer due to the slower kinetics. The impact of meteorology is
46
47 marked even for anaerobic digesters which generally have a temperature regulation
48
49 system. Yu et al. (2021) showed that inefficient temperature regulation due to
50
51 weather fluctuations can lead to a loss of methane production
52
53 by 20%. Temperature probably impacts even more strongly the emerging
54
55 algae/bacteria systems for wastewater remediation. These processes are seen
56
57
58

1
2
3
4
5
6
7
8
9
10 24 as a key player to enhance wastewater treatment by producing the oxygen
11 25 through photosynthesis, avoiding therefore the expensive cost of aeration
12 26 (Rossi et al., 2020b). In addition, the algal biomass has a valuable potential
13 27 to be used as byproduct (e.g. biofuels, biofertilizer and bioplastics), matching
14 28 a circular economy approach. Algae/bacteria are grown together in shallow
15 29 (typically less than 0.3 m) outdoor raceways, strongly depending on the so-
16 30 lar flux for photosynthesis (Milledge, 2011). Being shallow, these systems
17 31 have a low thermal inertia and temperature can very rapidly change in re-
18 32 sponse to meteorology, eventually leading to large variations in the medium
19 33 temperature (Béchet et al., 2011).

20 34 Better representing wastewater treatment processes have motivated two
21 35 decades of model development with the objective of supporting advanced pro-
22 36 cess supervision and optimization. The first models emerged for activated
23 37 sludge (ASM1,ASM3,(Henze et al., 2000a)) and anaerobic digestion (ADM1,
24 38 (Batstone et al., 2002)). A long list of variant models have been developed
25 39 (Janus and Ulanicki, 2010; Barrera et al., 2015; Buaisha et al., 2020) includ-
26 40 ing also models for the algae-bacteria processes (Broekhuizen et al., 2012;
27 41 Solimeno et al., 2019; Casagli et al., 2021b). A list of the most widespread
28 42 models for environmental processes can be found in Table 1.

29 43 Looking closer to these models, it turns out that they cannot be used
30 44 for forecasting, since they require medium temperature measurements, which
31 45 evolves, depending on the meteorology. Paradoxically, we are now in a situ-
32 46 ation where these models are not able to meet one of the key objective for

1
2
3
4
5
6
7
8
9 47 which they were designed: optimization of outdoor industrial processes. This
10
11 48 missing step for full predictions is somehow critic since most of the environ-
12
13 49 mental processes are permanently submitted to temperature variations due
14
15 50 to the nonstationarity of the solar flux combined with meteorology.

16
17 51 Predicting the dynamics of these processes needs first to get reliable
18
19 52 weather forecasts, at least for the short term and, second, a heat transfer
20
21 53 model for forecasting the reactor temperature dynamics. Forecasting temper-
22
23 54 ature in an outdoor process is not challenging in itself, and several thermal
24
25 55 models are available in the literature (la Cour Jansen et al., 1992; Sedory
26
27 56 and Stenstrom, 1995; Lippi et al., 2009). Nevertheless, integrated models
28
29 57 predicting at the same time medium temperature and biological activity are
30
31 58 still very rare, as well as their long-term validation.

32
33 59 This results from several bottlenecks, that together prevented the devel-
34
35 60 opment of fully predictive models. The first challenge is to coherently manage
36
37 61 the climatological information (solar flux, air temperature, wind velocity,...)
38
39 62 in the different submodels (heat transfer model, chemical model, biological
40
41 63 model). As a matter of illustration, the solar flux must be considered both in
42
43 64 the heat transfer model (solar irradiance at the ground level, in W m^{-2}) and
44
45 65 in the processes involving photosynthesis (Photosynthetically Active Radia-
46
47 66 tion, PAR, in $\mu \text{ mol m}^{-2} \text{ s}^{-1}$). The second challenge is to balance the model
48
49 67 complexity and its accuracy (Mairet and Bernard, 2019), with a similar treat-
50
51 68 ment for all the submodels. The accuracy of the biological model should be
52
53 69 similar to the one of the heat transfer model. Then, the same simulation
54
55
56
57
58

1
2
3
4
5
6
7
8
9 70 platform must be used for the two submodel, to automatically run the fully
10
11 71 predictive model embedding the set of interconnected submodels. Most of
12
13 72 the heat transfer models are run from computational fluid dynamics frame-
14
15 73 works, often requiring a human intervention. This prevent any automatic
16
17 74 use of the model for on-line control purpose. Finally, the precise way tem-
18
19 75 perature affects the enzymatic reactions governing microbial life and more
20
21 76 generally the growth rate of the involved organisms must have been well rep-
22
23 77 resented in the biological kinetics and accurately calibrated. Temperature
24
25 78 also affects the speciation of the chemical compounds and their availability
26
27 79 in the medium, and this temperature dependence must be implemented in
28
29 80 the model.
30
31

32 81 None of these issues taken separately represents a critical difficulty, but
33
34 82 the complexity of their combination probably explains the present lack of
35
36 83 fully predictive models.
37

38 84 The objective of this paper is to introduce the FLAME (Framework for
39
40 85 physical-biologicAl ModElS) framework, specifically developed for linking
41
42 86 the mass (C, N and P) and energy fluxes within the biological, physical
43
44 87 and chemical modules. The proposed approach leads to a framework where
45
46 88 full predictions become possible. This is the cornerstone for advanced mon-
47
48 89 itoring, design and control strategies opening the door to optimization of
49
50 90 the process efficiency, with simultaneous reduction of environmental impacts
51
52 91 (Klemeš et al., 2012; Yong et al., 2016; Van Fan et al., 2018, 2020).
53
54

55 92 The proposed approach is generic and can be applied to several out-
56
57
58
59
60
61
62
63
64
65

Table 1: Examples of models for WWT processes which could benefit from the FLAME modules. Green ticks point out the model implementation already done according to the proposed FLAME framework. Black ticks point out the FLAME modules that can be implemented. Red ticks point out the expected upgrading when using the FLAME framework, according to the current limitation: ¹ Only monoprotic acids and/or limited amount of chemicals considered; ² No evaporation; ³ Only O₂ stripping/dissolution considered (no CO₂ and NH₃).

WWT Process	Biological models (reference)	FLAME chemical	FLAME heat	FLAME I/O
Algae/Bacteria	ALBA Casagli et al. (2021b)	✓	✓	✓
	BIOALGAE2 Solimeno et al. (2019)	✓ ¹	✓	✓ ²
	ABACO Sánchez-Zurano et al. (2021)	✓	✓	✓
	Modified ASM3 Arashiro et al. (2017)	✓	✓	✓
	Modified RWQM1 Broekhuizen et al. (2012)	✓ ¹	✓	✓ ^{2,3}
	PHOBIA Wolf et al. (2007)	✓	✓	✓
	ASMA Wágner et al. (2016)	✓	✓	✓
	Activated sludge	ASM1, ASM2, ASM2d, ASM3 Henze et al. (2000b)	✓	✓
Anaerobic digestion	ADM1 Batstone et al. (2002)	✓ ¹	✓	..

door bioprocesses, but it is detailed and illustrated for the specific case of algae-bacteria systems. The high-fidelity biological ALBA (ALgae BActeria) model is used here for sake of illustration. It can be interchanged with other biological models to include a different description of the process. The FLAME framework is progressively described along the paper and its theory is illustrated point by point with algae-bacteria outdoor systems.

First, we present a brief review of existing heat transfer models which

1
2
3
4
5
6
7
8
9
100 have been developed for environmental bioprocesses. The following para-
101 graph details the material and methods used along the paper. We provide
102 a detailed description of the experimental data which were used to validate
103 the case study. Information on the model implementation are also provided.
104 In section 4 we introduce the FLAME framework, and the structure of the
105 general model. We detail and illustrate the different compartments using the
106 algae-bacteria process as example of application. We propose an effective
107 heat transfer model, and a general approach to represent chemical equilibria
108 in the process. Finally we provide details about the different fluxes from and
109 towards the environment. In section 5 we validate our approach with data
110 from a campaign (Casagli et al., 2021b) on an algae-bacteria process. The
111 fully predictive model turns out to be very accurate, even for winter periods.
112 The model highlights the difference in the microbial community between the
113 cold and the hot seasons. We show that temperature indirectly impacts al-
114 kalinity, with a strong influence on the dynamics of ammoniacal nitrogen
115 removal.

116 **2. Review of full predictive models for environmental biotechno-** 117 **logical processes**

118 The pioneer heat transfer model of la Cour Jansen et al. (1992) was
119 developed for an activate sludge process and validated along a full year with
120 data from a plant in Denmark. Later, another heat transfer model was
121 developed for an aeration tank by Sedory and Stenstrom (1995) and validated

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

122 in July and January across WWTP in the US. It turned out that predicting
123 temperature in winter was more challenging. This model was later improved
124 by Lippi et al. (2009). The model of Makinia et al. (2005) for activated
125 sludge tank was validated along the year in a WWTP in Oregon. Once
126 again the critical winter period was the less accurately represented. More
127 recently, Arnell et al. (2021) explicitly coupled a heat transfer model to the
128 BSM2 modelling framework with different tanks in a WWTP in Sweeden
129 and validated the temperature model along the year.

130 All these models are based on dynamical temperature simulations, resulting
131 from a first order model. The temperature influence on biological kinetics in
132 the most advanced cases is implemented with the Arrhenius law. Moreover,
133 the fluxes of C, N and P are not represented, and therefore, only a simplified
134 chemical model is typically implemented.

135 The temperature effect is more systematically included in the modelling
136 works dealing with microalgae based processes (Broekhuizen et al., 2012;
137 Solimeno et al., 2019; Casagli et al., 2021b). Indeed, solar radiation is key
138 for photosynthesis, and associated with the solar heat flux. However, for
139 all these models, temperature was assumed to be experimentally measured,
140 which definitely hinders the prediction capability of bioprocess models. The
141 model of Béchet et al. (2011) was previously developed for predicting the
142 temperature in raceway ponds producing microalgae. However, its imple-
143 mentation requires to integrate a partial differential equation (PDE) describ-
144 ing temperature in the ground, to determine the conductivity term. Such

1
2
3
4
5
6
7
8
9
10 145 computational complexity lead some authors to measure the ground temper-
11 146 ature in order to run the model (Rodríguez-Miranda et al., 2021). However
12
13 147 this solution jeopardizes any attempt to assess various operating strategies
14
15 148 or process implementation at a different location. A heat transfer model, ex-
16
17 149 tending the one of Béchet et al. (2011), is proposed here, replacing the PDE
18
19 150 by the temperature dynamics of the material enveloping the water mass,
20
21 151 which is partially in contact with the ground. Finally it leads to a differen-
22
23 152 tial equation of dimension 2 which is embedded in the FLAME framework.
24
25
26
27

153 **3. Materials and Methods**

154 *3.1. Pilot raceway application for validating the fully predictive ALBA model*

155 The experiments were carried out with an outdoor High Rate Algae Bac-
156 156 teria Pond (HRABP) located at INRAE, Narbonne, southern France (Lati-
157 157 tude: 43.15656, Longitude: 2.994438), with a total surface area of 56 m² and
158 158 a channel length of 15 m (see Figure 1).
159

159 The raceway was operated in continuous mode, from 15/05/2018 to 01/08/2019.
160 160 The influent flow rate was set to obtain a Hydraulic Retention Time (HRT)
161 161 of 5 days along the whole experimental period, except from one month
162 162 (29/08/2018-29/09/2018) during which different HRT values (ranging from 2
163 163 to 10 days) were tested. The HRABP was also equipped with online dissolved
164 164 oxygen, temperature, pH and incident PAR probes. Off-line measurements
165 165 of Total Suspended Solids, Chemical Oxygen Demand (total and soluble),
166 166 ammonium, nitrate and nitrite were carried out. The air temperature, wind
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200



Figure 1: High Rate Algae-Bacteria pond (HRABP) located in Narbonne (F).

167 speed and relative humidity data, necessary for determining the pond tem-
168 perature through the model, were acquired from the nearest weather station
169 (Béziers, France, Latitude: 43.3235, Longitude: 3.3539), located at approx-
170 imately 30 km from the pond. The local rainfall rate was recorded on-site.
171 Additional information on the experimental protocol can be found in Casagli
172 et al. (2021b), and they are also summarized in Appendix A.

173 *3.2. Model implementation*

174 To guaranty the accuracy in the implementation of this complex model,
175 it was independently implemented in Aquasim (Reichert, 1994) and Mat-
176 lab R2019a. Removing bugs and ensuring a safe model code is crucial,
177 and a double implementation guarantees the model soundness (Mairet and
178 Bernard, 2019). The numerical integration under Matlab was carried out

1
2
3
4
5
6
7
8
9
10 179 with the ode15s variable-step, variable-order solver based on the numerical
11 180 differentiation formulas of orders 1 to 5 (Shampine et al., 1999). The rel-
12 181 ative tolerance was set to 10^{-6} . Such solver for stiff Ordinary Differential
13 182 Equations (ODE) is necessary to well manage the integration with the pH
14 183 sub-model, running at a faster time scale. In Aquasim, the ODE (biological
15 184 and heat transfer) and the algebraic equations (chemical equilibria) are in-
16 185 tegrated according to the DASSL algorithm (Petzold, 1982; Reichert, 1998).
17
18
19
20
21
22
23
24

186 4. General FLAME modelling framework

187 4.1. General structure

188 The general predictive model structure results from the three following
189 key components:

- 190 1. A submodel for the heat transfer to predict the medium temperature
191 from solar flux, wind, air temperature and relative humidity.
- 192 2. A submodel representing the chemical processes, including the ionic
193 balances, the dissociation constants and their temperature dependence.
- 194 3. A model representing the mass exchange with the environment, in-
195 cluding the dissolved and particulate masses in the liquid (influent and
196 effluent) and the mass of gases entering or leaving the reactor, according
197 to meteorology.

198 The model consists in four coupled dynamical equations, whose structure
199 is illustrated in Figure 2. Each subsystem represents the dynamics of the

1
2
3
4
5
6
7
8
9
200 biochemical species (Equation (1)), of the reactor volume (Equation (2)), of
11 the temperature (Equation (3)) and of \hat{H}^+ ions (Equation (4)):
12
13
14
15
16

$$\dot{\xi} = K \cdot \rho(\xi, T, \theta, \hat{H}^+) + \Delta(\xi, \xi_{in}, T, \hat{H}^+) \quad (1)$$

$$\dot{V} = Q_{in} - Q_{out} + Q_{rain} - Q_{evap} \quad (2)$$

$$\dot{T} = \sum_j Q_j(T, \theta, \rho) \quad (3)$$

$$\dot{\hat{H}}^+ = \hat{K} \left(\Phi_{pH}(\hat{H}^+, \xi, T) - \hat{H}^+ \right) \quad (4)$$

202 Where ξ represents the set of state variables associated with dissolved (de-
30 noted S_{YY} according to the IWA convention) or particulate (denoted X_{YY}
31 according to the IWA convention) compounds, $[g.m^{-3}]$. $K = P^T$ is the sto-
32 ichiometric matrix (P being the Petersen matrix). $\rho(\xi)$ is the vector of the
33 biological reaction rates $[g.m^{-3}.d^{-1}]$. The vector of fluxes from and towards
34 the environment (considering all the phases: solid, liquid and gaseous) is
35 denoted Δ . ξ_{in} is the vector of influent concentrations $[g.m^{-3}]$.
36
37
38
39
40
41
42
43

209 The reactor volume V depends on Q_{in} , Q_{out} , Q_{rain} and Q_{evap} , respectively
44 the inflow rate, outflow rate, rain rate and evaporation rate $[m^3.d^{-1}]$; Finally,
45 the vector T contains the temperature of the key elements of the process.
46
47
48
49
50
212 In the applied example to algae-bacteria systems, the vector T includes the
51 temperature of the water body and the one of the concrete envelope in contact
52 with the ground. The various heat fluxes are denoted $Q_{h,i}$. These fluxes
53
54
55
214 depend on the meteorological variables vector $\theta(t)$, including solar heat flux,
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9 227 thus the biological reaction rates. A more detailed description of the heat
10
11 228 transfer model and the chemical sub-model can be found in sections 3.4 and
12
13 229 3.5.
14

15 230 Finally, a module computes the flux of compounds Δ from and towards
16
17 231 the environment external to the reactor. It consists in considering the flux
18
19 232 of soluble elements in the influent and effluent, the flux of solids (which have
20
21 233 been possibly recirculated or harvested) and the flux of gases exchanged with
22
23 234 the liquid phase (the speciation of the dissolved compounds, e.g. CO_2 and
24
25 235 NH_3 , quantified through the chemical model).
26
27

28 236 4.2. *The biological core model*

29 237 4.2.1. *Mass balance structure of biological models*

30
31
32 238 The classical structure of mass balance models for perfectly mixed biore-
33
34 239 actors consists in representing the mass transfer taking place between the
35
36 240 n_ξ state variables, through a set of n_ρ reactions (Bastin and Dochain, 1990;
37
38 241 Dochain and Vanrolleghem, 2001): $K \cdot \rho(\xi, T, I, [H^+])$
39
40

41
42 242 The underlying reaction network is represented by the stoichiometric ma-
43
44 243 trix K . Each column of this matrix correspond to a (macroscopic) reaction.
45
46 244 It is recommended that this reaction network conserves the elemental masses
47
48 245 (at least of C, N and P). The choice of the number of microbial species is
49
50 246 delicate and will definitely orientate the modelling, balancing accuracy and
51
52 247 complexity.
53

54
55 248 The two bricks of the biological model (reaction network and reaction
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9 249 kinetics) must be chosen with care, and this is the most difficult step in
10
11 250 developing a biological model (Mairet and Bernard, 2019).

12
13 251 The biological kinetics are affected by medium temperature (T_R), light
14
15 252 intensity, nutrient concentrations and pH. Appendix B recalls some standard
16
17 253 kinetics to represent these effects. For all the above mentioned reasons,
18
19 254 designing the biological model is a time demanding task. It is, however, the
20
21 255 core of the bioreactor dynamics and also the key for a further successful use
22
23 256 of the model for advanced control.

24
25
26 257 The main advantage of the proposed FLAME framework is that it is
27
28 258 straightforward to replace the biological core model, keeping the same chem-
29
30 259 ical, heat transfer and input/output model. Various competitive biological
31
32 260 models can then be implemented, comparing the inherent ability to well rep-
33
34 261 resent the process, independently of the heat-transfer or chemical framework
35
36 262 which stay unchanged (see Table 1). It is also the opportunity to benefit from
37
38 263 different models which all together can contribute to improve predictions by
39
40 264 proposing a coherent predictive framework (Mairet and Bernard, 2019).

41
42
43 265 As a matter of illustration, we present hereafter the fully predictive ALBA
44
45 266 model, according to the FLAME framework structure.

46 47 48 267 *4.3. Example of the ALBA biological core model*

49
50
51 268 A first version of the ALBA model has already been proposed to represent
52
53 269 algae-bacteria systems for wastewater remediation (Casagli et al., 2021b,a).
54
55 270 The ALBA model (Casagli et al., 2021b), simulates the dynamics of an out-
56
57
58

1
2
3
4
5
6
7
8
9
10 271 door algae-bacteria raceway. The biological sub-model considers a mixed
11 272 culture of algae (X_{ALG}), heterotrophic bacteria (X_H), Ammonium Oxidizing
12
13 273 Bacteria (X_{AOB}) and Nitrite Oxidizing Bacteria (X_{NOB}). The model includes
14
15 274 19 biological processes and involves 17 state variables. The associated sto-
16
17 275 ichiometric matrix (see Appendix D) has been computed so as to balance
18
19 276 elemental C, N, P, O and H .

21
22 277 In Appendix C we recall the main choices made in the construction of
23
24 278 the model. We refer the reader to Casagli et al. (2021b,a) for more details.

25
26 279 The model was successfully calibrated and validated using the data-
27
28 280 set relative to a demonstrative scale raceway treating synthetic municipal
29
30 281 wastewater (see Appendix A) located in Narbonne (France) and a pilot-
31
32 282 scale raceway treating piggery digestate located in Milano (Italy).

33
34 283 Altogether, 30 days were exploited for the calibration phase (from Nar-
35
36 284 bonne case study), while 602 days were used validating the model (from
37
38 285 Narbonne and Milan case study) based on a set of experimental data (pH,
39
40 286 $SO_2, S_{NH}, S_{NO_3}, S_{NO_2}, X_{ALG}$, TSS and soluble COD).

41
42 287 At this stage, the ALBA model requires a measurement of the reactor
43
44 288 temperature to run. The proposed FLAME framework extends this model
45
46 289 to make it fully predictive, *i.e.* depending only on the local meteorological
47
48 290 data.
49

50
51 291
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
292 4.4. Heat transfer model to predict the reactor temperature

11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
293 Here we focus on reactors with an active mixing that guaranties that the
294 biochemical concentrations and temperatures are homogeneous in the water
295 body. We can therefore take benefit from the universal temperature model
296 for high rate ponds developed by Béchet et al. (2011) to predict the water
297 temperature and the water level of the reactor. However this model has two
298 hindrances. First, implementing the temperature profile in the ground is
299 complex, making it difficult to use. Second, as it can be seen in Béchet et al.
300 (2018), it underestimates the actual thermal inertia of the system, simulat-
301 ing temperature fluctuations with a too large amplitude. The temperature
302 model of Béchet et al. (2011) was thus modified to account for the inertia
303 of the reactor support (assumed to be concrete in this case), especially at
304 the bottom under the liquid mass. An overall heat balance was then carried
305 out on the support, adding an equation describing its temperature evolution.
306 The considered heat fluxes for the water mass and the support are illustrated
307 on Figure 3.

43
44
45
46
47
48
49
308 The first heat balance considers the temperature dynamics in the reactor,
309 accounting for the heat exchanges with the material of the reactor :

50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

$$\begin{aligned} \rho_w V C_{p,w} \frac{dT_R}{dt} = & Q_{ra,p} + Q_{ra,s} + Q_{ra,a} + Q_{h,evap} + Q_{conv} + Q_{h,in} \\ & + Q_{h,out} + Q_{h,rain} - Q_{conv,cond_w,co} \end{aligned} \quad (5)$$

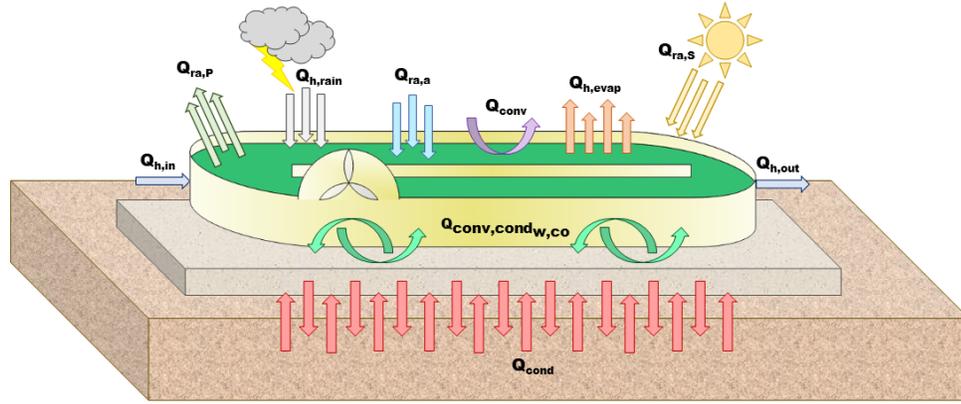


Figure 3: Heat balance on both water and reactor bodies and interaction with the ground.

311 where: T_R is the medium temperature in the reactor (K); ρ_w is the density
 312 of the water (kg m^{-3}); C_{pw} is the specific heat capacity of the water (J kg^{-1}
 313 K^{-1}); and V is the water volume (m^3). $Q_{ra,p}$ is the radiation from the reactor
 314 surface (W); $Q_{ra,s}$ is the total (direct + diffuse) solar radiation (W); and $Q_{ra,a}$
 315 is the radiation from the air to the water (W). $Q_{h,evap}$ is the evaporation flux
 316 (W), Q_{conv} is the convective flux at the water surface (W); $Q_{h,in}$ (resp. $Q_{h,out}$)
 317 is the heat flux associated with the influent (resp. effluent) water (W); and
 318 $Q_{h,rain}$ is the heat flux related to rain [W].

319 The term $Q_{conv,cond_w,i}$ is the conductive/convective flow related to the heat
 320 exchange between water and concrete:

$$Q_{conv,cond_w,co} = h_{w,co} \cdot (T_R - T_{co}) \quad (6)$$

321 The parameter $h_{w,co}$ ($\text{W m}^{-2} \text{K}^{-1}$) is the heat transfer coefficient between
 322 the water (w) and the reactor support (co), and T_{co} (K) is the temperature
 323 of the concrete.

324 The differential equation describing the temperature dynamics of the con-
 325 crete of the support is:

$$\rho_{co} V_{co} C_{p,co} \frac{dT_{co}}{dt} = h_{w,co} \cdot (T_R - T_{co}) + Q_{cond} \quad (7)$$

326 where Q_{cond} is the conductive heat flux with the ground at the reactor bot-
 327 tom (W). The conductive flux has a minor impact on the total heat balance
 328 (Béchet et al., 2011), therefore, a linear soil temperature profile was imple-
 329 mented for sake of simplicity, assuming that the ground temperature was
 330 approximately equal to the annual average air temperature at a depth of 3.5
 331 meters.

332 The evaporative and convective heat flux have a strong effect on the temper-
 333 ature prediction, and they were implemented according to the Buckingham
 334 theorem, depending on the dimensionless numbers of Sherwood, Schmidt and
 335 Reynolds. The Sherwood and Nusselt numbers were linearly interpolated for
 336 Reynolds numbers between 3×10^5 and 5×10^5 to ensure model calculations
 337 for Reynolds numbers in the transition from laminar to turbulent flow. To
 338 avoid a zero evaporation when there is no wind, a minimum wind speed (4

1
2
3
4
5
6
7
8
9
339 m s⁻¹) was considered in the calculation of the evaporative heat flux.

10
11 For the processes where the biological activity is associated to exothermic
12
13 reactions, a heat flux must be added proportional to the biological kinetics.
14
15 This is especially important for the exothermic heterotrophic bacteria growth
16
17 in activated sludge (Sedory and Stenstrom, 1995).
18

19
20 Also, a more suitable model for the conduction between the concrete
21
22 envelope and the ground must be implemented, when the tank is partially
23
24 buried, as for aeration basins (Sedory and Stenstrom, 1995).
25

26 27 4.5. *General principle of the chemical sub-model* 28

29
30 In most of the bioprocesses there is a broad range of involved molecules,
31
32 including species whose speciation depends on pH. It is therefore crucial to
33
34 well represent the pH and the dissociation state of the key chemical species
35
36 which affect the biological kinetics and the exchange with the environment.
37

38 For most of the models, this analysis is often carried out considering a
39
40 limited number of chemical species and using directly the measured pH to
41
42 estimate the chemical speciation in the reactor. The framework that we
43
44 propose is general and can be straightforwardly adapted to most of the case
45
46 studies.
47

48 The sub-model for pH prediction (H^+ ions concentration) results from
49
50 the dynamical balance between the chemical, physical and biological process
51
52 interactions. The proposed pH sub-model is based on dissociation equilibria
53
54 and mass balances of acids and bases, extending the one proposed in the
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
361 ADM1 model and on the charge balance, through which the concentration
10
362 of hydrogen ions is computed. Here the main contribution is the method to
11
12
13
363 systematically write the problem and to solve the algebraic equations system.
14
15
364 In the proposed pH model polyprotic acids speciation are considered, given
16
17
365 the wide range of pH variation (when it is not controlled) due to the photo-
18
19
366 synthetic activity, while in ADM1 only monoprotic acids were integrated.

20
21
22
367 The chemical submodule includes three components, represented in Table
23
24
368 2 which must be tailored to the specific case:

- 25
26
27
369 1. The mass balance equations for the state variables of the biological
28
370 model, which correspond to the sum of chemicals which dissociate in
29
30
371 the water. As an example to describe the total concentration of CO_2 ,
31
32
372 HCO_3^- and CO_3^{2-} in the ALBA model correspond to the state variable
33
34
373 inorganic carbon (denoted S_{IC} in the ALBA model):

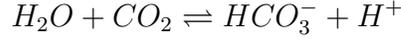
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

$$\frac{S_{IC}}{12} = CO_2 + HCO_3^- + CO_3^{2-}$$

374 Note that this equation can also account for the change in unit between
375 the state variables ($g.m^{-3}$) and the chemical model (which should be
376 in $mol.m^{-3}$).

- 377 2. The dissociation equations based on the affinity constants. They must
378 be rewritten in a form where only the H^+ ions concentration together
379 with the total amount of the element appears (represented by one of
380 the model state variable). For example, for the dissociation constant

1
2
3
4
5
6
7
8
9
381 associated with the CO₂ equilibrium:

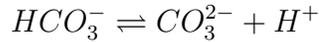


16
17 382 we get:

$$CO_2 = \frac{S_{IC}/12}{1 + \frac{K_{aCO_2}10^3}{H^+} + \frac{K_{aCO_2}K_{aHCO_3}10^6}{(H^+)^2}} \quad (8)$$

22 383 with $K_{A,H_2CO_3} = 4.27E-07M$.

24 384 And for the dissociation constant associated with the HCO₃⁻ equilib-
26 385 rium:

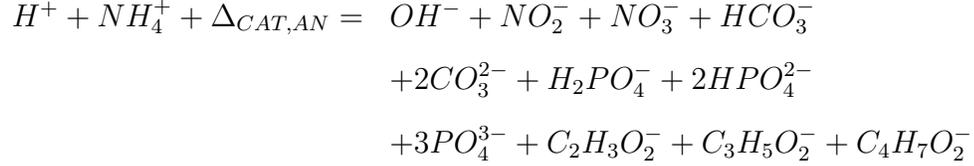


$$HCO_3^- = \frac{S_{IC}/12}{1 + \frac{H^+}{K_{aCO_2}10^3} + \frac{K_{aHCO_3}10^3}{H^+}} \quad (9)$$

36 386 with $K_{A,HCO_3} = 4.68E-11$.

- 39 387 3. The ionic balance equation representing the electroneutrality of the
41 388 medium, accounting for all the ions that are affected by the reactions,
43 389 and for those of constant concentration (denoted $\Delta_{CAT,AN}$) whose
45 390 concentrations are not modified by any biochemical reaction. As a
47 391 matter of illustration for WWT processes, a general electroneutrality

equation is:



Note that the notion of Total Alkalinity (TA) (mol m^{-3}) is directly derived from these considerations, as reported by Casagli et al. (2021a):

$$\begin{aligned} TA = & HCO_3^- + 2CO_3^{2-} + H_2PO_4^{2-} \\ & + 2PO_4^{3-} + OH^- + NH_3 + C_2H_3OO^- \\ & + C_4H_7OO^- + C_3H_5OO^- + C_5H_9OO^- + HS^- \\ & + 2S^{2-} - H^+ - HNO_2 - HNO_3 - H_3PO_4 \end{aligned} \quad (10)$$

Temperature has a fundamental influence on the parameters of chemical equilibria (i.e. the acidity constants), as specified by Batstone et al. (2002). This effect must be implemented for adapting the model for speciation to temperature oscillations (especially for the processes running along all the year). See Appendix G for the detailed expressions of the temperature dependencies.

4.5.1. Chemical sub-model for the ALBA model

As a matter of illustration, the chemical sub-model for the ALBA model follows the presented structure, considering the equilibria and mass conservation presented in Table 2. The ALBA model was validated also on a six months dataset of a raceway treating digestate. Since the digestate can

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

405 present significant concentrations of volatile fatty acids (VFA - acetate, bu-
406 tyrate, propionate and valerate) and hydrogen sulphide (H_2S), in that case
407 the algebraic equation system for the chemical equilibria should take them
408 into account, as proposed in Table J.4 (see Appendix J). As explained by
409 Batstone et al. (2002), the Van't Hoff equation is not effective for organic
410 acids. However, their acidity constants only marginally vary in the temper-
411 ature range 0-60 °C.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table 2: (Part I) Algebraic equations for the chemical sub-model: mass balances and dissociation state

Description	Expression [$mol\ m^{-3}$]	K_A [M]
<i>Ammoniacal nitrogen</i>		
1) Mass balance	$\frac{S_{NH}}{14} - NH_3 - NH_4^+ = 0$	
2) Dissociation	$NH_4^+ \rightleftharpoons NH_3 + H^+$	$K_{A,NH_4^+} = 5.62E-10$
<i>Nitrogen oxides</i>		
3) Mass balance	$\frac{S_{NO_2}}{14} - NO_2^- - HNO_2 = 0$	
4) Dissociation	$HNO_2 \rightleftharpoons NO_2^- + H^+$	$K_{A,HNO_2} = 4.47E-04$
5) Mass balance	$\frac{S_{NO_3}}{14} - NO_3^- - HNO_3 = 0$	
6) Dissociation	$HNO_3 \rightleftharpoons NO_3^- + H^+$	$K_{A,HNO_3} = 4.37E+01$
<i>Inorganic carbon</i>		
7) Mass balance	$\frac{S_{IC}}{12} - CO_2 - HCO_3^- - CO_3^{2-} = 0$	
8) Dissociation	$H_2O + CO_2 \rightleftharpoons HCO_3^- + H^+$	$K_{A,H_2CO_3} = 4.27E-07$
9) Dissociation	$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	$K_{A,HCO_3} = 4.68E-11$

Table 1: (Part II) Algebraic equations of the chemical sub-model: mass balances and dissociation state

<i>Orthophosphates</i>	
10) Mass balance	$\frac{S_{PO_4}}{31} - H_3PO_4 - H_2PO_4^- - HPO_4^{2-} - PO_4^{3-} = 0$
11) Dissociation	
$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$	$H_3PO_4 - \frac{S_{PO_4}/31}{1 + \frac{K_{\alpha H_3PO_4} 10^3}{H^+} + \frac{K_{\alpha H_3PO_4} K_{\alpha H_2PO_4} 10^6}{(H^+)^2} + \frac{K_{\alpha H_3PO_4} K_{\alpha H_2PO_4} K_{\alpha HPO_4} 10^9}{(H^+)^3}} = 0$
12) Dissociation	
$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	$H_2PO_4^- - \frac{S_{PO_4}/31}{1 + \frac{K_{\alpha H_2PO_4} 10^3}{H^+} + \frac{K_{\alpha H_2PO_4} K_{\alpha HPO_4} 10^6}{(H^+)^2}} = 0$
13) Dissociation	
$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	$HPO_4^{2-} - \frac{S_{PO_4}/31}{1 + \frac{K_{\alpha H_3PO_4} K_{\alpha H_2PO_4} 10^6}{(H^+)^2} + \frac{K_{\alpha HPO_4} 10^3}{H^+}} = 0$
14) Dissociation	
$H_2O \rightleftharpoons OH^- + H^+$	$OH^- - \frac{K_{aw} 10^3}{H^+} = 1.00E-14$

15) Charge balance $H^+ + NH_4^+ + \Delta_{CAT,AN} - OH^- - NO_2^- - NO_3^- - HCO_3^- - H_2PO_4^- - 2HPO_4^{2-} - 3PO_4^{3-} = 0$

1
2
3
4
5
6
7
8
9
412 *4.5.2. Chemical sub-model resolution*

413 The strategy for resolving the pH subsystem was inspired by Rosén and
414 Jeppsson (2006), extending it to polyprotic acids. The idea was to transform
415 the problem of resolution of a set of algebraic equations given in Table 1 into
416 the solution of a differential system. The way this system is solved, with the
417 example of the ALBA model is proposed in Appendix K.

22
23
24
25
26
27
28
29
30
31
32
418 *4.6. I/O fluxes from and towards the environment*

419 This module manages the exchanges of liquid, solid and gaseous fluxes
420 from and towards the environment. The liquid and solid fluxes are asso-
421 ciated to hydraulic retention time (HRT) and solid retention time (SRT)
422 respectively. HRT and SRT can differ in reactors where biomass is fixed to
423 a support, or with a separation system such as membranes. A submodel of
424 the different fluxes (recirculation, harvesting,...) is then needed.

425 The outflow of gases for which the dissolved molecules are at higher con-
426 centration than the solubility constant, or the inflow of gases at a lower
427 concentration than the solubility constants must be taken into account

428 The CO₂, O₂ stripping/dissolution, but also of other gases such as volatile
429 fatty acids or NH₃ must be considered, quantifying their rates through the
430 $k_L a$ and their diffusion coefficients (D_{S_j}):

51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

$$Q_j = k_L a_j(T_R) \cdot \left(\frac{D_{S_j}}{D_{S_{O_2}}} \right)^2 \cdot (S_{j,sat}(T_R) - S_j) \quad (11)$$

431 Finally, the flux of water by evaporation must also be quantified, as com-

1
2
3
4
5
6
7
8
9
432 puted by the heat transfer model, see Equation (12).

10
11 It becomes then possible to evaluate the water level variation, and then
12
13 the reactor volume:
14

$$S \frac{dh_L}{dt} = -\frac{m_e}{\rho_w} + Q_{rain} + Q_{in} - Q_{out} \quad (12)$$

15
16
17
18
19
20
21 where m_e is the evaporation rate ($Kg.s^{-1}m^{-2}$); ρ_w is the water density
22
23 ($Kg.m^{-3}$); Q_{rain} is the rain rate (ms^{-1}); Q_{in} and Q_{out} are the inflow and
24
25 outflow rate, respectively. ($m^3.s^{-1}$).
26
27
28

438 5. Results and discussion

439 5.1. Fully predictive ALBA model validation on an outdoor demonstrative- 440 scale

441 Simulations were run using all the model compartments within the FLAME
442 framework, in order to compare the fully predictive model accuracy with the
443 simulations based on the measured pond temperature.

444 First, the physical sub-model dealing with temperature turns out to accu-
445 rately predict the temperature dynamics on a long time scale (443 days). The
446 temperature predictions properly follow the seasonal variation trend (figure
447 4 and Table 2). The predicted temperature oscillations slightly overestimate
448 or underestimate the measurements along the validation period, with an av-
449 erage error standard deviation of 1.44° C. Considering all the experimental
450 period, the heat transfer model remains very accurate, with a R^2 of 0.96,

1
2
3
4
5
6
7
8
9
10 451 computed on 10555 measurement points, and p-value lower than 1E-06. The
11 452 heat transfer model was simulated using the nearby meteorological data 30
12
13 453 km away. Given the great influence of some input data on simulation results
14
15 454 (e.g: total irradiance, air temperature and wind velocity) model predictions
16
17 455 could be further improved by collecting data from a meteorological station
18
19 456 located exactly at the pond location, therefore providing a more accurate
20
21 457 description of the onsite environmental conditions.
22

23
24 458 The biological response for the most relevant variables of the algae-bacteria
25
26 459 pond for the fully predictive ALBA model are reported in figure 7 and Table
27
28 460 2. The experimental measurements of S_{NH} , S_{NO2} , S_{NO3} , S_{O2} , pH , TSS ,
29
30 461 X_{ALG} and COD_S are shown together with their standard deviation, while
31
32 462 the fully predictive model simulations are shown together with their error
33
34 463 bounds, computed according to the procedure presented by Casagli et al.
35
36 464 (2021b). In addition, in table 2, different model goodness of fit are reported,
37
38 465 in order to more accurately depict the difference between the full predictive
39
40 466 framework and the simulations based on temperature measurements.
41

42
43 467 The fully predictive ALBA model was able to simulate the main measured
44
45 468 variables in the HRABP with a very good level of accuracy, being very close
46
47 469 to the ones obtained when running the model with the measured tempera-
48
49 470 ture. As reported in Table 2, all the computed criteria confirmed the model
50
51 471 goodness of fit.
52

53
54 472 An advantage of an accurate mathematical model is its ability to recon-
55
56 473 struct the components of the microbial population, and the relative distri-
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

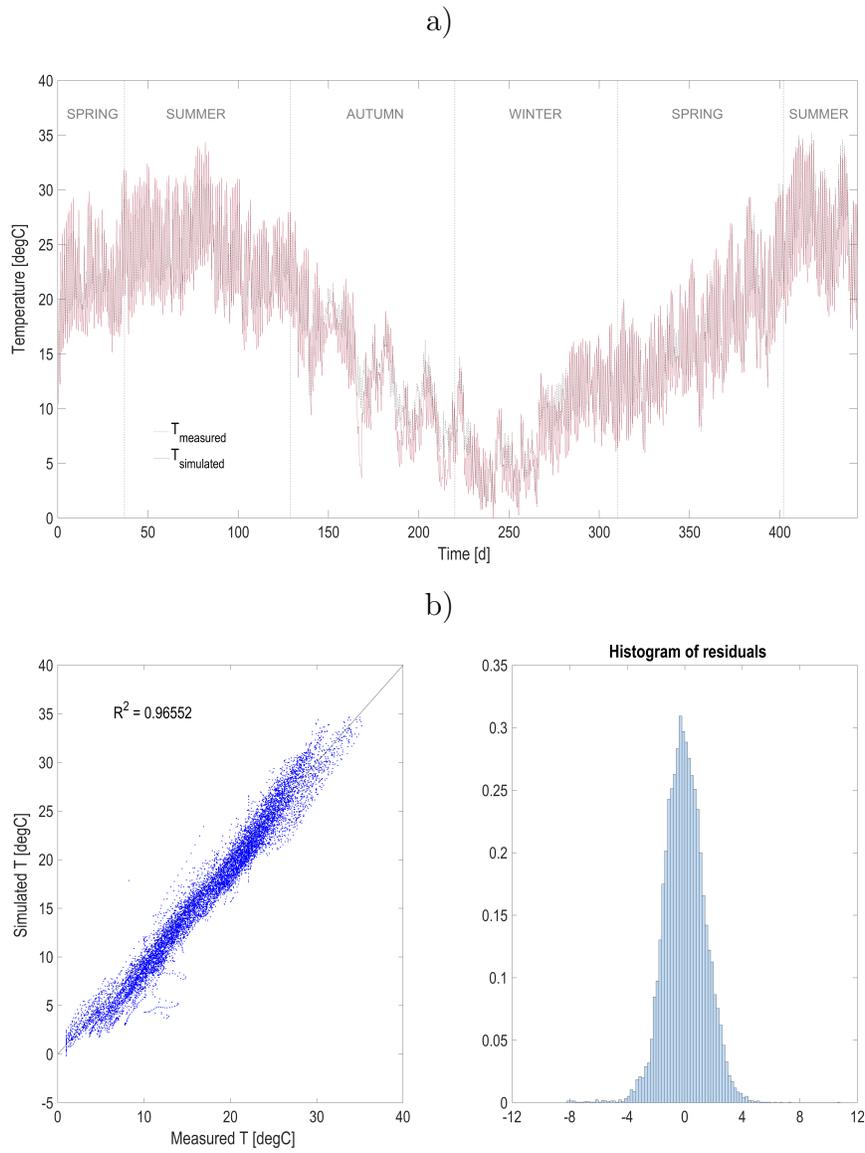


Figure 4: Heat transfer model validation over one year experimental measurements

1
2
3
4
5
6
7
8
9
10 474 bution between microalgae, heterotrophic bacteria and nitrifiers (AOB and
11 475 NOB). Direct measurements with phylogenetic markers (Junier et al., 2010)
12
13 476 would be challenging over a full year. Figure 5 shows how the microbial pop-
14
15 477 ulation partitioning is shaped by the seasons. Microalgae dominate the pop-
16
17 478 ulation along the year. During Spring and Summer the algal biomass, being
18
19 479 stimulated by higher temperatures and light intensities, it reaches the high-
20
21 480 est average concentrations ($348-367 \text{ gCODm}^{-3}$), while it is twofold reduced
22
23 481 in Autumn and Winter ($200-171 \text{ gCODm}^{-3}$). The biomass of heterotrophs
24
25 482 stays at a constant level along all the seasons ($60-93 \text{ gCODm}^{-3}$). Nitrifiers
26
27 483 are 50 times less abundant compared to the other biomasses, and they exhibit
28
29 484 a very different trend. AOB and NOB reach the highest concentration levels
30
31 485 in Summer and Autumn ($4.9-5.1 \text{ gCODm}^{-3}$ for AOB and $1-1.2 \text{ gCODm}^{-3}$
32
33 486 for NOB). The nitrifying biomass is reduced twofold in Winter, where tem-
34
35 487 peratures are too low for supporting its activity (2.6 gCODm^{-3} for AOB
36
37 488 and 0.4 gCODm^{-3} for NOB). The biomass composition is different when the
38
39 489 ecosystem is fed with digestate (see the case study presented in Appendix F,
40
41 490 figure F.9). AOB and NOB concentrations are higher ($16-33 \text{ gCODm}^{-3}$ for
42
43 491 AOB and $5-7 \text{ gCODm}^{-3}$ for NOB in summer and autumn, respectively), due
44
45 492 to the increased influent ammoniacal nitrogen concentration, exacerbated by
46
47 493 the longer biomass retention time. Nitrifiers are responsible for the main ni-
48
49 494 trogen fluxes. The heterotrophic bacteria concentration is much lower ($17-22$
50
51 495 gCODm^{-3} in summer and autumn, respectively) compared to the previ-
52
53 496 ous case, probably due to the reduced influent biodegradable organic matter
54
55
56
57
58
59
60
61
62
63
64
65

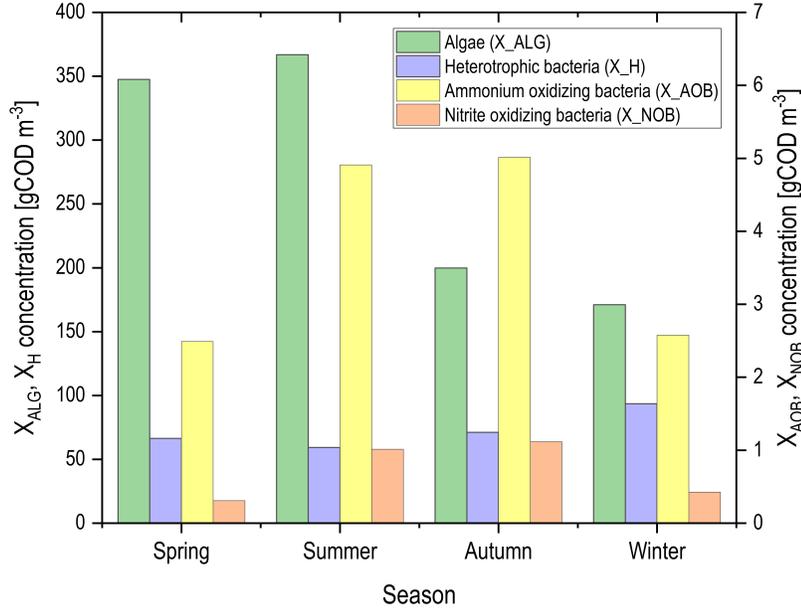


Figure 5: Average composition of the microbial population according to seasons, as estimated by the fully predictive model. Right axis: algae (X_{ALG}) and heterotrophic bacteria (X_H) concentration; left axis: nitrifying bacteria (X_{AOB} and X_{NOB}) concentration.

content. The highest algae concentration is reached again during Spring and Summer (498-592 $gCODm^{-3}$, respectively). These values are higher compared to the previous case. This is probably due to pH regulation with CO_2 injection, avoiding inorganic carbon limitation during the light periods.

5.2. How temperature affects alkalinity in HRABP

From the results shown in figure 7 and Table 2, it can be noticed that nitrate and nitrite predictions turn out to be sensitive to small biases in temperature simulations. This is possibly due to: i) the very low concentration of nitrifiers in this system, compared to the algal and heterotrophic

1
2
3
4
5
6
7
8
9
10 506 bacterial biomass, and ii) the high sensitivity of AOB and NOB to temper-
11 507 ature oscillations, being typically slow growers and therefore requiring more
12
13 508 time for adapting to oscillating environmental conditions. The difference
14
15 509 between nitrate simulated with both models resulted in a reduced R^2 and
16
17 510 a higher average relative error. The experimental data and the simulations
18
19 511 run based on temperature measurements, show a nitrate drop after reach-
20
21 512 ing a pick at day 410. For nitrate predicted in the FRAME framework,
22
23 513 this descendent trend is less marked and nitrate remain around an average
24
25 514 concentration of 26 gNm^{-3} . This is due to the higher predicted X_{NOB} con-
26
27 515 centration (1.12 gCODm^{-3} in average) compared to the one simulated using
28
29 516 the measured temperature (0.85 gCODm^{-3} in average). The explanation
30
31 517 of this phenomenon can be found in the temperature dependence function
32
33 518 of X_{NOB} growth rate, which peaks at $T_{opt} = 20^\circ \text{ C}$. Since the predicted
34
35 519 temperature, especially during night, slightly underestimates the real one,
36
37 520 a temperature closer to the optimal T_{opt} is simulated, enhancing the X_{NOB}
38
39 521 growth kinetic. This effect is amplified by the low concentration of nitrifiers,
40
41 522 while it is not producing significant variation for the other biomasses, whose
42
43 523 concentrations are one or two orders of magnitude higher.
44
45
46

47 524 It is worth remarking that the sensitivity of nitrifiers to temperature
48
49 525 have already been noticed (la Cour Jansen et al., 1992) and the challenges
50
51 526 to operate reactors at low temperature motivated the pioneer development
52
53 527 of heat transfer models to predict temperature dynamics.
54

55 528 The computed model error bars appropriately indicate this sensibility
56
57
58

1
2
3
4
5
6
7
8
9 529 during this period. The experimental data stay therefore within the model
10
11 530 uncertainty range (figure 7c). In the same period where X_{NOB} activity is
12
13 531 overestimated, the simulated total alkalinity (see Equation 10), resulted to
14
15 532 be slightly lower compared to the one simulated using the measured tem-
16
17 533 perature. The central role played by total alkalinity was shown by Casagli
18
19 534 et al. (2021a), and especially how it affects the level of inorganic carbon in
20
21 535 the system. Alkalinity must stay sufficiently high to allow a pool of inor-
22
23 536 ganic carbon that can support algae and nitrifiers activity. It is of utmost
24
25 537 importance to avoid competition for inorganic carbon between these two
26
27 538 populations, leading to favourable conditions for N_2O production and emis-
28
29 539 sions. Therefore, large errors in predicting the pond temperature can bring
30
31 540 to erroneous estimations of the distribution between ammonium, nitrate and
32
33 541 nitrite. It follows that alkalinity estimation will be biased and consequently
34
35 542 inorganic carbon concentration in the pond, with an overall uncertainty on
36
37 543 the N_2O emissions. The nitrifying activity was moderate (Casagli et al.,
38
39 544 2021b) for this case study, where the influent ammoniacal nitrogen is at low
40
41 545 concentration ($S_{NH_{in}}=8 \text{ gNm}^{-3}$), compared to the organic nitrogen fraction
42
43 546 ($S_{ND_{in}}=60 \text{ gNm}^{-3}$). Therefore no mechanisms of competitions for inorganic
44
45 547 carbon between algae and nitrifiers were observed. However, when studying
46
47 548 HRABPs treating digestate, as the one reported in Casagli et al. (2021a),
48
49 549 a very strong limitation for inorganic carbon caused by a drop in alkalinity
50
51 550 due to a strong nitrifying activity can be observed, despite the presence of
52
53 551 a pH control with CO_2 bubbling. In these cases, an approximate and raw
54
55
56
57
58
59
60
61
62
63
64
65

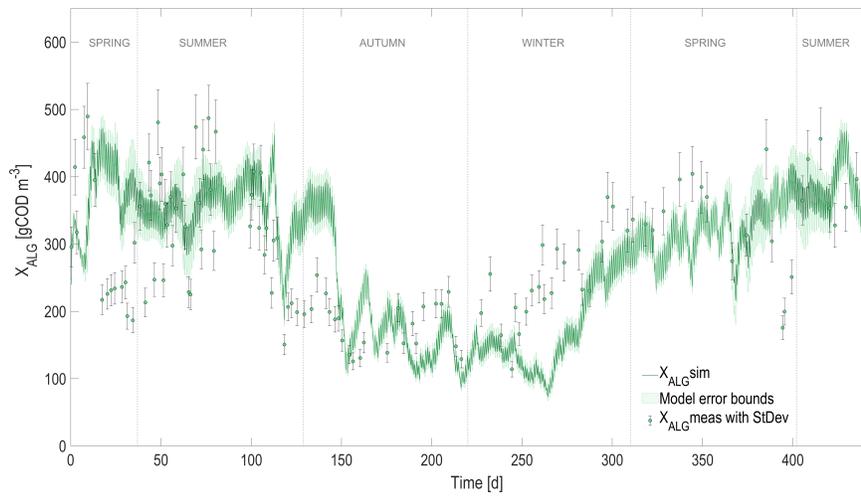
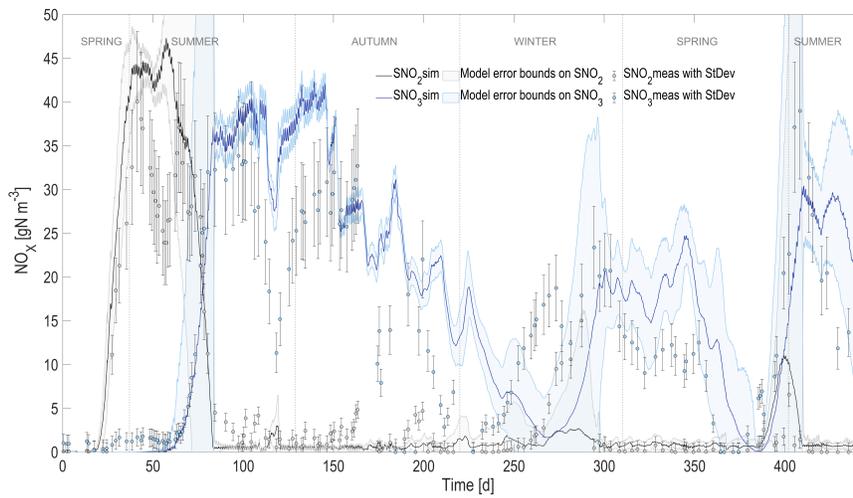
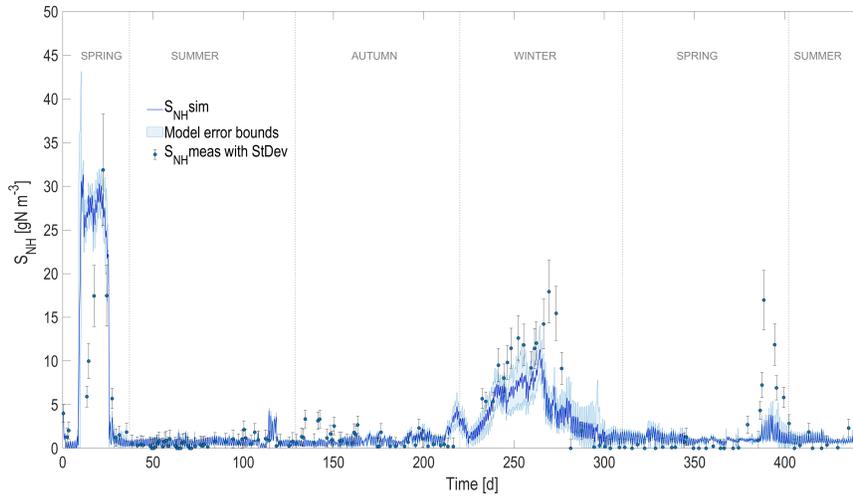
1
2
3
4
5
6
7
8
9
552 estimation of the pond temperature, might lead to a large bias in alkalinity
10
11 predictions, resulting in inefficient optimization strategies, potentially asso-
12
13 ciated with a risk of N₂O emission.
14

State variable	Err.St.Dev. (av)	TIC. (-)	Coeff.Var. (-)	R^2 (-)
S_{NH}	0.5435	0.0905	0.2254	0.98988
S_{NO2}	2.4545	0.1573	0.4659	0.95893
S_{NO3}	4.948	0.1962	0.323	0.86162
X_{ALG}	6.824	0.0224	0.0242	0.99582
TSS	8.6835	0.029	0.03	0.98365
COD_s	2.5589	0.0435	0.0465	0.95819
S_{O2}	0.7025	0.1163	0.0778	0.95861
pH	0.2663	0.0336	0.0292	0.93236
T^*	1.4477	0.081	0.0833	0.96552

30
31 Table 2: Comparison between simulation results using temperature measurement
32 and temperature predictions from the heat transfer model. The error standard
33 deviation, the absolute relative error, the variation and the correlation coefficients
34 are computed. (*): for temperature, the comparison is between the experimental
35 measurements and the predicted pond temperature with the heat transfer model.
36
37
38
39
40

555 5.3. Opening the door for Model Predictive Control

556 Model Predictive Control (MPC) is an advanced control approach (Cama-
557 cho and Alba, 2013; Hewing et al., 2020) for enhancing the process efficiency
558 by running a wide range of scenarios and selecting, among the ones satis-
559 fying some constraints, the ones offering the best performances. Combined
560 with weather forecasts, this approach can even anticipate the effect of the
561 meteorological evolution (De-Luca et al., 2017, 2019).



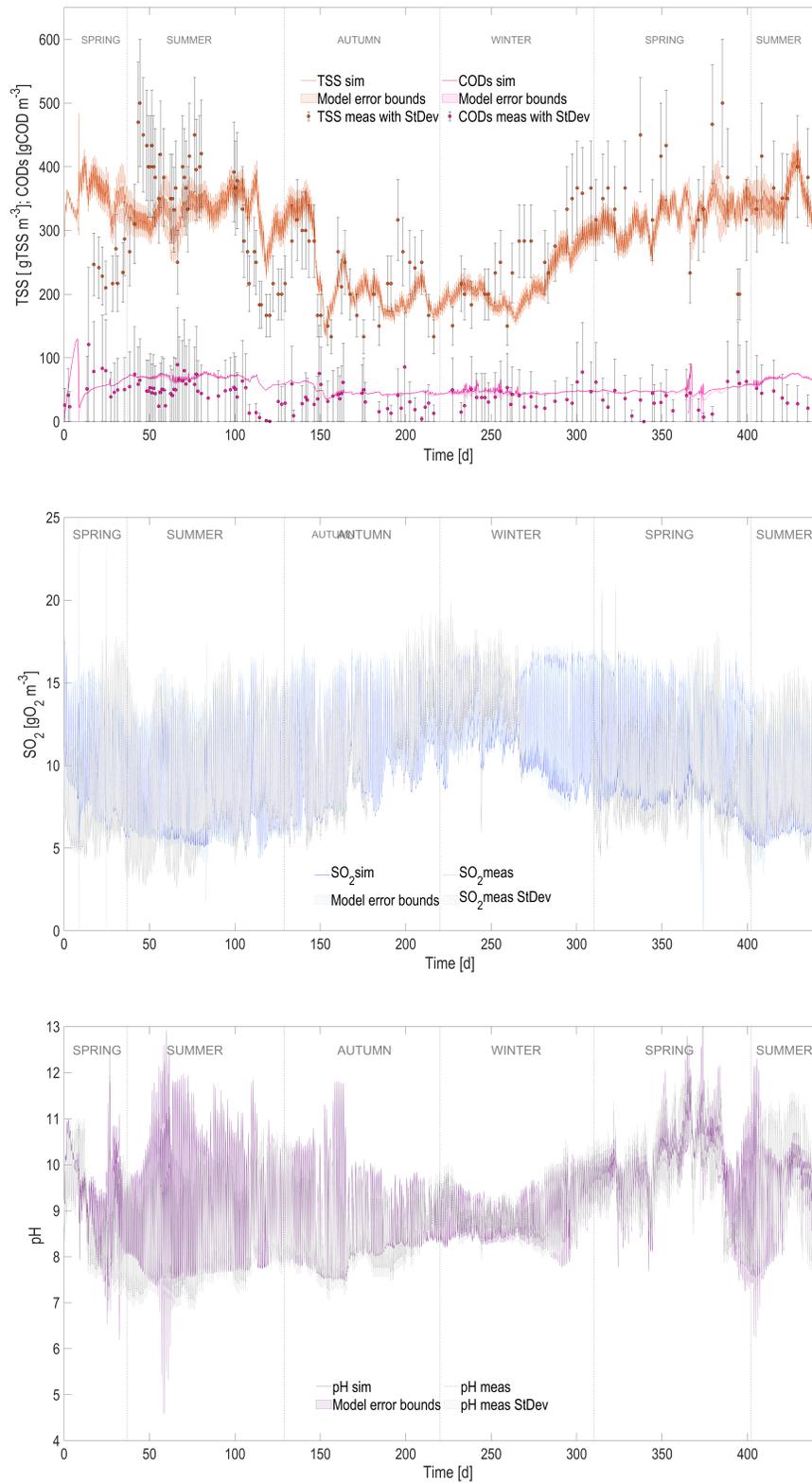


Figure 7: ALBA fully predictive model validation over one year. Experimental measurements and their Standard deviation, Error bounds for model predictions and simulation results: a) ammoniacal nitrogen; b) nitrite and nitrate; c) algal biomass; d) total suspended solids and soluble COD; e) dissolved oxygen; f) pH.

1
2
3
4
5
6
7
8
9 562 De-Luca et al. (2017, 2019) implemented a MPC strategy based on a
10 simple model accounting for temperature evolution in a mono-specific culture
11 563 of microalgae. By efficiently managing temperature and light use, it resulted
12 of microalgae. By efficiently managing temperature and light use, it resulted
13 564 in doubling algal productivity. This was achieved by on-line controlling the
14 in doubling algal productivity. This was achieved by on-line controlling the
15 565 water depth to anticipate the weather fluctuations and to better manage the
16 water depth to anticipate the weather fluctuations and to better manage the
17 566 hottest periods in summer. The FLAME framework makes it possible to
18 hottest periods in summer. The FLAME framework makes it possible to
19 567 apply similar strategies for more complex environmental processes.
20 apply similar strategies for more complex environmental processes.
21 568

22
23 569 The model can specifically be used to assess the sensitivity of outdoor
24 The model can specifically be used to assess the sensitivity of outdoor
25 570 biotechnological processes to temperature. It is capital to better understand
26 biotechnological processes to temperature. It is capital to better understand
27 571 which are the variables most affected by temperature. This also means that
28 which are the variables most affected by temperature. This also means that
29 572 the temperature predictions must be accurate for an efficient decision-making
30 the temperature predictions must be accurate for an efficient decision-making
31 573 process and for optimization. A biased temperature prediction at industrial
32 process and for optimization. A biased temperature prediction at industrial
33 574 scale can be critic for these variables resulting in a degradation in the control
34 scale can be critic for these variables resulting in a degradation in the control
35 575 performance or leading to inappropriate decisions.
36 performance or leading to inappropriate decisions.
37 576

38 576 As a matter of illustration, for the algae/bacteria process, nitrifiers turned
39 As a matter of illustration, for the algae/bacteria process, nitrifiers turned
40 577 out to be highly temperature sensitive. Accurately representing this popula-
41 out to be highly temperature sensitive. Accurately representing this popula-
42 578 tion is difficult, yet crucial to get a good description of ammonium, nitrate
43 tion is difficult, yet crucial to get a good description of ammonium, nitrate
44 579 and nitrite concentrations. A biased prediction of these quantities induces a
45 and nitrite concentrations. A biased prediction of these quantities induces a
46 580 wrong alkalinity estimation, with potential risk of inorganic carbon limitation
47 wrong alkalinity estimation, with potential risk of inorganic carbon limitation
48 581 and then the risk of N₂O emission. For these variables, it is thus key that
49 and then the risk of N₂O emission. For these variables, it is thus key that
50 582 the model is sufficiently accurate to make the management strategy efficient
51 the model is sufficiently accurate to make the management strategy efficient
52 583 in terms of wastewater remediation efficiency, nutrients recovery, and also of
53 in terms of wastewater remediation efficiency, nutrients recovery, and also of
54 584 greenhouse gas emissions.
55 greenhouse gas emissions.
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9 585 **6. Conclusions**

10
11 586 Temperature is a key factor affecting the enzymatic processes and shaping
12
13 587 the microbial communities. Medium temperature dynamics must be there-
14
15
16 588 fore accurately forecast, and also the way it affects the various biological
17
18 589 process represented.

19
20 590 The FLAME framework reveals to be particularly efficient to predict the
21
22 591 overall dynamics of an algae-bacteria process over 443 days. The proposed
23
24 592 heat transfer model, including the kinetic of both the liquid medium and the
25
26 593 reactor envelope is promising for better representing perfectly mixed reactors
27
28 594 in a WWTP.

29
30
31 595 The different models presented in Table 1 all could benefit from the
32
33 596 FLAME framework to become fully predictive. Coupled with weather fore-
34
35 597 casts, they can support a new generation of optimization strategies.

36
37 598 The FLAME framework also offers an opportunity to compare compet-
38
39 599 itive biological models that all have been developed to represent the same
40
41 600 process. Keeping the same chemical and physical modules, it proposes a
42
43 601 normalized way for benchmarking models. Several models can pass the val-
44
45 602 idation test and can then be kept to generate competitive predictions alto-
46
47 603 gether, improving the prediction accuracy, especially in situations far from
48
49 604 the calibration set.

50
51
52 605 The FLAME framework is a tool beyond the research world and can be
53
54 606 applied to large scale plants. It can be helpful during the scale-up phase for
55
56 607 preliminary economic assessments and for generating the data to support a

1
2
3
4
5
6
7
8
9
608 life cycle assessment in order to estimate the environmental footprint. It can
10
11 be used to guide the design and later, the management of outdoor industrial
12
13 bioprocesses.
14

611 **Acknowledgments**

612 This work benefited from the support of the ADEME Biomsa project and
613 from the ANR CtrlAB project (ANR-20-CE45-0014).
614

614 **References**

- 615 A.Pizzera, Scaglione, D., Bellucci, M., Marazzi, F., Mezzanotte, V., Parati,
616 K., Ficara, E., 2019. Digestate treatment with algae-bacteria consortia: A
617 field pilot-scale experimentation in a sub-optimal climate area. *Bioresource*
618 *Technology* 274, 232–243.
- 619 Arashiro, L.T., Rada-Ariza, A.M., Wang, M., Van Der Steen, P., Ergas,
620 S.J., 2017. Modelling shortcut nitrogen removal from wastewater using an
621 algal–bacterial consortium. *Water Science and Technology* 75, 782–792.
- 622 Arnell, M., Ahlström, M., Wärff, C., Saagi, R., Jeppsson, U., 2021. Plant-
623 wide modelling and analysis of wwtp temperature dynamics for sustainable
624 heat recovery from wastewater. *Water Science and Technology* 84, 1023–
625 1036.
- 626 Barrera, E.L., Spanjers, H., Solon, K., Amerlinck, Y., Nopens, I., Dewulf, J.,
627 2015. Modeling the anaerobic digestion of cane-molasses vinasse: Exten-

- 1
2
3
4
5
6
7
8
9 628 sion of the anaerobic digestion model no. 1 (adm1) with sulfate reduction
10
11 629 for a very high strength and sulfate rich wastewater. *Water research* 71,
12
13 630 42–54.
- 14
15
16 631 Bastin, G., Dochain, D., 1990. *On-line estimation and adaptive control of*
17
18 632 *bioreactors*. Elsevier, New York.
- 19
20
21 633 Batstone, D., Keller, J., Angelidaki, R., Kalyuzhnyi, S., Pavlostathis, S.,
22
23 634 Rozzi, A., Sandersand, W., Siegrist, H., Vavilin, V., 2002. The iwa anaero-
24
25 635 bic digestion model no.1 (adm1). *Water Science Technology* 45(10), 65–73.
- 26
27
28 636 Béchet, Q., Shilton, A., Guieysse, B., 2013. Modeling the effects of light
29
30 637 and temperature on algae growth: state of the art and critical assessment
31
32 638 for productivity prediction during outdoor cultivation. *Biotechnology ad-*
33
34 639 *vances* 31, 1648–1663.
- 35
36
37 640 Béchet, Q., Shilton, A., Park, J.B.K., Craggs, R.J., Guieysse, B., 2011. Uni-
38
39 641 versal temperature model for shallow algal ponds provides improved accu-
40
41 642 racy. *Environmental Science & Technology* 45, 3702–3709.
- 42
43
44 643 Béchet, Q., Sialve, B., Steyer, J.P., Shilton, A., Guieysse, B., 2018. Compar-
45
46 644 ative assessment of evaporation models in algal ponds. *Algal Research* 35,
47
48 645 283–291.
- 49
50
51 646 Bernard, O., Remond, B., 2012. Validation of a simple model accounting for
52
53 647 light and temperature effect on microalgal growth. *Bioresource Technology*
54
55 648 123, 520–7.

- 1
2
3
4
5
6
7
8
9 649 Bertolazzi, E., 2005. A combination formula of michaelis-menten-monod
10 type. *Computers & Mathematics with Applications* 50, 201–215.
11
12
13
14 651 Bougaran, G., Bernard, O., Sciandra, A., 2010. Modeling continuous cultures
15 of microalgae colimited by nitrogen and phosphorus. *Journal of theoretical*
16 652 *biology* 265, 443–454.
17
18
19 653
20
21 654 Broekhuizen, N., Park, J.B., McBride, G.B., Craggs, R.J., 2012. Modifica-
22 tion, calibration and verification of the iwa river water quality model to
23 655 simulate a pilot-scale high rate algal pond. *Water research* 46, 2911–2926.
24
25
26 656
27
28 657 Buaisha, M., Balku, S., Özalp-Yaman, S., 2020. Heavy metal removal investi-
29 gation in conventional activated sludge systems. *Civil Engineering Journal*
30 658 6, 470–477.
31
32
33 659
34
35 660 Camacho, E.F., Alba, C.B., 2013. *Model predictive control. Springer science*
36 & business media.
37
38 661
39
40 662 Casagli, F., Rossi, S., Steyer, J.P., Bernard, O., Ficara, E., 2021a. Bal-
41 ancing microalgae and nitrifiers for wastewater treatment: can inorganic
42 663 carbon limitation cause an environmental threat? *Environmental science*
43 & technology 55, 3940–3955.
44
45
46 664
47
48 665
49
50 666 Casagli, F., Zuccaro, G., Bernard, O., Steyer, J.P., Ficara, E., 2021b. Alba: A
51 comprehensive growth model to optimize algae-bacteria wastewater treat-
52 667 ment in raceway ponds. *Water Research* 190, 116734.
53
54
55 668
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6
7
8
9
669 la Cour Jansen, J., Kristensen, G., Laursen, K., 1992. Activated sludge
10
11 nitrification in temperate climate. *Water Science and Technology* 25, 177–
12
13 184.
14
15
16
672 De Baar, H., 1994. von Liebig's law of the minimum and plankton ecology
17
18 (1899–1991). *Progress in Oceanography* 33, 347–386.
19
20
21
674 De-Luca, R., Bezzo, F., Béchet, Q., Bernard, O., 2017. Exploiting mete-
22
23 orological forecasts for the optimal operation of algal ponds. *Journal of*
24
25 *Process Control* 55, 55–65.
26
27
28
677 De-Luca, R., Bezzo, F., Béchet, Q., Bernard, O., 2019. Meteorological data-
29
30 based optimal control strategy for microalgae cultivation in open pond
31
32 systems. *Complexity* 2019.
33
34
35
680 Dochain, D., Vanrolleghem, P.A., 2001. Dynamical modelling & estimation
37
38 in wastewater treatment processes. IWA publishing.
39
40
41
682 Henze, M., Gujer, W., Mino, T., van Loosdrecht, M.C., 2000a. Activated
42
43 sludge models ASM1, ASM2, ASM2d and ASM3. IWA publishing.
44
45
46
684 Henze, M., Gujer, W., Mino, T., Van Loosdrecht, M., 2000b. Activated
47
48 sludge models ASM1, ASM2, ASM2d and ASM3. IWA publishing.
49
50
51
686 Hewing, L., Wabersich, K.P., Menner, M., Zeilinger, M.N., 2020. Learning-
52
53 based model predictive control: Toward safe learning in control. *Annual*
54
55 *Review of Control, Robotics, and Autonomous Systems* 3, 269–296.
56
57
58

- 1
2
3
4
5
6
7
8
9 689 Janus, T., Ulanicki, B., 2010. Modelling smp and eps formation and degra-
10 dation kinetics with an extended asm3 model. *Desalination* 261, 117–125.
11
12
13
14 691 Junier, P., Molina, V., Dorador, C., Hadas, O., Kim, O.S., Junier, T., Witzel,
15 K.P., Imhoff, J.F., 2010. Phylogenetic and functional marker genes to study
16 692 ammonia-oxidizing microorganisms (aom) in the environment. *Applied*
17 693 *Microbiology and Biotechnology* 85, 425–440.
18
19
20
21 694
22
23 695 Klemeš, J.J., Varbanov, P.S., Huisingh, D., 2012. Recent cleaner produc-
24 tion advances in process monitoring and optimisation. *Journal of Cleaner*
25 696 *Production* 34, 1–8.
26
27
28
29
30 698 Lippi, S., Rosso, D., Lubello, C., Canziani, R., Stenstrom, M., 2009. Tem-
31 perature modelling and prediction for activated sludge systems. *Water*
32 699 *Science and Technology* 59, 125–131.
33
34
35 700
36
37
38 701 Luo, Y., Yao, J., Wang, X., Zheng, M., Guo, D., Chen, Y., 2020. Efficient
39 municipal wastewater treatment by oxidation ditch process at low temper-
40 702 ature: Bacterial community structure in activated sludge. *Science of The*
41 *Total Environment* 703, 135031.
42
43
44 704
45
46
47 705 Mairet, F., Bernard, O., 2019. Twelve quick tips for designing sound dynam-
48 ical models for bioprocesses. *PLoS Computational Biology* 15, e1007222.
49
50
51
52 707 Makinia, J., Wells, S.A., Zima, P., 2005. Temperature modeling in activated
53 sludge systems: A case study. *Water environment research* 77, 525–532.
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6
7
8
9 709 Martínez, C., Mairet, F., Bernard, O., 2018. Theory of turbid microalgae
10 cultures. *Journal of theoretical biology* 456, 190–200.
11
12
13
14 711 Milledge, J.J., 2011. Commercial application of microalgae other than
15 as biofuels: a brief review. *Reviews in Environmental Science and*
16
17
18 713 *Bio/Technology* 10, 31–41.
19
20
21 714 Morel, A., 1988. Optical modeling of the upper ocean
22 in relation to its biogenous matter content (case I wa-
23
24 715 ters). *J. Geophys. Res. Ocean.* 93, 10749–10768. URL:
25
26 716 <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/JC093iC09p10749>,
27
28 717 [doi:10.1029/JC093iC09p10749](https://doi.org/10.1029/JC093iC09p10749),
29
30 718 [doi:10.1029/JC093iC09p10749](https://doi.org/10.1029/JC093iC09p10749).
31
32
33 719 Osborne, J.M., Bernabeu, M.O., Bruna, M., Calderhead, B., Cooper, J.,
34 Dalchau, N., Dunn, S.J., Fletcher, A.G., Freeman, R., Groen, D., et al.,
35
36 720 2014. Ten simple rules for effective computational research. *PLoS Com-*
37
38 721 *putational Biology* 10, e1003506.
39
40
41
42 723 Petzold, L.R., 1982. Description of DASSL: a differential/algebraic system
43 solver. Technical Report. Sandia National Labs., Livermore, CA (USA).
44
45
46
47 725 Plósz, B.G., Liltved, H., Ratnaweera, H., 2009. Climate change impacts on
48 activated sludge wastewater treatment: a case study from norway. *Water*
49
50 726 *Science and Technology* 60, 533–541.
51
52
53
54 728 Reichert, P., 1994. Aquasim-a tool for simulation and data analysis of aquatic
55 systems. *Water Science and Technology* 30, 21.
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6
7
8
9
730 Reichert, P., 1998. Aquasim 2.0-tutorial. Swiss Federal Institute for En-
10
11 vironmental Science and Technology (EAWAG): Dübendorf, Switzerland
12
13
14
15
16
733 Rodríguez-Miranda, E., Acién, F.G., Guzmán, J.L., Berenguel, M., Visioli,
17
18 A., 2021. A new model to analyze the temperature effect on the microalgae
19
20 performance at large scale raceway reactors. *Biotechnology and Bioengi-*
21
22 neering 118, 877–889.
23
24
25
26
737 Rosén, C., Jeppsson, U., 2006. Aspects on ADM1 Implementation within the
27
28 BSM2 Framework. Department of Industrial Electrical Engineering and
29
30 Automation, Lund University, Lund, Sweden .
31
32
33
740 Rossi, S., Casagli, F., Mantovani, M., Mezzanotte, V., Ficara, E., 2020a.
34
35 Selection of photosynthesis and respiration models to assess the effect of
36
37 environmental conditions on mixed microalgae consortia grown on wastew-
38
39 ater. *Bioresource technology* 305, 122995.
40
41
42
744 Rossi, S., Sforza, E., Pastore, M., Bellucci, M., Casagli, F., Marazzi,
43
44 F., Ficara, E., 2020b. Photo-respirometry to shed light on microalgae-
45
46 bacteria consortia—a review. *Reviews in Environmental Science and*
47
48 *Bio/Technology* 19, 43–72.
49
50
51
748 Rosso, L., Lobry, J., Flandrois, J., 1993. An unexpected correlation between
52
53 cardinal temperatures of microbial growth highlighted by a new model.
54
55 *Journal of Theoretical Biology* 162, 447–463.
56
57
58

- 1
2
3
4
5
6
7
8
9 751 Rosso, L., Lobry, J.R., Bajard, S., Flandrois, J.P., 1995. Convenient model to
10 describe the combined effects of temperature and pH on microbial-growth.
11
12 752
13 Applied and Environmental Microbiology 61, 610–616.
14 753
15
16 754 Sánchez-Zurano, A., Rodríguez-Miranda, E., Guzmán, J.L., Acién-
17
18 755 Fernández, F.G., Fernández-Sevilla, J.M., Molina Grima, E., 2021. Abaco:
19
20 756 A new model of microalgae-bacteria consortia for biological treatment of
21
22 757 wastewaters. Applied Sciences 11, 998.
23
24
25 758 Sedory, P.E., Stenstrom, M., 1995. Dynamic prediction of wastewater aera-
26
27 759 tion basin temperature. Journal of Environmental Engineering 121, 609–
28
29 760 618.
30
31
32 761 Shampine, L.F., Reichelt, M.W., Kierzenka, J.A., 1999. Solving index-1 daes
33
34 762 in matlab and simulink. SIAM review 41, 538–552.
35
36
37 763 Solimeno, A., Gómez-Serrano, C., Acién, F.G., 2019. Bio_algae 2: improved
38
39 764 model of microalgae and bacteria consortia for wastewater treatment. En-
40
41 765 vironmental Science and Pollution Research 26, 25855–25868.
42
43
44 766 Van Fan, Y., Chin, H.H., Klemeš, J.J., Varbanov, P.S., Liu, X., 2020. Optimi-
45
46 767 sation and process design tools for cleaner production. Journal of Cleaner
47
48 768 Production 247, 119181.
49
50
51 769 Van Fan, Y., Varbanov, P.S., Klemeš, J.J., Nemet, A., 2018. Process effi-
52
53 770 ciency optimisation and integration for cleaner production.
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

771 Wágner, D.S., Valverde-Perez, B., Sæbø, M., de la Sotilla, M.B., Van Wa-
772 genen, J., Smets, B.F., Plosz, B.G., 2016. Towards a consensus-based
773 biokinetic model for green microalgae—the asm-a. *Water research* 103,
774 485–499.

775 Wolf, G., Picioreanu, C., van Loosdrecht, M.C., 2007. Kinetic modeling of
776 phototrophic biofilms: the phobia model. *Biotechnology and bioengineer-
777 ing* 97, 1064–1079.

778 Yong, J.Y., Klemeš, J.J., Varbanov, P.S., Huisingh, D., 2016. Cleaner en-
779 ergy for cleaner production: modelling, simulation, optimisation and waste
780 management. *Journal of Cleaner Production* 111, 1–16.

781 Yu, Q., Feng, L., Zhen, X., 2021. Effects of organic loading rate and tempera-
782 ture fluctuation on the microbial community and performance of anaerobic
783 digestion of food waste. *Environmental Science and Pollution Research* 28,
784 13176–13187.

785 Zouboulis, A., Tolkou, A., 2015. Effect of climate change in wastewater
786 treatment plants: reviewing the problems and solutions, in: *Managing
787 water resources under climate uncertainty*. Springer, pp. 197–220.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Simulating biotechnological processes affected by meteorology: application to algae-bacteria systems

Francesca Casagli^a, Olivier Bernard^{a,b*}

^c*BIOCORE, INRIA, Université côte d'Azur, BP 93, 06902 Sophia-Antipolis Cedex, France.*

^d*LOV, Sorbonne University, CNRS, UMR 7093, Station Zoologique, BP 28, 06234 Villefrance-sur-mer, France.*

SUPPORTING INFORMATION

788 **Appendix A. Experimental protocol (Narbonne case study)**

789 Details on the experimental protocol can be found in Casagli et al. (2021b).
790 Briefly, the HRABP was realized in concrete and placed on the ground over
791 a base of concrete (thickness 0.2 m). It was mixed with a paddle wheel,
792 operated to obtain a water linear velocity of 0.2 m s^{-1} , and an additional
793 mixing pump that was located at the opposite side of the paddle wheel (op-
794 erated at the flow rate of $182 \text{ m}^3 \text{ d}^{-1}$). The outflow was implemented
795 by gravity overflow, resulting in a variable liquid depth (min 0.257 m, max
796 0.368 m), measured with an ultrasonic distance sensor (Siemens, SITRANS
797 Probe 7ML5221-1BB11). The HRABP was also equipped with online dis-
798 solved oxygen (METTLER TOLEDO, InPro 6850i), temperature and pH

*Corresponding author

Email address: `olivier.bernard@inria.fr` (Olivier Bernard^{a,b*})

Preprint submitted to Journal of Cleaner Production

May 22, 2022

1
2
3
4
5
6
7
8
9
799 (METTLER TOLEDO, InPro4260(i)/SG/425) probes. The incident light
10
11 (expressed as Photosynthetically Active Radiation, PAR) was continuously
12
13 801 measured at the reactor surface, using a PAR meter (SKYE Instruments,
14
15 802 PAR 2625). All the online measurements were collected every five minutes,
16
17 803 using the dedicated SILEX-LBE acquisition system (INRAE-LBE, France).
18
19

20 804 **Appendix B. Recall of modelling principles**

21 22 23 805 *Appendix B.1. Modelling the influence of pH*

24
25 806 There are different kinetics models representing the influence of pH. The
26
27 807 most used being probably the one proposed by Rosso et al. (1995), i.e. the
28
29 808 Cardinal pH Model (CPM). The CPM is zero for $pH \notin [pH_{min}, pH_{max}]$,
30
31 809 where pH_{min} and pH_{max} are the minimum and the maximum pH thresholds
32
33 810 respectively. For $pH \in [pH_{min}, pH_{max}]$ the pH effect is described by f_{pH} ,
34
35 811 where pH_{opt} is the pH value at which f_{pH} is maximum:
36
37

$$38 \quad f_{pH} = \frac{(pH - pH_{max}) \cdot (pH - pH_{min})}{(pH - pH_{min}) \cdot (pH - pH_{max}) - (pH - pH_{opt})^2} \quad (B.1)$$

39
40
41 812

42 43 44 813 *Appendix B.2. Modelling the influence of temperature*

45
46 814 The temperature in outdoor open bioreactors fluctuates within large ranges
47
48 815 according to daily and seasonal dynamics. The fluctuations are of higher
49
50 816 amplitudes for the processes with lower depths. The temperature depen-
51
52 817 dence is often modelled through the Cardinal Temperature Model with In-
53
54 818 flection (CTMI), that requires three parameters, i.e. the cardinal temper-
55
56 819 atures: T_{max} , T_{min} and T_{opt} (Rosso et al., 1993). The CTMI is zero for
57
58

1
2
3
4
5
6
7
8
9
839 where the light extinction rate $\epsilon(\xi)$ is proportional to the biomass of algae in
10
11 most of the model, but can account for the background turbidity (Martínez
12
13 841 et al., 2018), possibly including other particulate compounds. It can even be
14
15 842 a nonlinear function of the algal biomass (Morel, 1988).

16
17 843 There are several ways of representing this effect (Béchet et al., 2013),
18
19 844 depending on if only the average light intensity or the average growth rate
20
21 845 are considered.

22 23 24 846 **Appendix C. Summary of the ALBA model development choices**

25
26
27 847 Here, we recall the main choices made in the construction of the model.
28
29 848 We refer the reader to Casagli et al. (2021b,a) for more details. Reaction
30
31 849 stoichiometry, rates and nomenclature are in line with the IWA modelling
32
33 850 works, i.e. Activated Sludge Models (ASMs) and Anaerobic Digestion Model
34
35 851 n°1 (ADM1), ((Batstone et al., 2002), (Henze et al., 2000b)).

36
37 852 The biokinetic rates are based on the Liebig’s minimum law (De Baar,
38
39 853 1994) for limiting substrates (carbon, nitrogen and phosphorus), meaning
40
41 854 that the most limiting nutrient drives the overall kinetics. The general ex-
42
43 855 pression describing the structure of bioprocess rates is:

$$44
45
46
47 \rho_j = \mu_{max_j} \cdot f_T \cdot f_{pH} \cdot \frac{K_n}{K_n + S_n} \cdot \min_i \left(\frac{S_i}{S_i + K_{S_i}} \right) \cdot X_{BM_i} \quad (C.1)$$

48
49
50
51 856 Where μ_{max_j} is the maximum specific growth rate [d⁻¹] related to the
52
53 857 process ρ_j ; f_T , f_{pH} and f_I are the functions describing temperature and pH
54
55 858 dependence, respectively; K_n is the inhibition constant for the inhibiting
56
57
58

1
2
3
4
5
6
7
8
9 substrate S_n , K_{S_i} is the half-saturation constant for the limiting substrate
10 S_i and $X_{BM,i}$ is the biomass associated to the process ρ_j .

11
12
13 The photosynthesis response to irradiance is described computing the
14 average algal growth rate for a given incident light and liquid depth. It
15 accounts for the light extinction through the Beer-Lambert law (B.3), and
16 for the actual growth rate at a certain depth. The chosen Haldane-type
17 function represents the limiting light in the darkest parts of the reactor and
18 photoinhibition at high irradiance close to the surface (Bernard and Remond,
19 2012):
20
21
22
23
24
25
26
27

$$\mu_{opt}(I(z)) = \mu_{max} \frac{I(z)}{I(z) + \frac{\mu_{max}}{\alpha} \left(\frac{I(z)}{I_{opt}} - 1 \right)^2} \quad (C.2)$$

28
29
30
31
32 The average growth rate in the reactor is then computed as follows:
33
34

$$\bar{\mu}(I_0, h) = \frac{1}{h} \int_0^h \mu(I(I_0, z)) dz \quad (C.3)$$

35
36
37
38 The temperature dependence for algae and bacteria growth is modelled
39 through the Cardinal Temperature Model with Inflection (CTMI), see Equa-
40 tion (B.2), (Rossi et al., 2020a).
41
42
43

44 The Arrhenius function, depending only on one parameter, was chosen
45 for the decay rates:
46
47
48
49

$$f_{T,2} = \theta^{T-20} \quad (C.4)$$

50
51
52 The pH strongly influences system dynamics, since it directly affects the
53 dissociation of the majority of soluble compounds (S_{IC} , S_{NH} , S_{NO_2} , S_{NO_3} ,
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

⁸⁷⁶ S_{PO_4}). The influence of pH on algae and bacteria bio-process rates is included
⁸⁷⁷ through CPM function proposed by (Rosso et al., 1995).

878 Appendix D. Petersen matrix for the ALBA model

component j →	X _{ALG} gCOD m ⁻³	X _{NOB} gCOD m ⁻³	X _{NOB} gCOD m ⁻³	X _H gCOD m ⁻³	X _S gCOD m ⁻³	X _I gCOD m ⁻³	S _S gCOD m ⁻³	S _I gCOD m ⁻³	S _C gCm ⁻³	S _{NO} gNm ⁻³	S _{NH} gNm ⁻³	S _{NO2} gNm ⁻³	S _{NO3} gNm ⁻³	S _{NO2} gNm ⁻³	S _{PO4} gPm ⁻³	S _{O2} gO ₂ m ⁻³	S _{PHO} gHm ⁻³
Algae																	
1	1								α _{1,9}	α _{1,11}					α _{1,15}	1	α _{1,17}
2	1							α _{2,9}				α _{2,13}			α _{2,15}	1	α _{2,17}
3	-1							α _{3,9}		α _{3,11}					α _{3,15}	-1	α _{3,17}
4	-1				α _{4,6}			α _{4,9}		α _{4,11}					α _{4,15}		
Heterotrophic bacteria																	
5			1				α _{5,7}		α _{5,9}	α _{5,11}					α _{5,15}		α _{5,16}
6			1				α _{6,7}		α _{6,9}			α _{6,13}			α _{6,15}		α _{6,16}
7			-1					α _{7,9}	α _{7,11}					α _{7,15}		-1	
8			1				α _{8,7}		α _{8,9}	α _{8,11}		α _{8,13}	α _{8,14}	α _{8,15}			
9			1				α _{9,7}		α _{9,9}	α _{9,11}	α _{9,12}			α _{9,15}			
10			-1					α _{10,9}	α _{10,11}		α _{10,12}	α _{10,13}	α _{10,14}	α _{10,15}			
11										α _{11,11}				α _{11,15}			
12					-1		α _{11,7}	α _{11,8}	α _{11,9}								α _{12,17}
13			-1		α _{13,5}	α _{13,6}			α _{13,9}		α _{13,11}				α _{13,15}		
Ammonium Oxidising Bacteria																	
14		1							α _{14,9}	α _{14,11}		α _{14,12}			α _{14,15}		α _{14,16}
15		-1							α _{15,9}	α _{15,11}					α _{15,15}		α _{15,16}
16		-1							α _{16,9}	α _{16,11}					α _{16,15}		
Nitrite Oxidising Bacteria																	
17			1						α _{17,9}	α _{17,11}	α _{17,12}	α _{17,13}			α _{17,15}		α _{17,16}
18			-1						α _{18,9}	α _{18,11}					α _{18,15}		α _{18,16}
19			-1						α _{19,9}	α _{19,11}					α _{19,15}		

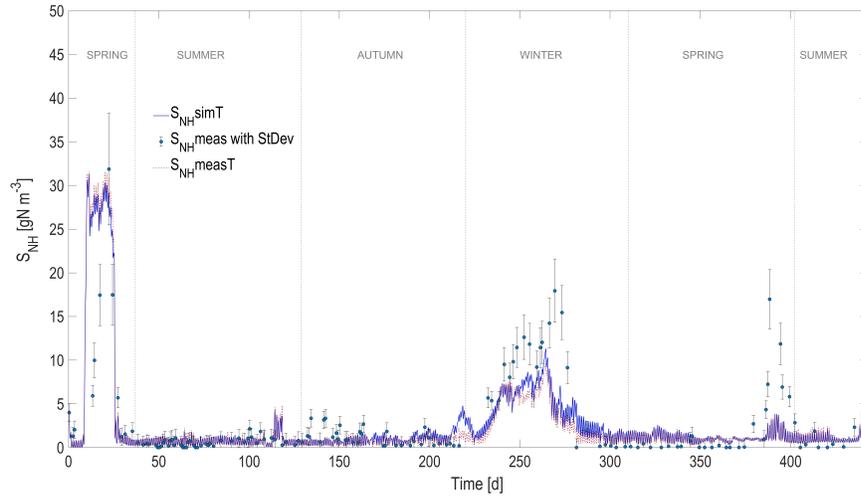
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

880 **Appendix E. Comparison between the fully predictive ALBA model**
881 **and simulations with measured temperature**

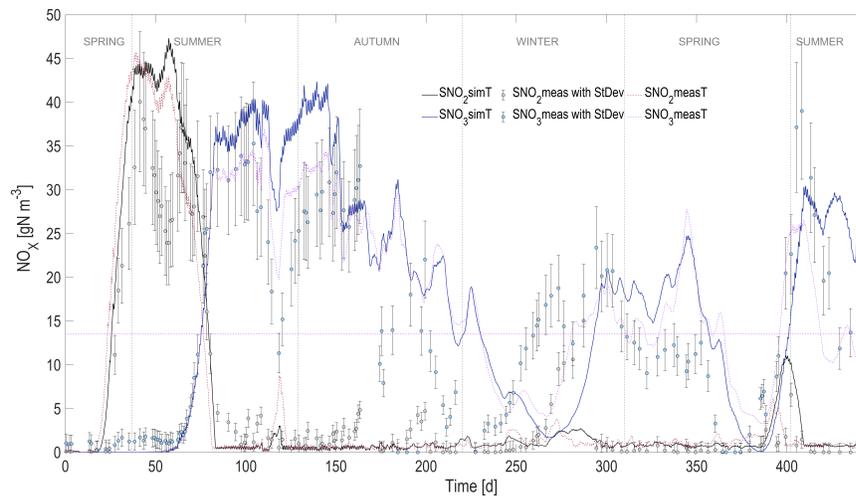
882 *Appendix E.1. Narbonne case study*

883 Figures E.1, E.2 and E.3 show the graphs already reported in Section 4,
884 superimposing the simulation results obtained using the measured tempera-
885 ture.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

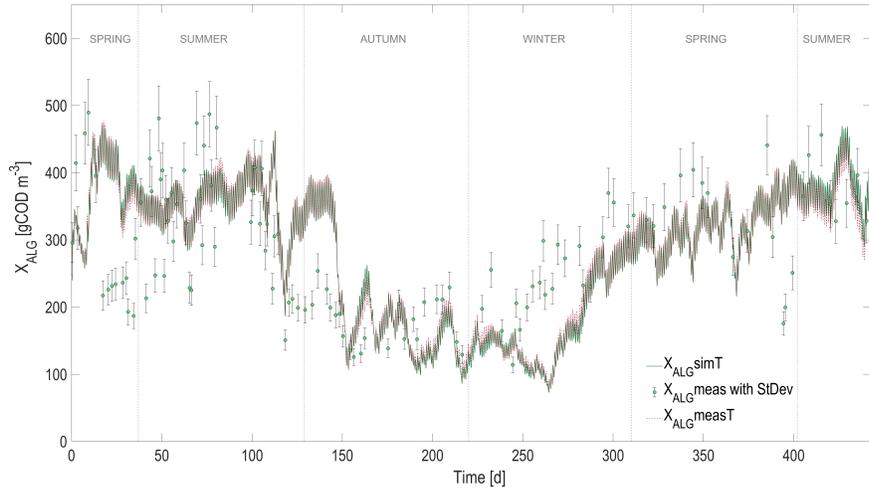


a)

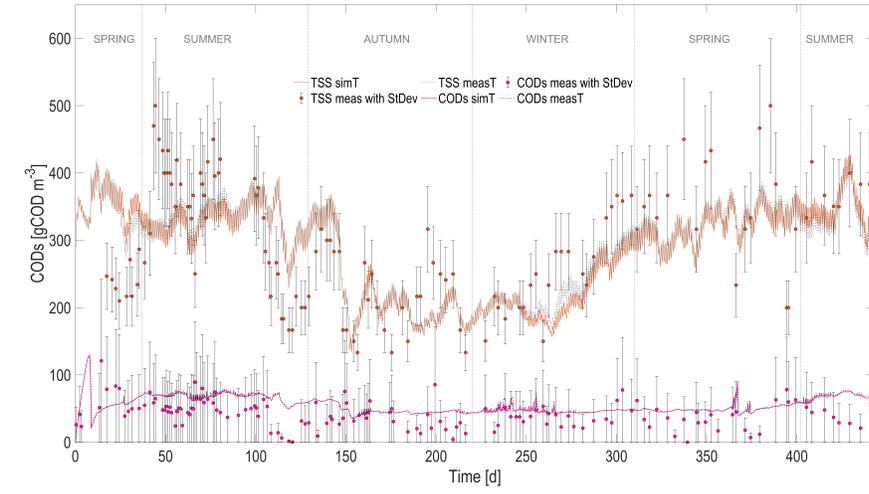


b)

Figure E.1: ALBA fully predictive model validation over one year. Experimental measurements (and their Standard Deviation), model predictions with simulated temperature and model predictions with measured temperature: a) ammoniacal nitrogen; b) nitrite and nitrate.



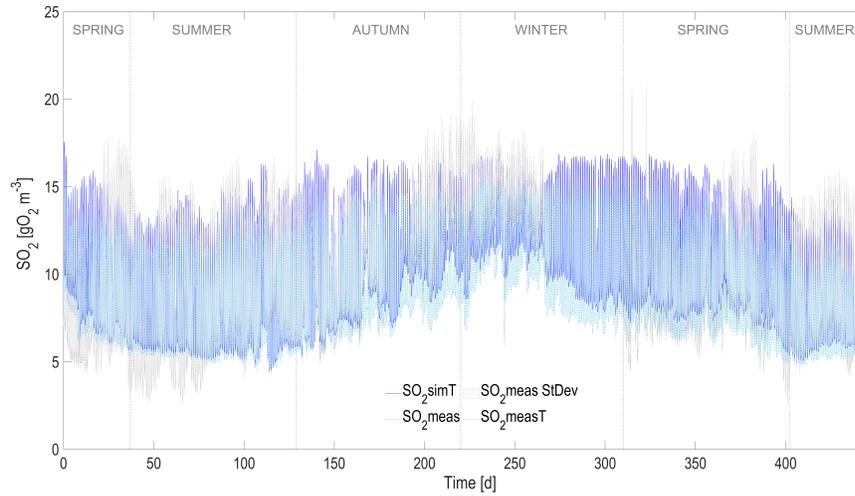
c)



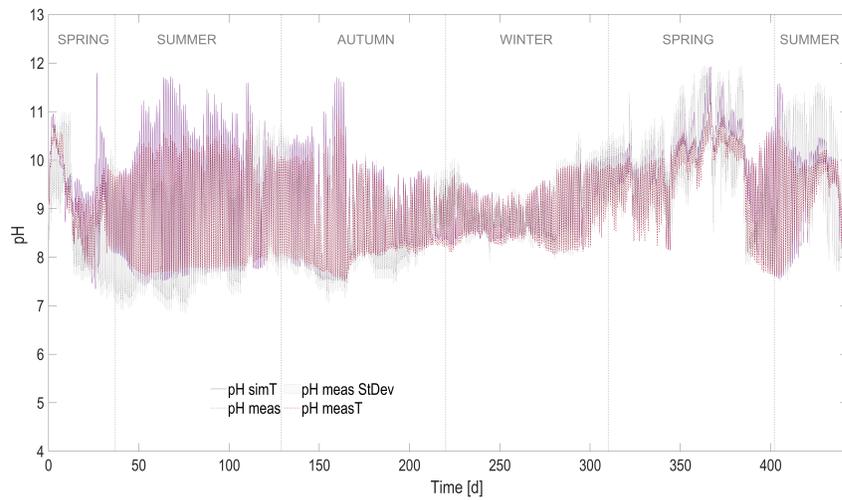
d)

Figure E.2: ALBA fully predictive model validation over one year. Experimental measurements (and standard deviation), model predictions with simulated temperature and model predictions with measured temperature: c) algal biomass; d) Total Suspended Solids and soluble COD

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65



e)



f)

Figure E.3: ALBA fully predictive model validation over one year. Experimental measurements (and their Standard Deviation), model predictions with simulated temperature and model predictions with measured temperature: e) dissolved oxygen; f) pH.

1
2
3
4
5
6
7
8
9
886 **Appendix F. Milan case study**

887 In figures F.5, F.6, F.7 and F.8 the validation results of the fully predic-
888 tive ALBA model, for another experimental application, are reported. The
889 fully predictive model was validated on experimental data from a pilot-scale
890 HRABP ($1m^3$) located in the northern part of Italy, treating the liquid frac-
891 tion of piggery digestate. The reactor configuration was different compared
892 to the one located in Narbonne, as shown in Figure F.4, so the heat trans-
893 fer model was adapted, removing the heat flux with the ground (conduction
894 term) and adding the conductive /convective term between the liquid, the
895 material of the pond and the air. More details concerning this experimenta-
896 tion can be found in A.Pizzera et al. (2019); Casagli et al. (2021a).

897 The model resulted to be very accurate in both the predictions of the pond
898 temperature and the main measured variables, as ammoniacal nitrogen, ni-
899 trite, nitrate, algal biomass and oxygen.

900 In figure F.6, F.7 and F.8, the dots represent the measurements with their
901 standard deviation, the continuous lines are the simulation results, while the
902 shaded areas are the error bounds for the model predictions, computed on
903 the first version of the ALBA model (i.e.where the measured temperature
904 was used). The continuous line falls always in the shaded areas and it fol-
905 lows very well the trend of the experimental data, confirming indirectly the
906 accuracy of the heat transfer model, applied also to this case study.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

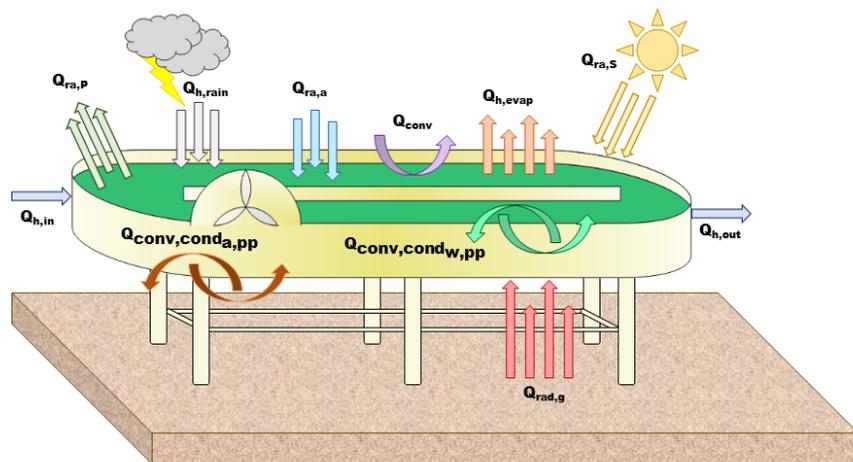
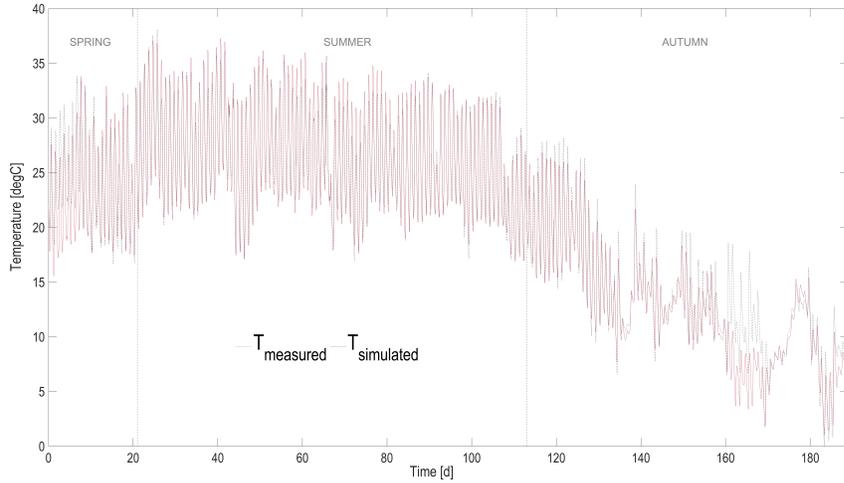
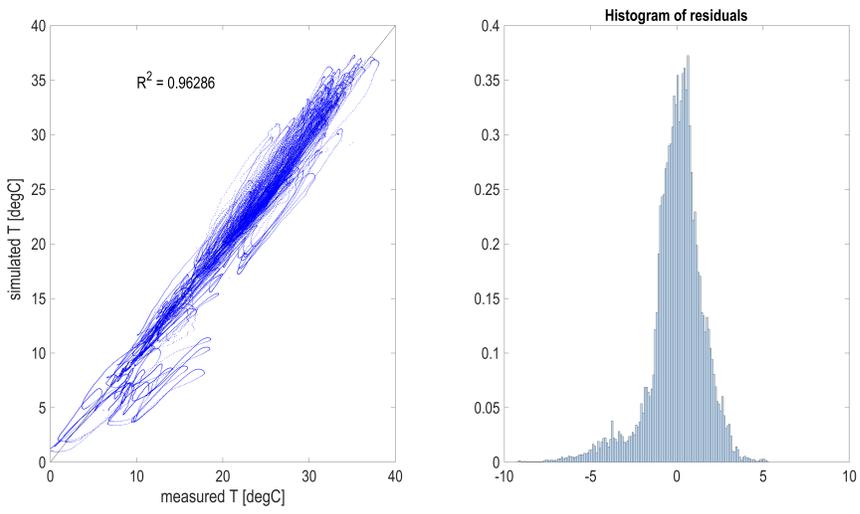


Figure F.4: Configuration of the HRABP located in Milan

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65



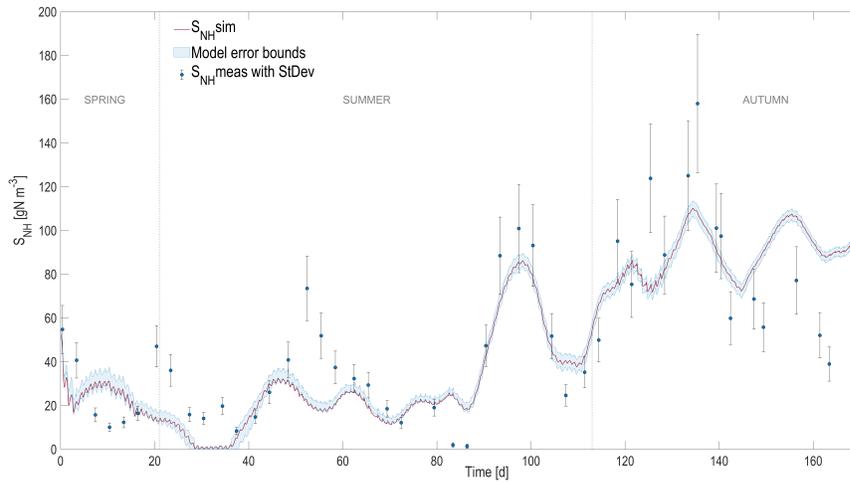
a)



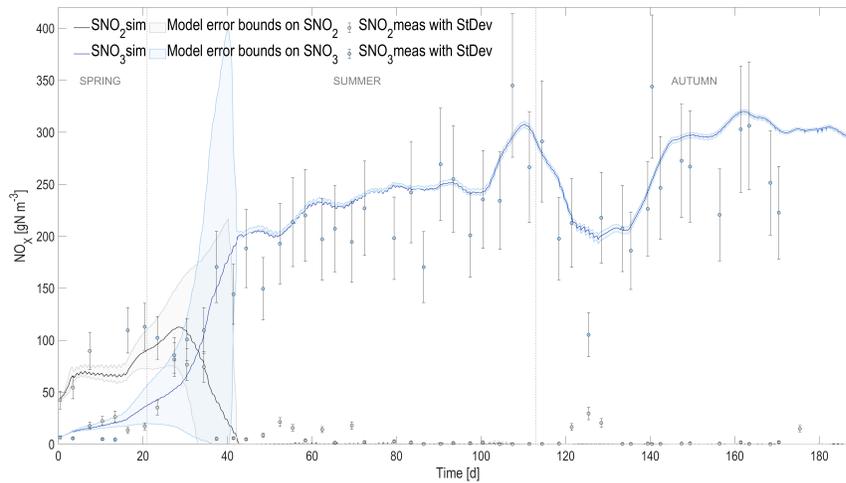
b)

Figure F.5: Heat transfer model validation over six months experimental measurements (54410 measured temperature values)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65



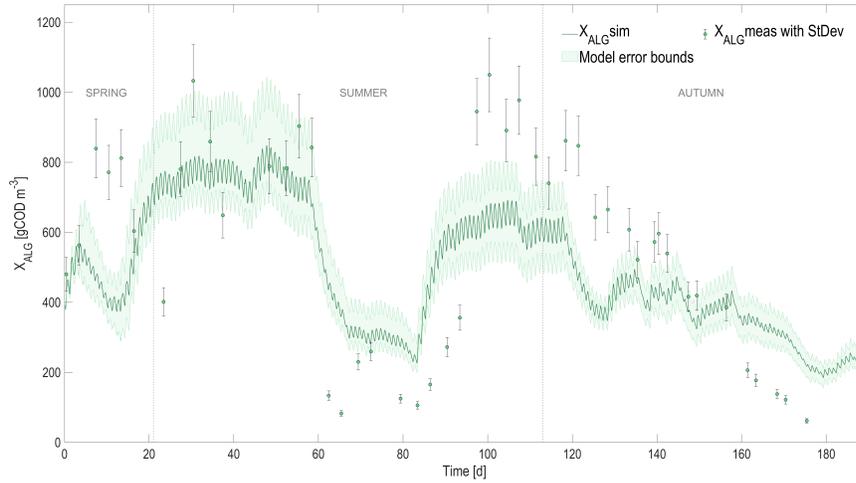
a)



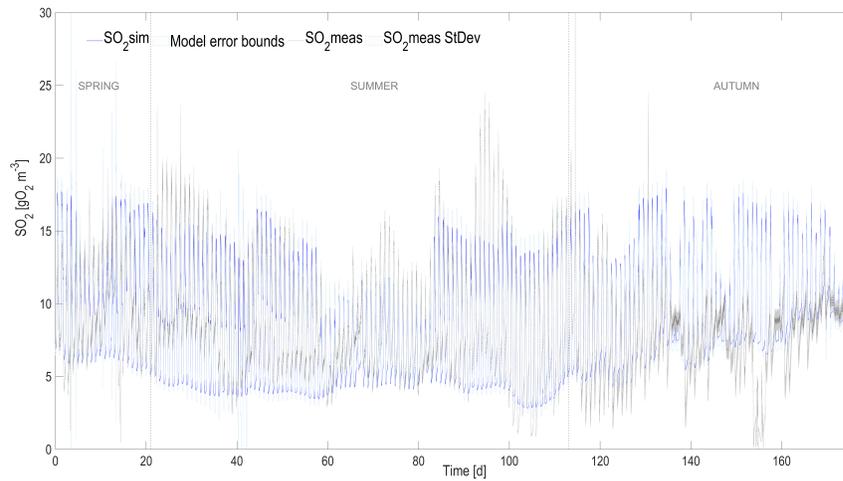
b)

Figure F.6: Full prediction capability of the coupled thermal-biology ALBA model. Comparison between predictions with simulated temperature (together with model error bounds) and measurements for: a) ammoniacal nitrogen; b) nitrite and nitrate.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65



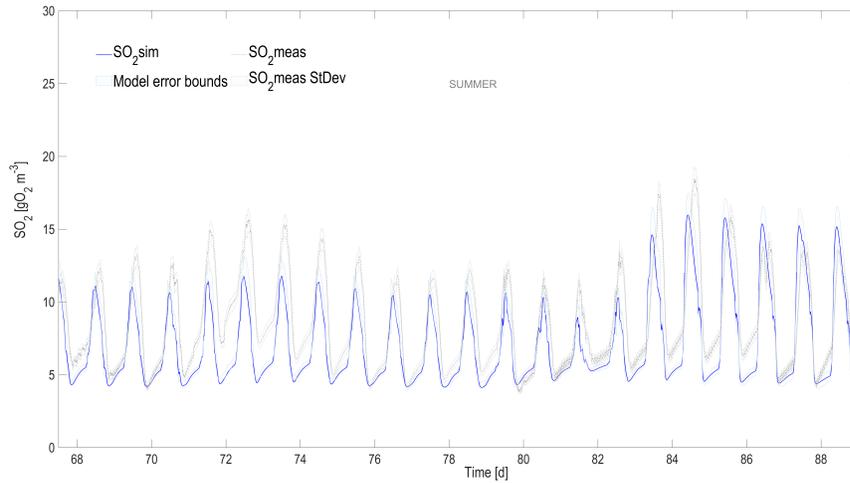
c)



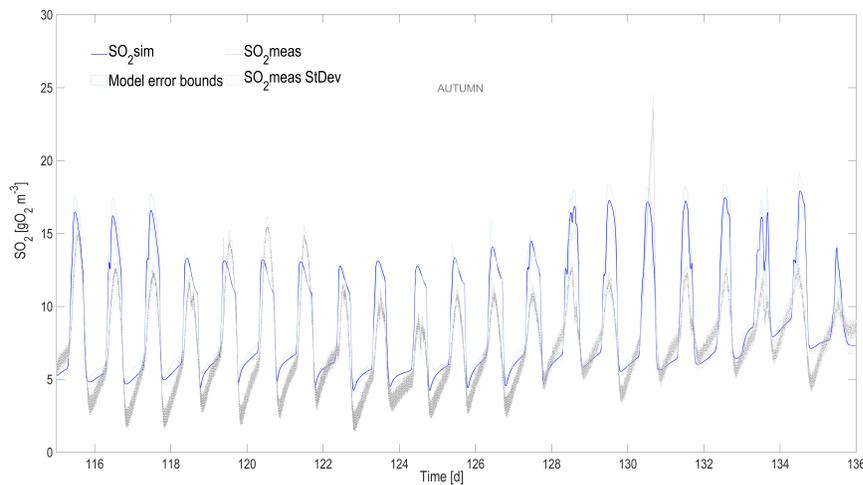
d)

Figure F.7: Full prediction capability of the coupled thermal-biology ALBA model. Comparison between predictions with simulated temperature (together with model error bounds) and measurements for: c) algal biomass; d) dissolved oxygen.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65



e)



f)

Figure F.8: Full prediction capability of the coupled thermal-biology ALBA model. Comparison between predictions with simulated temperature (together with model error bounds) and measurements for: e) dissolved oxygen: focus on summer season; f) dissolved oxygen: focus on autumn season.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

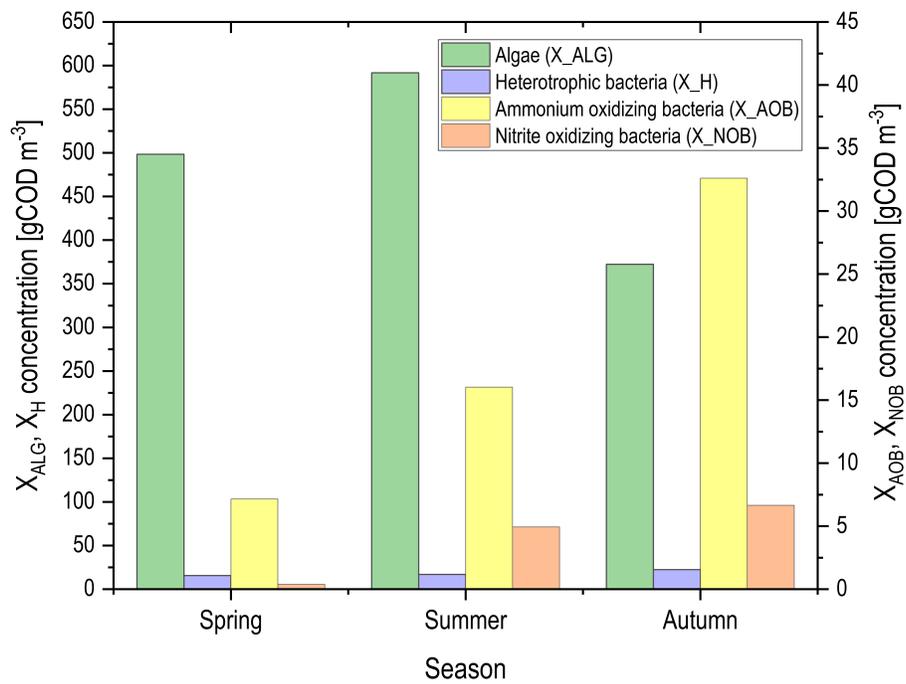


Figure F.9: Average composition of the microbial population according to seasons, as estimated by the fully predictive model. Right axis: algae (X_{ALG}) and heterotrophic bacteria (X_H) concentration; left axis: nitrifying bacteria (X_{AOB} and X_{NOB}) concentration.

1
2
3
4
5
6
7
8
9
907 **Appendix G. Temperature impact on equilibrium constants**

10
11
908 On the wave of the work performed from the ADM1 task group, the
12
13 temperature impact on the equilibrium coefficients ($K_{a,T}$, [$molL^{-1}$]) can be
909
14
15 taken into account by using the van't Hoff equation:
910
16
17

$$18 \ln \frac{K_{a,T}}{K_{a,T_{ref}}} = \frac{\Delta H}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T + 273.15} \right) \quad (G.1)$$

19
20
21
22

911 where T_{ref} is the standard temperature (i.e. 298.15 K) for which the value of
23
24 the equilibrium coefficient ($K_{a,T_{ref}}$, [$molL^{-1}$]) is known. R is the gas law con-
25
26 stant [$JK^{-1}mol^{-1}$] and ΔH is the heat of reaction at standard temperature
912
913 and pressure [$Jmol^{-1}$].
914
27
28
29
30
31

32 **Appendix H. Total alkalinity and inorganic carbon concentration:**
33
34 **effect of wrong temperature predictions in HRABPs**
915
916

35
36
917 In order to show the temperature effect on key variables as the inorganic
37
38 carbon (S_{IC}) and the total alkalinity (TA), additional simulations were run.
39
918 Specifically, the predictions obtained with the fully predictive ALBA model
40
41 were compared with the results obtained using the measured temperature
42
43 increased and decreased of 5 degC, respectively. The results of the compari-
44
45 son are reported in figure H.10. Concerning the total alkalinity, the average
919
920 absolute/relative error computed when increasing and decreasing the temper-
46
47 ature, is 26.74% and 16.65% respectively, while the maximum one is 140.59%
921
922 and 144.04% respectively. Focusing on the total inorganic carbon, the aver-
48
49 age and maximum absolute/relative error, when increasing the temperature,
923
924 are 50.84% and 295.39% respectively. When decreasing the temperature, the
925
926
927
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

928 average and maximum absolute/relative error are 32.64% and 201.65% re-
929 spectively.

930 It is therefore shown how much the total alkalinity and the inorganic carbon
931 trends are affected by a relatively small temperature variation ($\pm 5degC$).

932 In addition, these two variables are strictly linked to: i) photoautotrophic
933 and autotrophic growth (algae and nitrifiers); ii) CO_2 stripping and iii) suit-
934 able conditions for N_2O production (if occuring inorganic carbon limitation).

935 Therefore, an accurate temperature prediction in the reactor is required.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

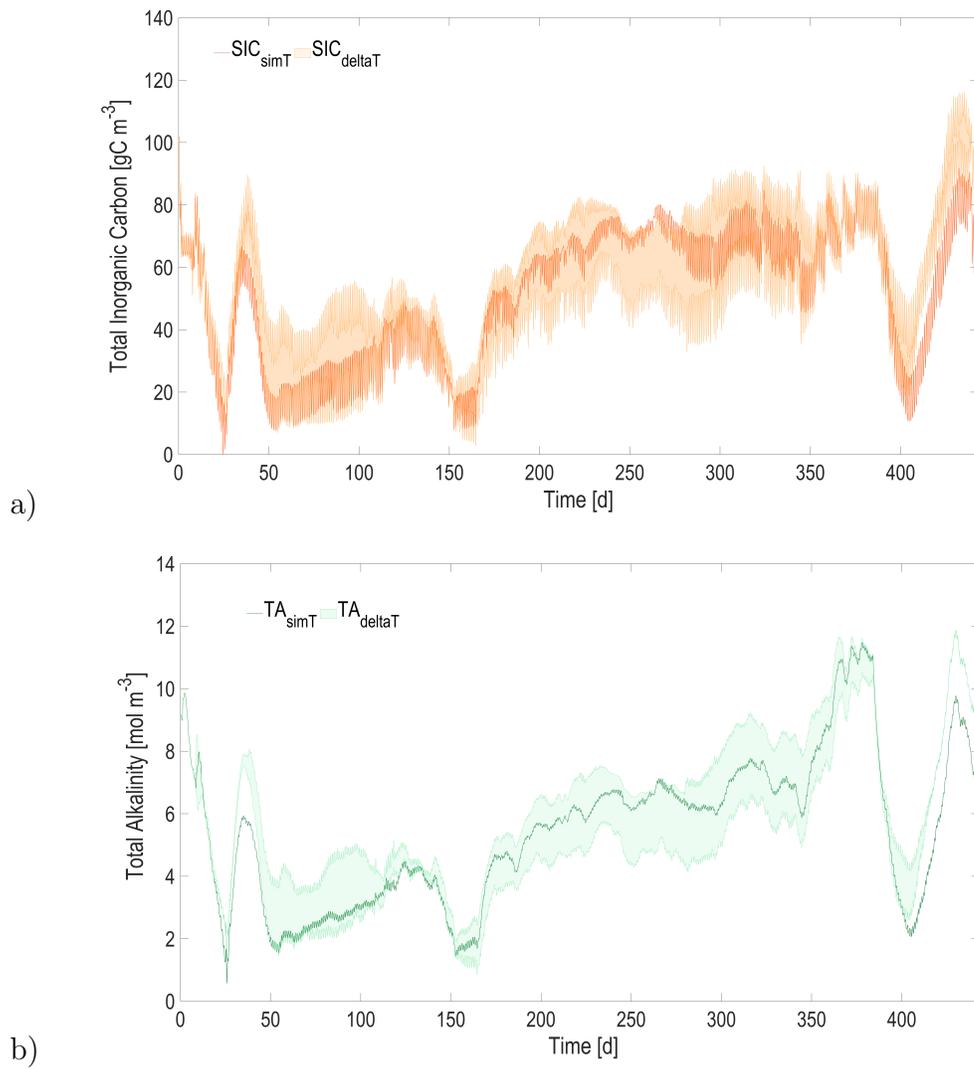


Figure H.10: Predicted values for total alkalinity (a) and inorganic carbon (b): the continuous lines represent the simulation results obtained using the fully predictive model; the shaded areas represent the total alkalinity and inorganic carbon range of variation for temperature $\pm 5^\circ \text{C}$.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

936 **Appendix I. Parameters used for the extended version of the heat**
937 **transfer model**

938 The parameters required for running the heat transfer model are reported
939 in the following Table I.3.

Table I.3: Parameter values for the heat transfer model.

Symbol	Definition	Unit	Value
<i>Water parameters</i>			
ρ_w	Water density	kg m ⁻³	998
Cp_w	Water heat capacity	J kg ⁻¹ K ⁻¹	$4.18 \cdot 10^3$
L_w	Water latent heat	J kg ⁻¹	$2.45 \cdot 10^6$
ϵ_w	Water emissivity	-	0.97
M_w	Water molecular weight	kg m ⁻³	0.018
<i>Soil parameters</i>			
k_s	Soil thermal conductivity	W m ⁻¹ K ⁻¹	2
Cp_s	Soil specific heat capacity	J kg ⁻¹ K ⁻¹	$1.25 \cdot 10^3$
ρ_s	Soil density	kg m ⁻³	$1.9 \cdot 10^3$
$l_{s,ref}$	Depth at which the soil temperature is constant over the year	m	5
$T_{s,ref}$	Soil temperature at $l_{s,ref}$	°C	10
<i>Air parameters</i>			
ϵ_a	Air emissivity	-	0.8
ν_a	Air kinematic viscosity	m ² s ⁻¹	$1.5 \cdot 10^{-5}$
λ_a	Air thermal conductivity	W m ⁻¹ K ⁻¹	$2.6 \cdot 10^{-2}$
Pr_a	Air Prandtl number	-	0.7
ρ_a	Air density	kg m ⁻³	1.2
α_a	Air thermal diffusivity	m ² s ⁻¹	$2.2 \cdot 10^{-5}$
$D_{w,a}$	Mass diffusion coefficient of water vapor in air	m ² s ⁻¹	$2.4 \cdot 10^{-5}$
<i>Pond parameters</i>			
V	Pond volume	m ³	variable
S	Pond surface	m ²	56
L	Pond length	m	15
z	Wind velocity height	m	0.5
z_0	Wind sensor height	m	2.6
q_i	Inflow rate	m ³ s ⁻¹	0
f_a	Algal absorption fraction	%	2.5
α	Power law exponent	-	0.29
<i>Concrete parameters</i>			
s_{co}	concrete thickness	m	0.3
ρ_{co}	concrete density	Kg m ³	2500
Cp_{co}	concrete heat capacity	J Kg ⁻¹ K ⁻¹	$1 \cdot 10^3$
$h_{co,w}$	Conductive-convective term (water on concrete)	W m ⁻² K ⁻¹	8.5^a
<i>Universal constants</i>			
σ	Stephan-Boltzmann constant	W m ⁻² K ⁻⁴	$5.67 \cdot 10^{-8}$
R	Ideal gas constant	Pa m ³ mol ⁻¹ K ⁻¹	8.314

^a computed considering: i) concrete thermal conductivity $2.6 \text{ W m}^{-1} \text{ K}^{-1}$; ii) water thermal convection coefficient $10^3 \text{ W m}^{-2} \text{ K}^{-1}$

940 **Appendix J. Extending the pH submodel in the presence of VFA**

941 .

Table J.4: Chemical sub-model extension when volatile fatty acids are present in the medium.

HAc : CH_3COOH , Ac^- : CH_3COO^- HBr : $CH_3CH_2CH_2COOH$, Br^- : $CH_3CH_2CH_2COO^-$ HPr : CH_3CH_2COOH , Pr^- : $CH_3CH_2COO^-$, HVa : $CH_3CH_2CH_2CH_2COOH$, Pr^- : $CH_3CH_2CH_2CH_2COO^-$

Description	Expression [$mol\ m^{-3}$]	K_A [M]
<i>Acetic acid</i>		
1) Mass balance	$\frac{S_{Ac}}{60.05 \cdot 1.07} - HAc - Ac^- = 0$	
2) Dissociation	$HAc \rightleftharpoons Ac^- + H^+$	
	$HAc - \frac{\frac{S_{Ac}}{60.05 \cdot 1.07}}{1 + \frac{K_{A,Ac} 10^3}{H^+}} = 0$	$K_{A,Ac} = 1.74E-5$
<i>Butyric acid</i>		
3) Mass balance	$\frac{S_{Bu}}{88.11 \cdot 1.82} - HBu - Bu^- = 0$	
4) Dissociation	$HBu \rightleftharpoons Bu^- + H^+$	
	$HBu - \frac{\frac{S_{Bu}}{88.11 \cdot 1.82}}{1 + \frac{K_{A,Bu} 10^3}{H^+}} = 0$	$K_{A,Bu} = 1.51E-5$
<i>Propionic acid</i>		
5) Mass balance	$\frac{S_{Pr}}{74.08 \cdot 1.51} - HPr - Pr^- = 0$	
6) Dissociation	$HPr \rightleftharpoons Pr^- + H^+$	
	$HPr - \frac{\frac{S_{Pr}}{74.08 \cdot 1.51}}{1 + \frac{K_{A,Pr} 10^3}{H^+}} = 0$	$K_{A,Pr} = 1.32E-5$
<i>Valeric acid</i>		
7) Mass balance	$\frac{S_{Va}}{102.13 \cdot 2.04} - HVa - Va^- = 0$	
8) Dissociation	$HVa \rightleftharpoons Va^- + H^+$	
	$HVa - \frac{\frac{S_{Va}}{102.13 \cdot 2.04}}{1 + \frac{K_{A,Va} 10^3}{H^+}} = 0$	$K_{A,Va} = 9.77E-6$
<i>Hydrogen sulphide</i>		
9) Mass balance	$\frac{S_{H_2S}}{32.07} - H_2S - HS^- - S^{2-} = 0$	
10) Dissociation	$H_2S \rightleftharpoons HS^- + H^+$	
	$H_2S - \frac{\frac{S_{H_2S}/32.07}{1 + \frac{K_{a,H_2S} 10^3}{H^+} + \frac{K_{a,H_2S} K_{a,HS^-} 10^6}{(H^+)^2}}}{1 + \frac{K_{a,H_2S} 10^3}{H^+} + \frac{K_{a,HS^-} 10^3}{H^+}} = 0$	$K_{A,H_2S} = 8.91E-8$
11) Dissociation	$HS^- \rightleftharpoons S^{2-} + H^+$	
	$HS^- - \frac{\frac{S_{H_2S}/32.07}{1 + \frac{K_{a,H_2S} 10^3}{H^+} + \frac{K_{a,HS^-} 10^3}{H^+}}}{1 + \frac{K_{a,H_2S} 10^3}{H^+} + \frac{K_{a,HS^-} 10^3}{H^+}} = 0$	$K_{A,HS^-} = 1.29E-13$

1
2
3
4
5
6
7
8
9
942 **Appendix K. Solving the pH submodel**

10
11
12 .
13
14 The way the pH submodel is numerically solved is illustrated for the
15 ALBA model. It consists in determining 15 unknown (NH_3 , NH_4^+ , NO_2^- ,
16 HNO_2 , NO_3^- , HNO_3 , CO_2 , HCO_3^- , CO_3^{2-} , H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} ,
17 PO_4^{3-} , OH^- and H^+) from the 5 state variables S_{PO_4} , S_{NO_2} , S_{NO_3} , S_{NH} and
18 S_{IC} supporting the 5 mass balances and the 9 equations for the dissociation,
19 plus the one for the charge balance. To solve this system, the charge balance
20 equation can be rewritten accounting for the dependence of the dissociated
21 fractions from the H^+ ions and from the total amount of compounds.
22
23
24
25
26
27
28
29
30
31

$$\begin{aligned}
 H^+ &+ NH_4^+(H^+, S_{NH}) + \Delta_{CAT,AN} - OH^-(H^+) \\
 &- NO_2^-(H^+, S_{NO_2}) - NO_3^-(H^+, S_{NO_3}) - HCO_3^-(H^+, S_{IC}) \\
 &- 2CO_3^{2-}(H^+, S_{IC}) - H_2PO_4^-(H^+, S_{PO_4}) \\
 &- 2HPO_4^{2-}(H^+, S_{PO_4}) - 3PO_4^{3-}(H^+, S_{PO_4}) = 0
 \end{aligned} \tag{K.1}$$

32
33
34
35
36
37
38
39
40
41 952 which can be rewritten as

$$H^+ = \Phi_{pH}(H^+, S_{PO_4}, S_{NO_2}, S_{NO_3}, S_{NH}, S_{IC}) \tag{K.2}$$

42
43
44
45
46
47
48 953 The physical root of this equation can be solved by an algebraic solver.
49 Here we prefer to compute the variable \hat{H}^+ which is an estimate of H^+ . The
50 estimator equation is given by
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

$$\frac{d\hat{H}^+}{dt} = \hat{K} \left(\Phi_{\text{pH}}(\hat{H}^+, S_{PO_4}, S_{NO_2}, S_{NO_3}, S_{NH}, S_{IC}) - \hat{H}^+ \right) \quad (\text{K.3})$$

956 where \hat{K} is a constant tuning the rate for solving the pH equation. Note
957 that, for each equilibrium, \hat{H}^+ automatically satisfies Equation (K.2). At
958 the time scale defined by $\frac{1}{\hat{K}}$, the other state variables can be considered as
959 constant (fast-slow system).