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Mathematical and numerical modeling for a bio-chemical aquarium

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Abstract

Based on bio-chemical ground we derive an aquarium mathematical model useful for predicting dangerous situations as well as for the startup cycle. This model is a basic step toward a more complex advection–diffusion–reaction model in 3D space variables: it defines the reaction part of the more complex partial differential equations model. For the numerical solution of our aquarium model we apply a low complexity second order method combined with a simple adaptive step-size selection procedure. The low accuracy and complexity of the resulting numerical algorithm are motivated because of the high complexity of the final 3D model. The reported numerical results, and comparisons with the know-how available in literature, show the validity of the proposed model.

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Keywords: Bio-chemical aquarium model; Initial value problems for ODEs; Adaptive numerical methods

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1. Introduction

The main contribution of this paper is the formulation of a mathematical model that can be used to simulate the bio-chemical evolution of a prototype aquarium. This model can be considered as the reaction part of a more complex advection–diffusion–reaction model in 3D space variables. To validate the proposed model we report on results obtained for five numerical tests performed by using a low complexity second order numerical method coupled with a simple step-size selection procedure. Both the low complexity method and the simple adaptive mesh selection procedure were considered in view of the huge computational task represented by the 3D final model. We are interested to the evolution of the system for a long period, let us say 10 days or 8 weeks. Those are the typical intervals between two water changes, and the time required for the start-up of an efficient aquarium. Fishes may be introduced during the start-up period, but at higher risk and in any case they should be feed minimally and the water properties monitored constantly.

The bio-chemical cycle in any aquarium takes the following steps: (1) the fishes produce waste products that, with the residual food, are transformed into ammonium hydroxide (NH_3), lethal for the fishes at determined concentrations, and its derived ammonia (NH_4) which by contrast is not so dangerous; (2) provided the availability of oxygen *Nitrosomonas*, *Nitrosospira*, and other autotrophic bacteria (see [11]), take NH_3 and NH_4 and produce nitrogen dioxide (or nitrous acid NO_2) also known as nitrite salts which is lethal for the fishes at low concentrations, and has to be transformed as soon as possible; (3) that is the duty of *Nitrobacter*, *Nitrospira*, and other suitable bacteria, (see [11]), that from NO_2 and oxygen derive nitrate (NO_3); (4) nitrate are used by algae and plants for their living, in particular plants at fast grow like *Ceratophyllum demersum*, *Egeria densa*, *Ludwigia palustris* or others, for their living; (5) finally, algae and plants are heated by some species of fishes: *Xyphophorus variatus*, *Xyphophorus helleri*, etc.

Nitrification is a microbial process by which reduced nitrogen compounds (primarily ammonia) are sequentially oxidized to nitrite and nitrate. The nitrification process is primarily accomplished by two groups of autotrophic nitrifying bacteria that can build organic molecules using energy obtained from inorganic sources, in this case ammonia or nitrite. Recent studies on nitrifying biofilms suggest that *Nitrosomonas* and *Nitrobacter* are the most active species at high ammonia and oxygen concentrations while at low ammonia concentration the *Nitrosospira* and *Nitrospira* are the prevalent species, [8]. A corresponding concentration decrease in dissolved oxygen can be noted within this process, [9, pp. 205–211]. Uptake of nitrogen in the form of nitrate, nitrite or ammonia is normal in the nitrogen cycle within a closed environment like an aquarium. Because of the slow growth rate of nitrifying bacteria, it may take 4–8 or more weeks for them to colonize the biological filter and for water quality

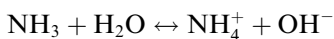
to stabilize. Bacterial colonization occurs naturally; although suspensions of concentrated bacteria are available commercially and may be added to the water to stimulate and faster colonization. Alleman [1] reports at least six condition under which an elevated nitrite concentration can be observed in a nitrification system, including reduced temperature, limited amount of O_2 , elevated pH, high free ammonia concentration, decomposing matter, and acute process loadings.

We note that, when the availability of dissolved oxygen becomes insufficient, the anaerobic bacteria (*Pseudomonas* family) begin to use nitrate as an oxidizing agent [5]. This is an extreme behavior and will not be considered in this study. Moreover, for the sake of simplicity, in our model we assume that the action of the plants with respect to the nitrogen cycle is minimal. This hypothesis is verified if we have a small population of plants or else if our plants are at lengthy grow. In those cases we are allowed not to take into account the carbon cycle. This is in part also justified by the consideration that the effect of that cycle is to stabilize the pH value within the aquarium. Indeed, the main source of carbon to the aquarium is by far given by the unheated food given to the fishes [6] and this can be taken under control for a small aquarium. On the other hand, the carbon cycle is fundamental in the case of a study concerning the plants life.

Based on the bio-chemical conditions discussed so far, in the next section we define a simple, space independent, aquarium model. This model is a basic step toward a more complex advection–diffusion–reaction 3D one: it defines the reaction part of the more complex partial differential equations model described in the last section. In Section 4, we report some test cases used to validate the proposed space independent model. The presented numerical solutions were obtained by the second order Heun method coupled with a step selection procedure (see [7]), which are briefly described in Section 3.

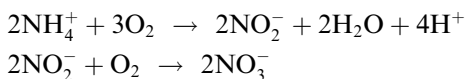
2. The mathematical model

There is a simple chemical reaction between ammonium hydroxide (NH_3) and ammonia (NH_4) in water:



where the \pm superscripts stand for a positive or negative ion, respectively. The \leftrightarrow symbol means that, at any time, there is an equilibrium between the two components. Moreover, the percentage of the dangerous ammonium hydroxide is minimal and grows with temperature and alkalinity of the water (see [4]). So that, we can apply the point of view of taking into account only the amount of the total ammonia.

It is now important to consider the nitrogen cycle, that is involved within any aquarium, described by the following chemical reactions:



where we recall that NO_2 and NO_3 are nitrite and nitrate, respectively. So that a simple mathematical model that takes into account the above cycle can be formulated as follows:

$$\begin{aligned} \frac{dc_1}{dt} &= p_1(1 - q_1c_1) - \mu_1c_1^2c_2^3, \\ \frac{dc_2}{dt} &= p_2(1 - q_2c_2) - \mu_1c_1^2c_2^3 - \mu_2\sqrt{c_2}c_3, \\ \frac{dc_3}{dt} &= \mu_1c_1^2c_2^3 - \mu_2\sqrt{c_2}c_3 - p_3c_3, \\ \frac{dc_4}{dt} &= \mu_2\sqrt{c_2}c_3 - p_4c_4, \end{aligned} \tag{2.1}$$

where t is the time and c_j for $j = 1, 2, 3, 4$ are NH_4 , O_2 , NO_2 , and NO_3 concentrations, respectively. Ammonia and oxygen, nitrite and nitrate are measured in milligram per liter, the time scale is in seconds. The solubility of oxygen in water is a decreasing function of temperature: from tabulated experimental values we have 9.2 mg/l at 20 °C, 8.3 mg/l at 25 °C and 7.7 mg/l at 30 °C. Safe values of c_1 (ammonia) should be below of 0.05 mg/l; a maximum value that can be tolerated only for a small period is 0.25 mg/l. Safe values of c_3 (NO_2 , nitrite) are below 0.05 mg/l. At concentrations of 50–60 mg/l of nitrate some fishes become to suffer, and 100 mg/l is dangerous indeed, then, c_4 should belong within the range 5–10 mg/l.

For the parameters involved within the model we have to take into account several factors. One important factor is the amount of water, measured in liters, of the aquarium: a large aquarium is simpler to be controlled than a smaller one. Other useful indicators to consider are the number of fishes and the amount of food that is not heated by the fishes. It is common to quantify the fishes population by their total length, but by a simple dimensional analysis [3, pp. 22–27] we can prove that their weights represent better indicators. Next, we must consider the efficiency of the filter available for the treatments of the water and the evolution of the bacteria population. At the start up of the system we have to expect a grow of the ammonia concentration, followed by the growing of the bacteria; we note that the *Nitrosomas* bacteria are able to colonize an aquarium faster than the *Nitrobacter*. All these considerations were used in order to define the model parameters. So that, $p_1(t)$, p_k for $k = 2, 3, 4$, q_1 , q_2 , $\mu_1(t)$, and $\mu_2(t)$, take into account, respectively:

$p_1(t)$ the ammonia NH_4 production,

$$p_1(t) = \gamma [\arctan(\tau(t)) - \arctan(\tau(0))],$$

where γ is a given constant, and

$$\tau(t) = \frac{x_{\max} - x_{\min}}{\vartheta} t + x_{\min},$$

x_{\min} , x_{\max} are constants, and ϑ is a reference time. This function is related to the fish population and their by-products such as food not heated, etc.

p_2 the oxygen O_2 production within the aquarium;

p_3 the nitrite consumption due to chemical additives;

p_4 the nitrate consumption by algae and plants;

q_1 a limiting coefficient for the ammonia grow, assumed here to be equal to $1/\max c_1$ where $\max c_1$ is a top dangerous concentration;

q_2 a limiting coefficient for the oxygen grow, equal to $1/\max c_2$ where $\max c_2 = 8.5$;

$\mu_1(t)$ the *Nitrosomonas*, *Nitrospira*, etc., efficiency,

$$\mu_1(t) = \gamma_1 [\arctan(\tau_1(t)) - \arctan(\tau_1(t_{\min}))],$$

where γ_1 is constant,

$$\tau_1(t) = \frac{y_{\max} - y_{\min}}{\vartheta} t + y_{\min}$$

y_{\min} , and y_{\max} are constants;

$\mu_2(t)$ the *Nitrobacter*, *Nitrospira*, etc. efficiency,

$$\mu_2(t) = \gamma_2 [\arctan(\tau_2(t)) - \arctan(\tau_2(t_{\min}))],$$

where γ_2 is constant,

$$\tau_2(t) = \frac{z_{\max} - z_{\min}}{\vartheta} t + z_{\min},$$

z_{\min} , and z_{\max} are reference values.

The functions $p_1(t)$, $\mu_1(t)$, and $\mu_2(t)$, for $x_{\min} = 0$, $x_{\max} = 24\pi$, $y_{\min} = -6\pi$, $y_{\max} = 5\pi$, $z_{\min} = -6\pi$, $z_{\max} = 2\pi$, $\gamma = 5 \times 10^{-6}$, $\gamma_1 = 2 \times 10^{-8}$, $\gamma_2 = 3 \times 10^{-6}$ and ϑ given by a reference time of 6 weeks (in seconds), are shown in the left frame of Fig. 1. We note that, in this figure, the μ_1 parameter is magnified by a factor of 100.

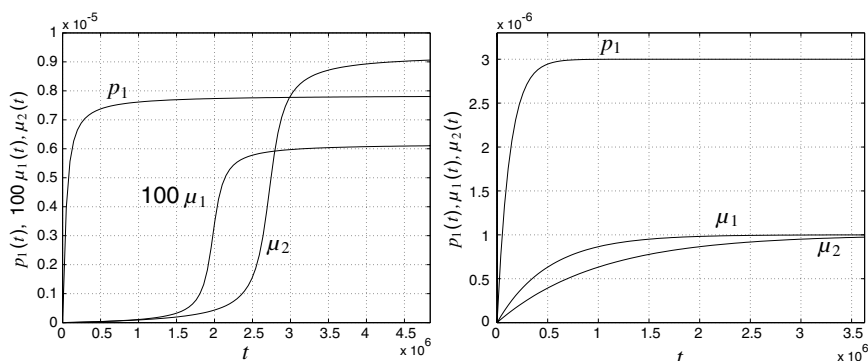


Fig. 1. Aquarium model: two different models for $p_1(t)$, $\mu_1(t)$, and $\mu_2(t)$.

A different model for those functions is reported on the right frame of the same figure: in this case the functional form $f(x) = \alpha(1 - \exp(-\beta t))$, was considered, with α and β constants. Some preliminary numerical experiments pointed out that the first model for the considered parameters provides better results than this last one. Henceforth, for the sake of brevity, only results obtained by the first parameters model will be reported in the following.

3. Numerical method and adaptive strategy

Let us rewrite the governing system in vectorial form

$$\frac{d\mathbf{c}}{dt} = \mathbf{R}(\mathbf{c}),$$

where $\mathbf{c} = (c_1, c_2, c_3, c_4)^T$ and $\mathbf{R} = (R_1, R_2, R_3, R_4)^T$, with

$$\begin{aligned} R_1 &= p_1(1 - q_1 c_1) - \mu_1 c_1^2 c_2^3, \\ R_2 &= p_2(1 - q_2 c_2) - \mu_1 c_1^2 c_2^3 - \mu_2 \sqrt{c_2} c_3, \\ R_3 &= \mu_1 c_1^2 c_2^3 - \mu_2 \sqrt{c_2} c_3 - p_3 c_3, \\ R_4 &= \mu_2 \sqrt{c_2} c_3 - p_4 c_4. \end{aligned}$$

For the numerical results reported in the next section we apply the explicit second order Heun method:

$$\mathbf{c}^{n+1} = \mathbf{c}^n + \frac{\Delta t}{2} [\mathbf{R}(\mathbf{c}^n) + \mathbf{R}(\mathbf{c}^n + \Delta t \mathbf{R}(\mathbf{c}^n))]. \quad (3.1)$$

The choice of a second order method is motivated by the awareness that the final 3D model can be solved by a combination of second order numerical methods. Moreover, due to the huge computational complexity of this 3D

model we are particularly interested to an adaptive method with very low complexity.

We give here a brief description of the adaptive procedure used with the above Heun method, for more details see [7]. Given a step size Δt^n and an initial value \mathbf{c}^n at time t^n , the method computes an approximation \mathbf{c}^{n+1} at time $t^{n+1} = t^n + \Delta t^n$. We define the following monitor function:

$$\eta^n = \frac{\|\mathbf{c}^{n+1} - \mathbf{c}^n\|_\infty}{\|\mathbf{c}^n\|_\infty + \epsilon_M},$$

where $\epsilon_M > 0$ is of the order of the machine precision, so that we can require that the step size is modified as needed in order to keep η^n between user defined tolerance bounds.

In all the reported numerical tests we used the following conditions:

- step-size limitations: $10^{-4} \leq \Delta t^n \leq 10^4$;
- monitor function bounds: $10^{-4} \leq \eta^n \leq 10^{-3}$;
- step-size increment: $\Delta t^{n+1} = 2 \cdot \Delta t^n$ as soon as $\eta^n < 10^{-4}$;
- step-size reduction: we chose to repeat the same step when $\eta^n > 10^{-3}$ with a reduced step size given by $\Delta t^n = \Delta t^n/2$.

4. Numerical tests

In this section, we report on five tests that were used to validate the proposed aquarium model. In all tests, we considered a time period of 8 weeks, because this is the period usually used for monitoring the start up of any aquarium. Moreover, typical values of the introduced parameters, might be as follows:

$$\begin{aligned} \gamma &= 5 \times 10^{-6}, \quad p_2 = 10^{-4}, \quad p_3 = 0, \quad p_4 = 2 \times 10^{-7}, \\ q_1 &= 1/\max c_1, \quad q_2 = 1/\max c_2, \\ \gamma_1 &= 2 \times 10^{-8}, \quad \gamma_2 = 3 \times 10^{-6}, \\ \max c_1 &= 5 \text{ mg/l}, \quad \max c_2 = 8.5 \text{ mg/l}. \end{aligned} \tag{4.1}$$

As a first test we try to reproduce the eight weeks start-up of a new aquarium. This is the most critical period in any aquaculture experience. Fig. 2 reports on results obtained by direct measurements for a typical nitrification system.

It is easily seen that, initially, the dissolved oxygen in the aquarium is at its maximum concentration; ammonia, nitrite and nitrate are absent. So that, we have to consider the following initial conditions:

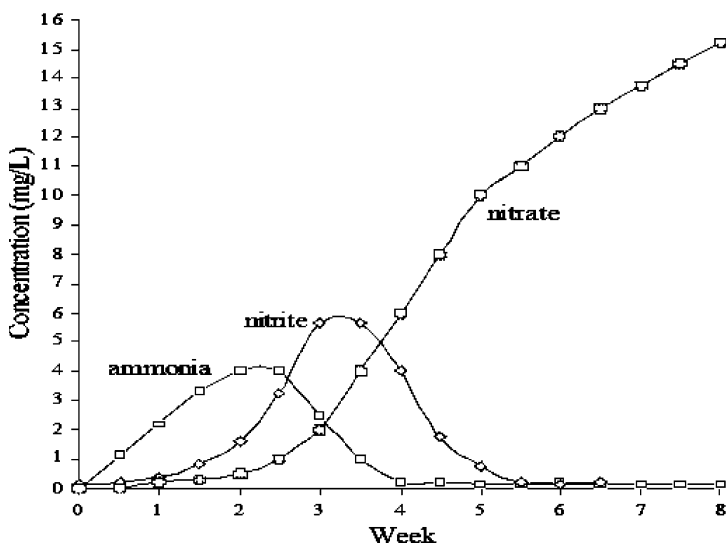


Fig. 2. Aquarium model: normal start-up measures.

$$c_1(0) = 0, \quad c_2(0) = 8.5, \quad c_3(0) = 0, \quad c_4(0) = 0. \quad (4.2)$$

The numerical results obtained for this test case are plotted in Fig. 3. The proposed model provides a prediction on the necessity to use more than 5 weeks to allow the aquarium to arrive at a safe steady state bio-chemical condition. In Fig. 4 we show the step-size selection, as well as the monitor function. We can notice that, we get a discontinuity on monitor function η for any change in the step-size value. Moreover, a fast variation of the step-size value can be noticed at the beginning of the computation. This is normal for any adaptive strategy when a first time step is not chosen carefully. We can remark that the step-size selection criterion used here is able to modify the used step-size quickly enough so that this particular aspect of the adaptive process can be forgotten by the user.

Naturally, we are particularly interested to the extreme situations corresponding, for instance, to a cycle without fishes and plants ($p_1 = 0$), or to insufficient availability of oxygen ($p_2 \approx 0$), etc. To this end we performed two other tests. We consider, first, the situation of an aquarium without a sufficient water circulation and without plants. In this case, the oxygen concentration in the water will become, soon or later, insufficient to allow the chemical reactions. To see how our model can simulate this case we assume directly that $p_2 = 10^{-6}$ and we start with the same initial conditions (4.2) of the first test. The obtained numerical results are reported in Fig. 5. It is now evident that in such a state of affairs the aquarium will not arrive at a safe steady state regime for the fish population.

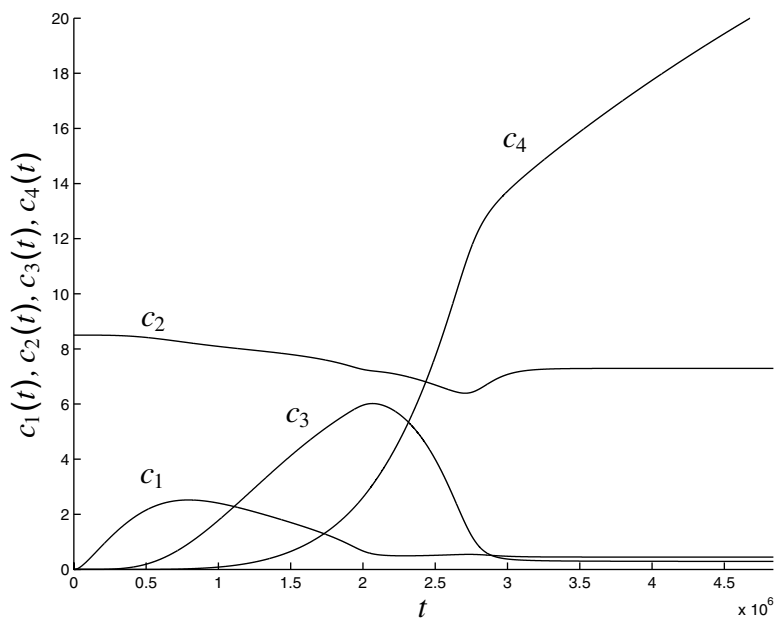


Fig. 3. Test 1: normal start-up numerical solution.

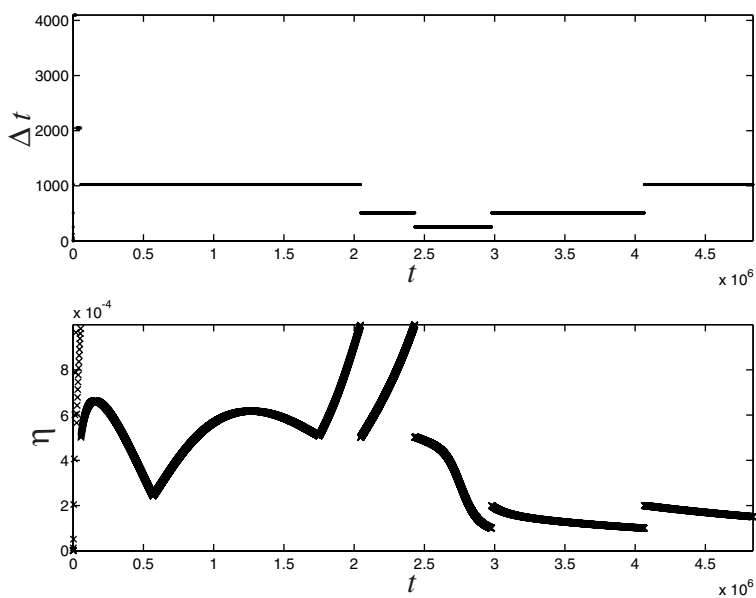


Fig. 4. Test 1: step-size selection (top), and monitoring function (bottom).

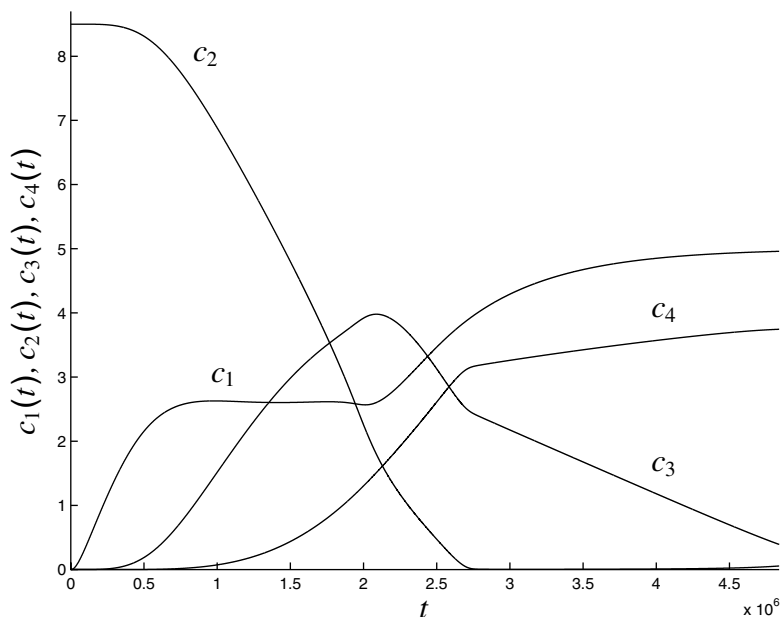


Fig. 5. Test 2: $p_2 = 10^{-6}$, the production of oxygen is inadequate to support the chemical reactions.

As a thirdly test, we assume that the aquarium already arrived, for some accident, at dangerous conditions for the fishes. To simulate this case, we choose the initial conditions:

$$c_1(0) = 0, \quad c_2(0) = 0.5, \quad c_3(0) = 5, \quad c_4(0) = 2, \quad (4.3)$$

that is, ammonia is absent but nitrite are at dangerous peak, oxygen is at a low level and nitrate is within the norm. In this situation, a wise decision is to save the fishes by taking them off of the aquarium and finding for them a suitable recover (bearing them to friend's aquaria or to some aquarium shop). So that, we assume that the fishes are out of the aquarium. The obtained numerical results are reported in Fig. 6. It is evident from the reported results that in this case the aquarium needs more than two months in order to return to a safe state, hence it is certainly a good advise to proceed by a massive water change. From Figs. 5 and 6, we can notice how the positivity of the oxygen concentration is verified.

We report now two final tests that have been performed to make a comparison with batch experiments made by Anthonisen et al. [2]. These authors consider a system where the production and consumption of nitrogen components are absent, this implies that at any time we must have conservation of the total amount of nitrogen (ammonia plus nitrite plus nitrate). Within the proposed

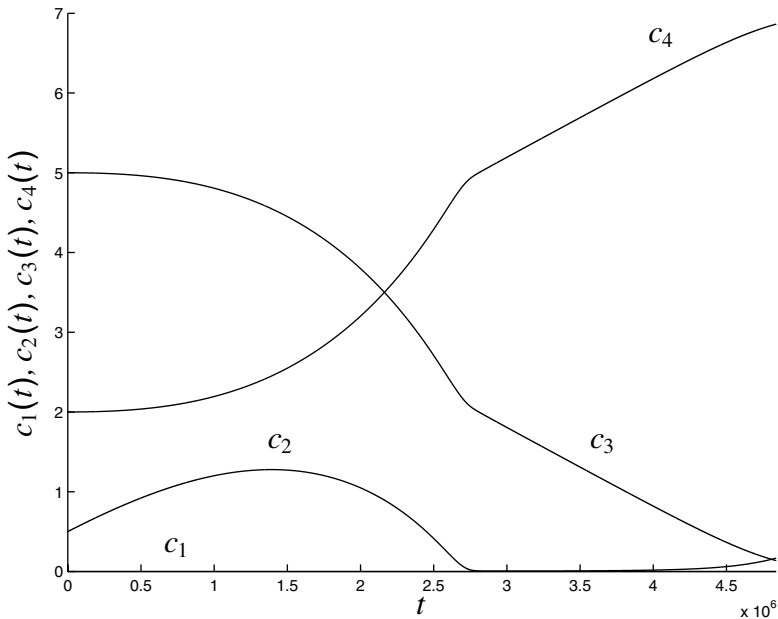


Fig. 6. Test 3: $p_1 = 0$, there is not production of ammonia to support the chemical reactions; but now the initial conditions are given by (4.3).

aquarium model such a state of affairs can be imposed by setting $p_3 = p_4 = 0$ and $p_1(t) = 0$ for all times. Our fourth test case is a noninhibited nitrification process with initial conditions modified as follows:

$$c_1(0) = 5, \quad c_2(0) = 8.5, \quad c_3(0) = 0, \quad c_4(0) = 0, \quad (4.4)$$

that is, ammonia and oxygen are at their maximum peaks and nitrite and nitrate are initially absent. The numerical results for this test case are reported in Fig. 7.

The final test case is concerned with a inhibited nitrite oxidation and can be simulated by setting $\gamma_2 = 5 \times 10^{-9}$. Fig. 8 shows the corresponding numerical results. As expected, the inhibited nitrification process results in an upsurge of the dangerous nitrite concentration. We have already reported in Section 1 that such a possibility is related with several circumstances, such as reduced temperature, limited amount of O_2 , elevated pH, high free ammonia concentration, decomposing matter, and acute process loadings (see [1]).

We remark that, as it can be easily noted by looking at the two last figures, the total amount of nitrogen components is, indeed, constant. Moreover, as far as the ammonia, nitrite and nitrate species are concerned, we can verify that the positivity requirement for the concentrations is fulfilled.

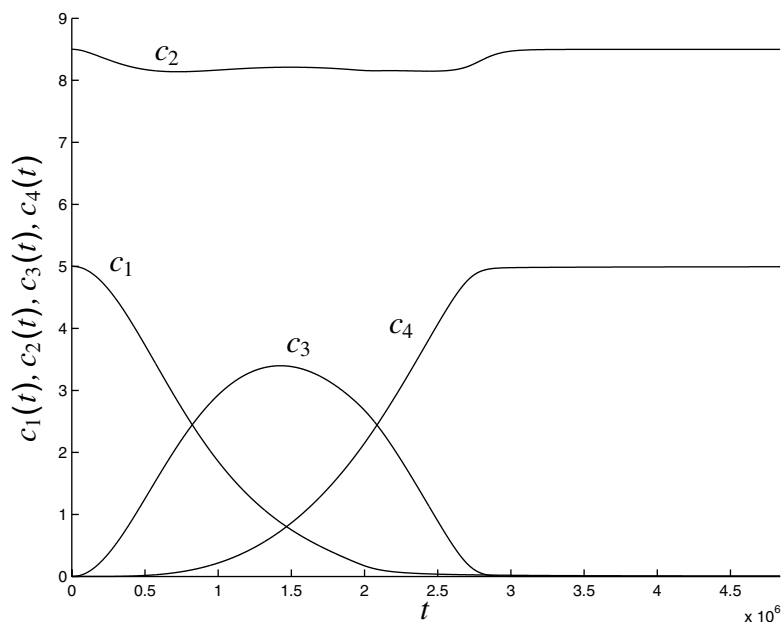


Fig. 7. Test 4: noninhibited nitrification process.

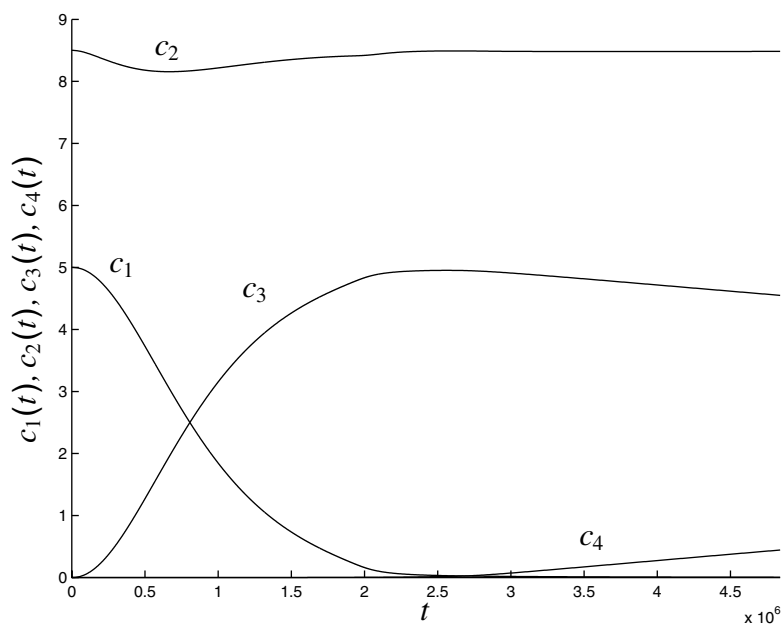


Fig. 8. Test 5: inhibited nitrite oxidation. The initial conditions are given by (4.4).

5. Conclusions and remarks

In Section 1 we described, from a bio-chemical point of view, the nitrogen cycle. Nitrogen dioxide and nitrate in aquaria are produced by bacteriological nitrification of excreted ammonium nitrogen. The aquarium model, introduced on the basis of this nitrogen cycle, is indeed a simplified version of a more complex model. In fact, we have omitted to consider the dependence of the dependent variables on the aquarium physical dimensions: that is, we have assumed the simplifying hypothesis that at each point of the aquarium we have the same bio-chemical conditions. This may be a reasonable hypothesis for a steady state situations and in order to carry on the proposed preliminary study. However, some cases of real interest cannot be investigated within the range of validity of the above hypothesis. Consider, for instance, the case of a concentrated release of pollutant material within the aquarium: a dead fish, some overdone amount of food, or a decomposing plant. Moreover, as soon as we take into account the action of a pump, a partial water change, or the use of additives we have to take into account the action of a velocity field acting on the water particles.

All the above reasoning leads us to consider a three-dimensional advection–diffusion–reaction model governed by the following system of equations:

$$\frac{\partial \mathbf{c}}{\partial t} + \nabla \cdot (\mathbf{v}\mathbf{c}) - \nabla \cdot (D\nabla \mathbf{c}) = \mathbf{R}(\mathbf{c}), \quad (5.1)$$

where $\mathbf{c} = \mathbf{c}(\mathbf{x}, t)$ with $\mathbf{c} \in \mathbb{R}_4$ and $\mathbf{x} \in \Omega \subset \mathbb{R}_3$ t and \mathbf{x} denote time and space variables, respectively; the water velocity field \mathbf{v} and the diffusion coefficients matrix D are, usually, supposed to be given. Here, the water velocity depends on the pump action and diffusion matrix takes into account the property of the chemical species to be diluted in water.

A simple numerical approach for the solution of (5.1) is the so-called operator splitting, due to Strang [10], uncoupling the time evolution of the advection–diffusion part of the system with respect to the reaction part. An elementary justification for the popularity of the Strang approach is that the left-hand side of (5.1) has a scalar nature, that is each component of the field variables \mathbf{c} is governed by a scalar partial differential equation, in contrast with its right-hand side where all the components are coupled. Moreover, the time evolution of each component of the left-hand side is determined by a partial differential equation whereas the time evolution of the right-hand side has a local (in space) dependence.

In this paper, we have used five test cases to verify that the proposed aquarium model can be used to predict the typical operation regimes. The obtained results have been favorable compared with the available literature experimental data.

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