BioSystems 115 (2014) 1–4

Contents lists available at ScienceDirect

BioSystems

journal homepage: www.elsevier.com/locate/biosystems

Kinetic Monte Carlo simulation of the initial phases of chlorophyll fluorescence from photosystem II

Ya Guo, Jinglu Tan *

Department of Biological Engineering, University of Missouri, Columbia, MO 65211, USA

ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form 16 October 2013
Accepted 21 October 2013

Keywords:
Chlorophyll fluorescence
Kinetic Monte Carlo
Reaction kinetics
Photosynthesis

ABSTRACT

Kinetic Monte Carlo (KMC) simulation is employed to represent the photochemical reactions involved in the initial phases of chlorophyll fluorescence (ChlF) emission from photosystem II (PSII). Comparison with a differential equation representation reveals similarities and differences. Both KMC and differential equation models can describe the kinetic variations and show the main characteristics of ChlF emission. Differential equation models are simpler to implement but have limitations that warrant future improvements.

1. Introduction

In the plant photosynthetic process, absorbed light energy by chlorophyll molecules may be transferred forward and used for photochemical reactions, or dissipated as heat or fluorescence (Butler, 1978; Goltsev et al., 2003; Krause and Weis, 1991; Lavergene and Trissl, 1995; Stribet et al., 1998; Vredenberg, 2004; Taiz and Zeiger, 2006). Because chlorophyll fluorescence (ChlF) competes for energy with photochemical reactions (Lubitz et al., 2008), the dynamics of ChlF is affected by photosynthetic activities (Kautsky and Hirsch, 1931; Stribet and Strasser, 1996; Rohacek and Bartak, 1999; Rohacek, 2002). This makes ChlF a useful indicator of plant physiology and environmental changes (DeEll and Toivonen, 2003; Guo and Tan, 2010; Rodriguez and Greenbaum, 2009; Zivcak et al., 2008).

Kinetic models are used to describe ChlF dynamics and to extract quantitative information from measured ChlF (Lazár, 2009; Lazár and Jablonský, 2009; Vredenberg, 2000, 2008, 2011; Vredenberg and Prasil, 2009). Differential equations have been commonly employed to represent the reaction kinetics (Chernev et al., 2006; Baake and Schloder, 1992; Goltsev and Yordanov, 1997; Guo and Tan, 2009, 2011; Lazár and Schansker, 2009; Zhu et al., 2005). While differential equations are compact and convenient to use, they have limitations in representing certain aspects of the process. These limitations may or may not be significant for a given application but need to be analyzed and understood.

Each reaction center (RC) functions as an individual unit and each has one plastoquinone A (Q_A) site and one plastoquinone B (Q_B) site (Guo and Tan, 2009; Guo et al., 2010). An electron entering an RC is carried first by Q_A, then Q_B and later steps (Goltsev and Yordanov, 1997; Blankenship, 2002). The individuality of the RCs and the order of events within an RC can be represented by first-order differential equations with possible combinations of Q_A and Q_B states as state variables as was done in Guo et al. (2010). ChlF emission, however, involves numerous antennas and a pool of plastoquinones corresponding to each RC. There are then thousands of combinations of redox or excitation states, which makes it practically impossible to use first-order kinetics to represent the reactions. Tokarčík (2012) attempted to model ChlF from PSII by using pi-calculus though potential limitations of differential equations were not specifically discussed. Using concentrations of individual chemical species as state variables result in a compact set of second-order differential equations as done in Guo and Tan (2011). The second-order differential equations, however, implicitly assume a well-mixed system. The effects of this assumption have not been demonstrated. Xin et al. (2013) simulated PSII ChlF by the Monte Carlo method with explicit description of PSII activities; however, a comparison of the results from Monte Carlo simulation and differential equations was not provided.

In this work, kinetic Monte Carlo (KMC) simulation (Gillespie, 1976, 1977) is used to represent the discrete events involved in the initial phases of PSII ChlF emission. Since KMC simulation can represent a large number of individual RCs and other members of the electron transport chain without resorting to assumptions, this gives an opportunity to compare KMC and differential equation models.

---

* Corresponding author.
E-mail address: tanj@missouri.edu (J. Tan).

0303-2647/$ – see front matter © 2013 Elsevier Ireland Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biosystems.2013.10.004

2. KMC simulation of ChlF

Light may excite a PSII antenna complex (A). An excited antenna complex (A^*) may dissipate the absorbed energy as heat or ChlF, or it may transfer the absorbed energy forward for photochemical reactions. When A^* transfers the absorbed energy to P680 (PSII chlorophylls), P680 becomes excited (P680*) and may pass the excited electron through a pheophytin molecule to plastoquinone Q_A, thus reducing Q_A (Goltsev and Yordanov, 1997; Blankenship, 2002). The electron carried by the reduced Q_A ($Q_A{}^-$) may be transferred back to the antenna complex (Goltsev and Yordanov, 1997, Guo and Tan, 2009), or may be transferred to another plastoquinone (Q_B), which is capable of receiving two electrons. Q_A is tightly bound in the thylakoid membrane, but Q_B is loosely bound. After receiving two electrons, $Q_B{}^{2-}$ will combine with two protons to become plastoquinol (QH_2) and QH_2 will diffuse from the Q_B site to the thylakoid lumen. A plastoquinone (PQ) molecule from a PQ pool will then move to the vacated Q_B site and become a new Q_B. QH_2 will be oxidized later and becomes a PQ. The resulting PQ will return to the PQ pool (Goltsev and Yordanov, 1997). These processes have been modeled at different levels of complexity in the literature and a comparison can be found in Lazár and Jablonský (2009). Some of the models reported have 50 or more state variables. While these models reach a high degree of completeness in representing the activities involved, they cannot be practically used for simulation and analysis because the complexity does not allow easy determination of model parameters from experimental data. To make model parameter estimation possible, Guo and Tan (2011) developed a minimized model for the initial phase of PSII ChlF based on the following 10 chemical reactions.

$$A \underset{k_2}{\overset{k_1 u}{\rightleftarrows}} A^* \tag{1}$$

$$A^* + Q_A \underset{k_4}{\overset{k_3}{\rightleftarrows}} A + Q_A{}^- \tag{2}$$

$$Q_A{}^- + Q_B \underset{k_6}{\overset{k_5}{\rightleftarrows}} Q_A + Q_B{}^- \tag{3}$$

$$Q_A{}^- + Q_B{}^- \underset{k_8}{\overset{k_7}{\rightleftarrows}} Q_A + Q_B{}^{2-} \tag{4}$$

$$Q_B{}^{2-} + PQ \xrightarrow{k_9} Q_B + QH_2 \tag{5}$$

$$QH_2 \xrightarrow{k_{10}} PQ \tag{6}$$

where u is the excitation light intensity, k_1 is the light-capture efficiency of antennas, k_2 is the dissipation rate through heat and fluorescence, k_3 is the rate at which Q_A is reduced in the presence of A^*, k_4 is the overall rate of charge recombination, k_5 through k_8 are the forward or backward rates of electron transfer between Q_A and Q_B sites, k_9 is the overall rate at which $Q_B{}^{2-}$ is protonated and then replaced by a new Q_B from the PQ pool, k_{10} is the net rate of QH_2 oxidation.

By assuming continuous mixing and continuously varying concentrations or probabilities of occurrence of A^*, $Q_A{}^-$, $Q_B{}^-$, $Q_B{}^{2-}$, and PQ, the reactions in Eqs. (1)–(6) were modeled with five continuous-time differential equations with the initial phases of ChlF being proportional to k_2A^* in previous work (Guo and Tan, 2011). These assumptions have also been made in other differential equation models for ChlF in the literature (Goltsev and Yordanov, 1997; Zhu et al., 2005).

The chemical reactions in Eqs. (1)–(6) can be simulated by using the KMC method. Since it can represent the reactions as discrete stochastic events as they occur in individual reaction centers, KMC simulation should be a much closer presentation of reality than the differential equations. The general procedure for KMC modeling can be found in Gillespie (1976, 1977). KMC simulation of the 10 reactions is summarized below.

Table 1
Reaction velocities.

Reaction rates	Reaction velocities at the *p*th step
$k_1 u$	$r_{p1} = k_1 u(A_0 - A^*) = k_1 u(A_0 - x_{p1})$
k_2	$r_{p2} = k_2 A^* = k_2 x_{p1}$
k_3	$r_{p3} = k_3 A^* Q_A = k_3 x_{p1}(1 - x_{p2})$
k_4	$r_{p4} = k_4\ A Q_A{}^- = k_4(A_0 - x_{p1})\,x_{p2}$
k_5	$r_{p5} = k_5 Q_A{}^- Q_B = k_5 x_{p2}(1 - x_{p3} - x_{p4})$
k_6	$r_{p6} = k_6\ Q_A Q_B{}^- = k_6(1 - x_{p2})x_{p3}$
k_7	$r_{p7} = k_7\ Q_A{}^- Q_B{}^- = k_7 x_{p2} x_{p3}$
k_8	$r_{p8} = k_8\ Q_A Q_B{}^{2-} = k_8(1 - x_{p2})x_{p4}$
k_9	$r_{p9} = k_9\ Q_B{}^{2-} PQ = k_9\ x_{p4}\ x_{p5}$
k_{10}	$r_{p10} = k_{10} QH_2 = k_{10}(PQ_0 - x_{p5})$

where A_0 and PQ_0 are the number of antenna complexes and PQ pool size per reaction center, respectively.

Table 2
Events to carry out.

j	Events to carry out
1	A^* increased by 1
2	A^* decreased by 1
3	A^* decreased by 1, $Q_A{}^-$ set to 1
4	A^* increased by 1, $Q_A{}^-$ set to 0
5	$Q_A{}^-$ set to 0, $Q_B{}^-$ set to 1
6	$Q_A{}^-$ set to 1, $Q_B{}^-$ set to 0
7	$Q_A{}^-$ set to 0, $Q_B{}^-$ set to 0, $Q_B{}^{2-}$ set to 1
8	$Q_A{}^-$ set to 1, $Q_B{}^-$ set to 1, $Q_B{}^{2-}$ set to 0
9	$Q_B{}^{2-}$ set to 0, PQ decreased by 1
10	PQ increased by 1

The reactions involve five independent chemical species (A^*, $Q_A{}^-$, $Q_B{}^-$, $Q_B{}^{2-}$, and PQ) and 10 reactions (represented by k_1u through k_{10}). The amount of the ith species at iteration p is denoted as x_{pi} ($i = 1, 2, \ldots, 5$), and the reaction velocity for the jth ($j = 1, 2, \ldots, 10$) reaction at iteration p is denoted as r_{pj}, where p is an integer to denote Monte Carlo iterations. The simulation steps are:

Step 1: Set time $t = 0$ and iteration index $p = 0$.
Step 2: Initialize the species (x_{0i}, $i = 1, 2, \ldots, 5$).
Step 3: Compute the 10 reaction velocities at iteration p (r_{pj}) according to the current values of x_{pi} ($i = 1, 2, \ldots, 5$) as summarized in Table 1.
Step 4: Calculate the cumulative reaction velocities $R_{pj} = \sum_{q=1}^{j} r_{pq}$, $j = 1, 2, \ldots, 10$.
Step 5: Sample a uniformly distributed random number $\mu \in (0, 1]$.
Step 6: Determine the event (j) to carry out for which $R_{p(j-1)} < \mu R_{p10} \le R_{pj}$ ($R_{p0} = 0$). Note that the condition and the definition of R_{pj} in *Step* 4 mean that events associated with greater reaction velocities are more likely to occur and events for later reactions (larger j values) would not occur right after excitation light u is applied to an initially dark-adapted leaf.
Step 7: Carry out event j as summarized in Table 2.
Step 8: Draw another uniformly distributed random number $\mu' \in (0, 1]$.
Step 9: Update time with $t = t + \ln(1/\mu')/R_{p10}$. Note $\mu' = 1$ leads to no time increase.
Step 10: Increment p and go to *Step* 3.

It is worth noting that in the KMC algorithm, many RCs can be simulated and each RC is simulated individually. This means that different RCs may have different model parameters. For example, when k_5 is set to zero for an RC, the Q_B site in the RC is rendered