

OPTICS AND SPECTROSCOPY

MATHEMATICAL MODEL AND ANALYSIS OF THE CAUSES OF DELAYED LUMINESCENCE OSCILLATIONS IN LEAVES OF HIGHER PLANTS

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Using a previously developed model including primary processes and the Calvin cycle, delayed luminescence oscillations have first been obtained, and assumptions as to the mechanism responsible for their development have been made.

The oscillatory behavior of delayed luminescence was experimentally discovered in 1990. The oscillatory photosynthesis kinetics is of great interest to investigators, for it is a vivid manifestation of the regulatory linkages in the system.

Depending on the particular experimental conditions, the observed behavior of the variables describing the process of photosynthesis [1, 2], including the damped fluorescence intensity and Calvin-cycle metabolite concentration oscillations due to variations in the environmental conditions (light intensity, gas composition of the medium, phosphate concentration), can vary. As noted in [1], with the kinetics being nonmonotonic as it is, most pronounced are the regulatory processes that provide for the optimal functioning of the complex system of reactions involved in the process. A mathematical model of the latter allows one to distinguish the reactions most essential for the development of oscillations. In this connection, the quantitative study of the regulatory linkages and the development of models describing the system under damped oscillation conditions become topical. Delayed luminescence provides a means to experimentally study regulatory linkages in photosynthetic systems. Delayed luminescence develops in the reaction center of photosystem 2 (PS2) in the course of the reverse electron transport reactions leading to the development of an excited special pair of the reaction center PS2 ($P680^*$). Insofar as different electron carriers can participate in charge-carrier recombination, delayed luminescence following a light flash consists of many components occurring on the scale of characteristic times from a few hundreds of nanoseconds to a few seconds. The transport of electrons between photosystems is most frequently studied in terms of delayed luminescence occurring on the millisecond time scale, which is apparently associated with charge-carrier recombination in the states $Z+P680PheoQ_{A-}$, $S+ZP680PheoQ_A$ (reduced quinone Q_A) and $Z+P680PheoQ_AQ_{B-}$ (reduced quinone Q_B) [3] because it can easier be recorded than the other components. Besides, Q_B is the slowest link in the electron-transport chain. Therefore, it might be expected that recombination involving Q_{A-} and Q_{B-} will prove very sensitive to the electron-transport chain condition. Delayed luminescence is also more sensitive to variations in the functioning rate of the Calvin cycle than fast luminescence [4]. Delayed luminescence was discovered by Strehler and Arnold [5] in 1951. Sorokin [6] was the first to quantitatively describe the relationship between the concentration of the reduced and oxidized PS2 carriers and the delayed luminescence intensity.

At the present time there exist mathematical photosynthesis models that satisfactorily describe the photosynthesis steady-state conditions and monotonic kinetics. However, to describe the oscillatory photosynthesis behavior, some not quite completely justified assumptions should be made.

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Let us consider some of these models.

In the model developed by Laisk and co-workers [7], an idea based on the phosphorus cycle in photosynthesis was suggested to explain the oscillatory behavior. The homeostasis of phosphates and sugar phosphates is maintained through the regulation of the activity of citosol fructose-biphosphatase and ADP-glucose-pyrophosphorylase in the chloroplast. Thus, oscillations were obtained only on the assumption that the regulators operated with a 10–20 s lag phase. To this end, they artificially introduced into their equations a delay in the form of a lagging variable whose physical meaning was not defined. Another simplified model version suggested by Horton and Nicholson [8] contained a similar delay in the activation of the synthesis of saccharose by triose phosphates and their inactivation under the effect of inorganic phosphates. Oscillations could not be obtained in the model but for this not quite justified assumption. Besides, as noted by the authors, isolated chloroplasts can also exhibit oscillations [9], and this means that the source of oscillations should be sought for in the internal reactions of the chloroplasts. An important feature of the above models is the allowance made for the regulation of the enzymes of the Calvin cycle by its various intermediates. Most of these models pay inadequate attention to the light and dark photosynthesis processes that we consider important for the development of damped oscillations.

Giercsh [10] suggested a different approach to the study of oscillations. He studied simplified models and analytically calculated those values of the parameters, which marked the development of oscillations. In one of his works, he considered the two-equation model known as the “basic oscillator” (a model Calvin cycle allowing for the existence of two kinase reactions competing for ATP). However, the oscillations obtained in this model die out much faster (by two orders of magnitude) than the oscillations observed experimentally [1]. This is probably because the model ignores the interaction of light and dark reactions. In another model [11] consisting of three equations and taking into account the transport of electrons through NADPH, the authors attained a better agreement with the experiment. However, neither fluorescence, nor release of CO_2 (and it is exactly these phenomena that are as a rule observed in experiments) was included in explicit form in the equations, and so this agreement is fairly difficult to judge.

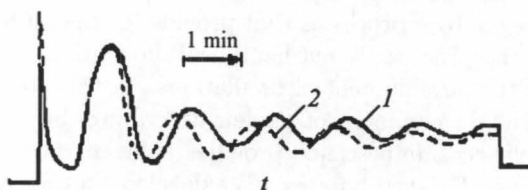


Fig. 1

Variation kinetics of the 10-ms afterglow component in wheat leaves. CO_2 concentration in the leaf atmosphere: (1) 0.03%, (2) 3%.

In 1990, Damdinsuren [12] discovered delayed luminescence oscillations (Fig. 1). Neither of the above models could help to study delayed luminescence, for it was not explicitly expressed in terms of the model variables. It was earlier demonstrated that under certain conditions the time variation of delayed luminescence could differ from that of fast fluorescence [13]. In this connection, it would be of interest to consider a photosynthesis model that would make it possible to obtain not only fluorescence oscillations, but also delayed luminescence oscillations on the millisecond time scale.

Investigators at the Department of Biophysics developed a model allowing for both light processes (absorption of light quanta by pigments, electron transport) and dark processes (CO_2 absorption in the Calvin cycle). The model is a system of 15 equations [14] (Fig. 2) to be solved numerically by means of a Delphi program.

To study delayed luminescence, this program provides for a periodic switching-on of light, i. e., illumination intervals alternate with darkness intervals (around 10 ms in duration). At some model parameter values the system develops oscillations similar to those observed experimentally (Fig. 3).

It has turned out that most important parameters for the occurrence of such oscillatory behavior are the rate of ATP consumption in the phosphorylation reactions P_{11} and P_{13} , the rates of the linear and cyclic electron transport P and P_3 , the rate of CO_2 absorption, the light intensity, and the phosphorylation-

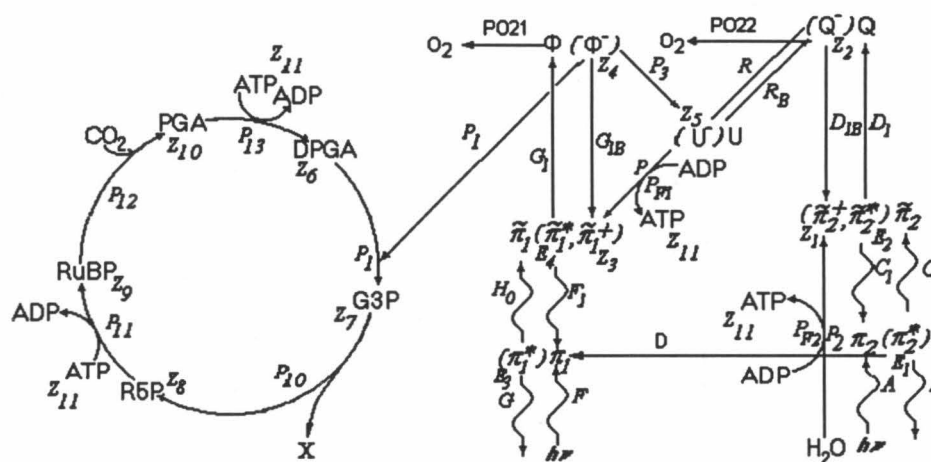


Fig. 2

Scheme of reactions: π_1, π_2 — antenna pigments, $\tilde{\pi}_1, \tilde{\pi}_2$ — PS1 and PS2 reaction centers, $Q, U,$ and Φ — electron carriers, DPGA — 1,3-P2D-glycerate, PGA — phosphoglyceric acid, R5P — ribulose-5-phosphate, RuBP — ribulose bisphosphate, G3P — glyceraldehyde-3-phosphate, ATP — adenosine triphosphate.

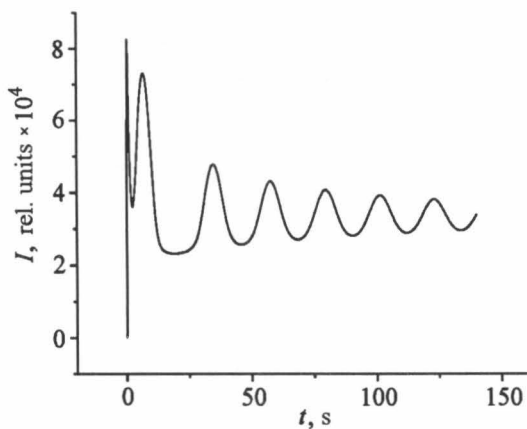


Fig. 3

Model oscillatory behavior of delayed luminescence.

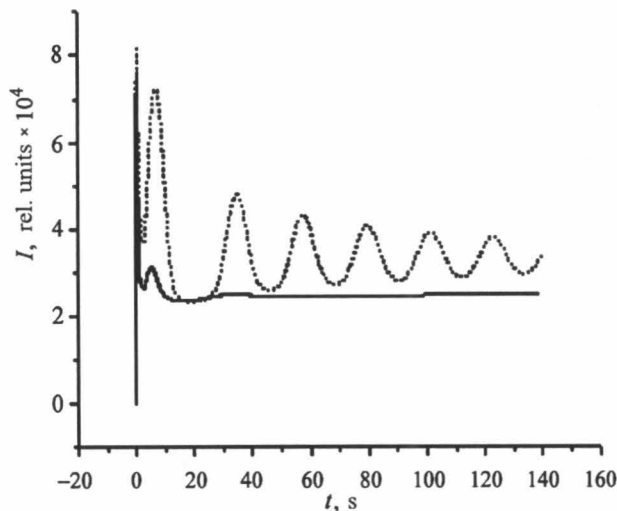


Fig. 4

Photosynthesis kinetics at $P_{F1} = 0.019$ (solid line) and $P_{F1} = 0.009$ (dotted line).

electron-transport coupling constant P_{F1} (see Fig. 2), the behavior being sensitive to variations of even a single parameter. To illustrate, as the parameter P_{F1} grows, the system practically ceases oscillating (Fig. 4). The value of the parameter $P_{CO_2} \cdot P_{12}$ is equal to 0.0005, which corresponds to the absorption of five CO_2 molecules per reaction center molecule for 10 s, i.e., approximately corresponds to normal conditions. The intensity of light is such that a single chlorophyll molecule in PS2 absorbs 1 quantum in 10 s, which also approximately corresponds to normal illumination.

Within the first ten seconds following the switching-on of light, complex transient processes occur, whose character depends on the initial conditions. Analysis of the time dependences of Fig. 5 shows that following the switching-on of light, it is first of all the noncyclic electron transfer that starts working actively, and ATP and NADPH begin accumulating. Because of the nonoptimal proportion between the resultant ATP and NADPH concentrations, the Calvin cycle works slowly, which leads to the

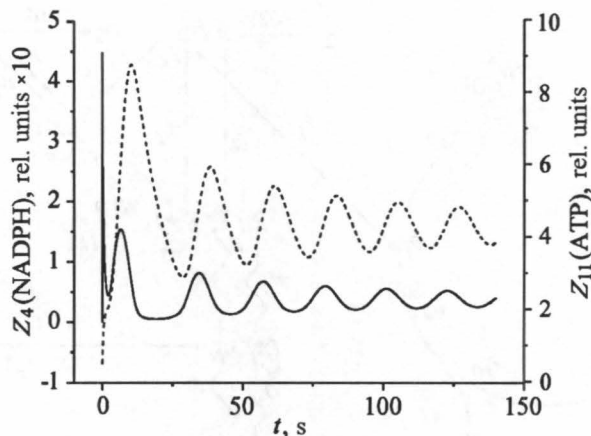


Fig. 5

Temporal variation of the NADPH and ATP concentrations.

growth of the NADPH concentration, so that the cyclic electron transport starts operating. As a result, the ATP concentration grows, and 1,3-P2D-glycerate—a Calvin cycle metabolite, which enters into reaction with NADPH and oxidizes it, accumulates. This results in a reduction of the cyclic electron flow and hence reduces the ATP synthesis. The Calvin cycle slows down, a great number of reduced acceptors of photosystem 1 (PS1) accumulates, and this leads to an increase of fluorescence. For this reason, the ATP minimum (approximately within 5–10 s) is followed by a maximum of the quantity Z_4 proportional to the NADPH concentration and of the quantity E_1 proportional to the concentration of the FS2 chlorophyll molecules in the excited state and, hence, of the pertinent delayed luminescence intensity.

Thus, photosynthesis oscillations can be due to the disturbance of the NADPH/ATP balance. The regulation of this proportion is ensured by the coupling between the amount of the reduced PS1 acceptors and the ATP synthesis. This coupling is effected by the cyclic electron flow in turn coupled to the ATP synthesis through the intermediary of ATP-synthase. And it is precisely the parameter P_{F1} that is responsible for the operating efficiency of this system, and so its reduction causes such changes in the system's behavior as illustrated in Fig. 4.

As distinct from the results obtained earlier by means of this model, in the present work we have managed to achieve characteristic times closer to those observed experimentally. This is explained by the fact that in the early works (see [14]) the values of some constants were overrated by an order of magnitude or two compared to the values estimated on the basis of the experimental data in order to accelerate computer calculations. In this work, the constants were selected proceeding from the following considerations. The rate constants of the primary processes were taken approximately equal to $1/t_i$, where t_i are the characteristic times of these processes.

The rate constants of the individual reactions in the Calvin cycle are fairly difficult to measure. To estimate them, use is made of indirect methods utilizing the Michaelis constants for each stage of the enzymatic reactions in the Calvin cycle and the appropriate free energy values. We used a different approach: the values of the constants were estimated on the basis of the experimental data on the absorption of CO_2 and consumption of NADPH. Besides, some parameters in the present work were specially adjusted to attain the best possible fit to experiment.

We note in conclusion that to achieve oscillatory photosynthesis behavior we made no extra suppositions in addition to those contained in the original system of equations describing the suggested scheme of reactions (see Fig. 2). The further analysis of this system will help one gain a better understanding of the photosynthesis regulation pathways.

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