DIFFERENTIAL EQUATIONS FOR DELAYED FLUORESCENCE KINETICS IN LIVING PLANTS

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The slow decay of the delayed fluorescence (DF) of living plants seems to have a complicated kinetics. A system of differential equations is derived, which takes into account that DF results from a recombination of electrons at the oxidized reaction-center P680 of Photosystem II (PS II). We use a resistor-accumulator (capacitor) equivalent-circuit to describe the Z-scheme. The main characteristic of the model is that the electron-pools of the transport-chain of PS I and PS II are coupled in series by the plastoquinon-molecules.

In this model we use the equivalence between the energy diagram of the DF (thermally activated fluorescence) and the discharge of an accumulator as shown in Fig. 1. The intensity of DF is the average of photons emitted from all  $P680^{\circ}$ -molecules that are reduced by the activation-process. In comparison, the discharge-current of the accumulator is the sum of electrons/time, which lose their chemical potential within the molecules of the accumulator. The discharge current will be zero, if there are no electron-donator- and electron-acceptor-molecules left and the inner resistor  $R_1$  of the accumulator becomes infinity. Because the transition probability  $S_1 \rightarrow S_0$  is high compared to  $PQ \rightarrow S_1$  we have to choose  $R_1 \gg R_a$ .





Fig. 1: Comparison between the DF and the discharge of an accumulator.



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In Fig. 2 a simplified equivalent-circuit of the Z-scheme of photosynthesis is shown. The accumulators are charged by the photodiodes PoSO and P7OO. The accumulator Edwhich drives  $R_{CALVIN}$  gains twice the voltage of Q and PQ, because the photodiodes are connected in series. It should be noted that the darkprocesses of the Calvin-Cycle, here represented by  $R_{CALVIN}$ , may have a nonlinear response. The response of the photosystem can be studied in both cases: the input of photons (inhomogeneous differential equations) should correspond to the induction of photosynthesis as can be measured by the induction-curves of the 0%5 nm fluorescence. The relaxation to the dark-adapted state is described by the homogeneous differential equations and can be measured by DF. To get a first approximation for the differential equations for the kinetics of the DF, we have omitted the transport-chain between the water-splitting encyme and some pool-molecules of PS I and PS II, as well as the electron-storage capability of the membrane and the Calvin-Cycle, which can deliver electrons to POSO<sup>4</sup> even after very long times.

Fig. 3 shows this simplified resistor-accumulator-circuit, which we used to get the differential equations by application of Kirchhoff's rules (see Fig.4).



 $\frac{di_1}{dt} + \frac{1}{R_1 \Omega} \cdot i_{\Omega} = 0$   $\frac{di_2}{dt} - \frac{1}{R_2 \Omega} \cdot i_{\Omega} + \frac{1}{R_2 P \Omega} \cdot i_{2} = 0$   $\frac{di_3}{dt} - \frac{1}{R_3 P \Omega} \cdot i_{P \Omega} + \frac{1}{R_3 F_d} \cdot i_{3} = 0$   $^{1}1 = i_{2} + i_{\Omega}$   $^{1}2 = i_{3} + i_{P Q}$ 

Fig. 3:

Discharge of the resistor-accumulatorcircuit for deriving the homogeneous differential equations.  $R_{CALV}$  was not taken into account.

Differential equations.

Fig. 1:

To derive more sophisticated differential equations (taking into account more electron-storage pools) the equivalent-circuit can be easily altered.

By numerical integrating the differential equations we have obtained the curves shown in Fig. 5, which base on the initial conditions that Fd starts with 1.0 V and Q and PQ start with .5 V. This agrees with the chemical potential of an electron at Fd and FdR, which is about twice that of an electron at PQ.

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Fig. 5: Solution-curves of the homogeneous differential equations by numerical integration;  $i_1$  corresponds to the decay of DF.



Fig. 6: Experimental and fitted curves of the decay of DF at 8.8 C and 28.8 C.

The characteristic increase in intensity is produced by those electrons coming from the pool-molecules between PS I and the Calvin-Cycle, which can recharge Q and PQ by means of their higher chemical potential.

Fig. 6 gives an example of fitted curves for the decay of DF of Chlorella algae at 8.8 C and 28.8 C. Compared to the model of Fig. 4 another storage pool of PS II between Q and PQ was added. At higher temperatures the pools of PS I can be discharged more rapidly as can be seen from the data for 28.8 C. From this temperature-dependence we can derive an activation-energy for the electrons delivered from Fd(PS I) of  $\triangle E \approx .7$  eV.

Using the obtained analytical expressions for the kinetics of DF we are able to compare them to in-vivo measurements of DF. Different results should point to disturbances within the photosystem of the plant.

## Acknowledgement

We thank the "Rechenzentrum der Universität Regensburg" for good collaboration.