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Research Paper for Bioelectrochemistry

Investigation of quinone reduction by microalgae using fluorescence - Do "lake" and "puddle" mechanisms matter?

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§ Léna Beauzamy deceased in March 2022 before completion of the final version of this manuscript. Her coauthors dedicate this study to her memory

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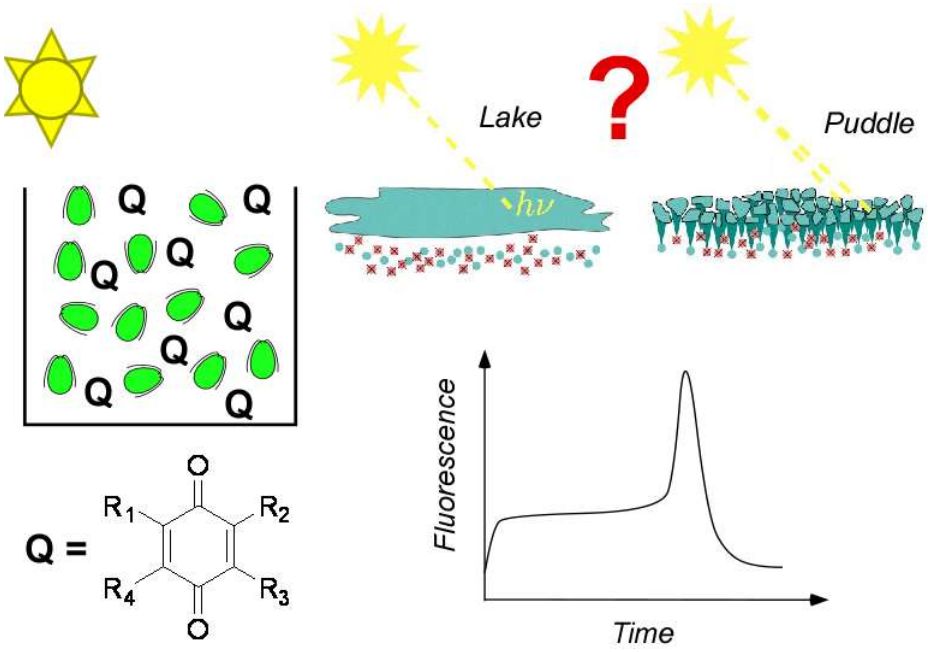
Graphical Abstract



Fluorescence data for investigating the ability of quinones to extract photosynthetic electrons are revisited in the case of microalgae. In particular, two light capture mechanisms (lake vs. puddle) are considered which plays an important role in how to quantify the effect of quinones. The results for both mechanisms are compared and the best way to assess the effect of quinones is discussed.

ABSTRACT

Photosynthesis is a fundamental process used by Nature to convert solar energy into chemical energy. For the last twenty years, many solutions have been explored to provide electrical power from the photosynthetic chain. In this context, the coupling between microalgae and exogenous quinones is an encouraging strategy because of the capability of quinones to be reduced by the photosynthetic chain. The ability of a quinone to be a good or bad electron acceptor can be evaluated by fluorescence measurements. Fluorescence analyses are a convenient tool helping to define a diverting parameter for some quinones. However, this parameter is implicitly designed on the basis of a particular light capture mechanism by algae. In this paper, we propose to revisit previous fluorescence experimental data by considering the two possible mechanisms (lake vs. puddle) and discussing their implication on the conclusions of the analysis. In particular, we show that the maximum extraction efficiency depends on the mechanism (in the case of 2,6-dichlorobenzoquinone – 2,6-DCBQ, (0.45 ± 0.02) vs (0.61 ± 0.03) for lake and puddle mechanisms respectively) but that the trends for different quinones remain correlated to the redox potentials independently of the mechanism.

Keywords: photosynthesis; quinones; fluorescence; microalgae; electron harvesting

1. Introduction

Photosynthesis is a fascinating process that many research groups are trying to take advantage of.[1-10] In the case of oxygenic photosynthesis, the illumination of the photosynthetic organism (algae, cyanobacteria, plants) leads to light capture by reaction centers. More particularly, a first charge separation then occurs at the PSII level and is then followed by a series of electron transfers along the photosynthetic chain which results in the oxidation of water and a H^+ gradient indirectly leading to the reduction of carbon dioxide (**Scheme 1**). Anoxygenic photosynthesis (for some bacteria) globally obeys the same principle even if some reagents (hydrogen sulfide, H_2) or products (sulfur) are comparatively different. In any case, in the current context of renewable energies, it is therefore a challenge to harvest or divert the electron flow of this hidden battery by using a collecting electrode that competes with the electron acceptors within the PETC (photosynthetic electron transfer chain).[11-13]

In the last twenty years, the field of electricity production from natural photosynthesis has considerably grown.[14, 15] Basically, a photoanode (or sometimes a photocathode) is built by combining a collecting electrode and the photosynthetic target.[16] It can be associated with the complementary half-cell as biophotoelectrochemical cell or investigated as a single half-cell by polarizing the working electrode.[13] From the numerous studies on the subject, one of the main key points and bottlenecks is the electron transfer efficiency that strongly relies on the connection between the collecting electrode and the photochemical converter originating from photosynthesis.[17] The nature of the photosynthetic target can be particularly diverse (isolated photosystem, isolated thylakoid membrane, choroplast, entire organism).[18-22] Indeed, this is a crucial point because photosynthetic chain fragments are less stable while PETC is less accessible within whole organisms.[17] Therefore, the electrode-PETC connection can be improved by means of exoelectrogenesis electron carriers performing a mediated electron transfer. Such electron relays may be either soluble (benzoquinones, $Fe(CN)_6^{3-}$, phenazines…) or non soluble (Osmium or benzoquinone polymers…) mediators.[23]

Because they are soluble, lipophilic and PSII acceptors, quinones are considered as good candidates to reach this purpose (**Figure 1A**).[24] Thus, the quinone is added in its oxidized form (Q) which is then reduced throughout the photosynthetic chain to the reduced form (QH_2) which is finally oxidized at the surface of the collecting electrode, thus regenerating the original Q form (**Figure 1B**).[25-27] This choice seems all the more relevant as photosynthesis also involves endogenous quinones to promote some electron transfers along the PETC. In this

context, exogenous quinones should compete with endogenous plastoquinones. Although photocurrents can be obtained by combining photosynthetic organisms under illumination with exogenous quinones, the interactions involved remain not completely understood even though the extraction site (PSII or plastoquinone pool), quinone concentration and light intensity are all important parameters.[28-30]

For the last ten years, we have been studying by fluorescence and electrochemistry the interactions between exogenous quinones and a model microalga, *Chlamydomonas reinhardtii*.[31, 32] In particular, fluorescence measurements can be used to provide quantitative data on the ability of quinones to extract photosynthetic electrons.[33, 34] However, there may be some bias related to the light capture mechanism of the photosynthetic organism. Indeed, the mode of capture of photons by the chlorophyll antennae can be seen in two models (see an excellent description in reference [35]).[36] In the first one, the reaction centers are not connected ("puddle"). In other words, a collected photon can be recovered either on a center open to photosynthesis or on a closed center. In the second model ("lake"), the centers are always connected and a captured photon will always be recovered by an open center. These two extreme cases of a complex phenomenon can have an important role on the calculations performed from the fluorescence measurements. In our previous work, we had implicitly considered the "puddle" model. Because the "lake" type description is now commonly admitted, we report in this article the comparison of the processing of these former fluorescence data based on the two mechanisms possibly involved and we demonstrate why the conclusions reported before are still relevant.

2. Materials and Methods

2.1. Cell culture and preparation

ΔpetA mutant *Chlamydomonas reinhardtii* were used in the present work.[37] This strain lacks cytochrome b_6f complex whose absence prevents the reoxidation of the plastoquinol generated by light-induced Photosystem II centers. These properties make this strain an appropriate target for investigating the ability of exogenous quinones to be reduced by the photoinduced electron flow from PSII by means of fluorescence measurements. In short, *ΔpetA* algae were grown in Tris Acetate Phosphate aqueous medium (TAP = Tris base (20 $mmol.L^{-1}$), NH_4Cl (7 $mmol.L^{-1}$), $MgSO_4$ (0.83 $mmol.L^{-1}$), $CaCl_2$ (0.45 $mmol.L^{-1}$), K_2HPO_4 (1.65 $mmol.L^{-}$

^{1}), KH_2PO_4 (1.05 mmol.L^{-1}), CH_3CO_2H (0.3 mmol.L^{-1})) at 25°C under rather dim light conditions (50 µE.m^{-2}.s^{-1}) prior to further measurements. From a cell suspension at 10^6 cells.mL^{-1}, algae are resuspended (after centrifugation at 4000 g) into Tris-minimal medium (= TAP without acetate) for fluorescence experiments (final concentration of 10^7 cells.mL^{-1}).[29, 33, 34] Algae suspensions are maintained under stirring between two measurements.

2.2. Chemical materials and solutions preparation

All chemicals (including quinones) have been purchased from Sigma-Aldrich and have been used without further purification. Practically, quinones were dissolved in absolute ethanol to make fresh mother solutions (10 mmol.L^{-1}). Appropriate volumes of these solutions were thus directly added to the algae suspension (a cuvette containing the algae suspension; V = 2 mL) for subsequent fluorescence experiments. Of note, these experimental conditions correspond to a large excess of quinone compared to the considered PSII amount (quinone/PSII ratio ~ 1000 depending on the quinone concentration range).

2.3. Spectroscopy measurements

Within this paper, we analyzed the fluorescence measurements from the reference [33]. According to the procedure already described in our previous works, [29-31, 33, 34] fluorescence is recorded by using a JTS-10 spectrophotometer (Biologic, Grenoble, France). Photosynthetic activity is triggered by an actinic red light (λ = 640 nm) at different intensities (56; 135; 340 or 800 µE.m^{-2}.s^{-1}) during few seconds and ranging from an initial fluorescence value (F_0) to a steady state fluorescence level (F_{stat}). A short supersaturating pulse (250 ms; λ = 640 nm; I° = 5000 µE.m^{-2}.s^{-1}) of exciting light is then applied and corresponds to the maximum fluorescence level (F_{max}; measured 100 µs after the pulse was turned off). Such measurements allow one to calculate the quantum yield of PSII chemistry or the open center fraction according to lake and puddle mechanisms (see text below). The detecting light for sampling fluorescence was provided by white LEDs and the wavelength (440 nm) defined by a combination (3 mm BG39 and BG3) of Schott filters. Each experiment was replicated three times.

All plots, fittings and statistical analyses (s.e.m. with n = 3) were performed using SIGMA Plot 10.0 software (Systat Software Inc., Richmond, CA, USA).

3. Fluorescence measurements of algae-quinones interactions – Lake vs puddle mechanism

3.1. How to measure and analyze the interactions between algae and quinones?

A suitable way to evaluate the interactions between the photosynthetic chain and a given exogenous quinone is to perform fluorescence measurements with *ΔpetA Chlamydomonas reinhardtii* mutants.[37] Due to the lack of cytochrome b_6f complex, the PETC is interrupted downstream of the PSII, which helps to specifically study of the output PSII electron flow. Furthermore, after light capture at the chlorophyll antennae, the stored energy can effectively lead to a charge separation at the PSII level but also to a fluorescence emission. Thus, fluorescence is a proxy for photon/electron conversion by the photosynthetic chain and especially PSII. It is therefore related to the proportion of light that led to the electron flow from PSII. In practice, fluorescence induction curves are made by submitting an algae suspension to actinic light and then to a supersaturating pulse (**Figure 2A**).

The fluorescence level before irradiation (noted F_0) increases until a steady state value (F_{stat}) under actinic light. Of note, F_0 corresponds to dark conditions where the PSII photochemical conversion ability is maximum. Conversely, the supersaturating pulse has the effect of saturating the chain at the PSII level and leads to the highest fluorescence level (F_{max}) since the photochemical conversion ability is then zero. The use of these extreme fluorescence values (F_0 and/or F_{max}) and of the measurement under actinic light should make it possible to provide a parameter indicating the electron flow along the PETC as explained in some articles and reviews.[38-41] As a consequence, such a parameter should be thus sensitive to the presence of quinones and to their diverting effect of electron flow. Besides, a similar shape is observed for wild-type algae (only the beginning of the curve differs; see **Figure S1**), which would enable the data treatment. However, working on *ΔpetA* mutant provides a more specific approach to characterize the interactions between quinones and PSII.

3.2. How is light captured? "Lake" vs "Puddle"

Calculations involving fluorescence measurements can be based on how light is captured by the photosynthetic organism. In practice, two mechanisms can be considered.[42] Indeed, it is firstly important to note that the charge separation at PSII causes the oxidation of P680 and the reduction of Q_A (**Figure 2B**). The presence of the Q_A form defines an open center when Q_A^- defines a closed center. Thus, the fluorescence level before irradiation (F_0) is a situation where all centers are open. The steady state fluorescence level (F_{stat}) under actinic light thus corresponds to a fraction of open centers lower than 1. The supersaturating pulse closes all centers. The irradiation can no longer lead to charge separation which leads to the maximum fluorescence level (F_{max}). As mentioned above, two light capture mechanisms can be considered.[35] In the "**puddle**" model, reaction centers are not connected and have their own independent antennae. In this view, the site where the photon is captured is important (**Scheme 2**). If it is absorbed by an antenna that is connected to a closed center, no photosynthesis occurs. If the connected center is open then the photon is likely to be involved into the chain and trigger photosynthetic activity. Conversely, in the "**lake**" model, all the reaction centers are connected. In other words, when a photon is absorbed by a chlorophyll, a delocalized exciton is formed on the whole "lake" (**Scheme 2**). So, the site of capture of the photon does not matter since each open center competes to collect this exciton that will finally induce photosynthesis.

3.3. Which relevant parameters from fluorescence measurements?

3.3.1. Φ_{PSII}

As mentioned above, after being captured by the chlorophyll antennae at PSII, the incident photon causes the excitation of the P680 reaction center. This excess energy then gives rise to charge separation, i.e. the oxidation of P680 to $P680^+$ and the reduction of the embedded quinone Q_A to Q_A^- which can then transfer an electron along the photosynthetic chain. It is therefore important to quantify the yield of this photon/electron conversion. Therefore, the **photochemical PSII efficiency** (or yield; $\boldsymbol{\Phi_{PSII}}$) is defined as the fraction of photons converted to electrons along the photosynthetic chain from PSII. Φ_{PSII} can be calculated according to (see details in **Supplementary information**):[42]

$$\Phi_{PSII} = \frac{F_{max} - F_{stat}}{F_{max}} \quad (1)$$

The way to determine Φ_{PSII} does not depend on the light capture mechanism.[40-42] This is therefore a very reliable and robust way to make use of fluorescence data. Using the measured fluorescence data from the reference [33], **Figure 3** displays Φ_{PSII} values for a suspension of *Chlamydomonas reinhardtii* algae (*ΔpetA* mutants; see experimental part) as a function of 2,6-DCBQ concentrations for different light irradiances (**Figure 3A**) and for three quinones (2,6-DCBQ, 2,6-DMBQ and PPBQ) at 340 $\mu E.m^{-2}.s^{-1}$ (**Figure 3B**). The photochemical efficiency of PSII is theoretically the most relevant parameter since the electron harvesting at PSII by exogenous quinones should alleviate the limiting downstream steps. Indeed, the exogenous quinones should be reduced by the embedded quinone Q_A^- (or possibly the pool of plastoquinones in their reduced form, see **Scheme 1**) thus increasing the photoconversion rate. The increase in such a photon/electron conversion yield, i. e. Φ_{PSII}, is therefore expected. This trend is indeed observed in most cases. However, there are also conditions where Φ_{PSII} values decrease at high concentrations. This unexpected decrease is due to the fact that the photochemical yield of PSII may be indirectly affected by the quenching behaviour of quinones.[25]

Indeed, these compounds are known to quench fluorescence at chlorophyll antennae (Chl).[33, 43, 44] Knowing that only the oxidized form of quinones (i.e. Q and not QH_2) has such properties,[29], the mechanism involved is probably not a direct energy transfer since the absorption spectra of quinones and chlorophylls have a very low overlap.[45] The favored mechanism should be related to the formation of an adduct (Chl* + Q → [Chl*, Q]) followed by an electron transfer ([Chl*, Q] → [Chl^+, Q^-]).[46] The resulting ionic pair eventually decays to the ground state ([Chl^+, Q^-] → Chl + Q).

Because this is an alternative pathway involving quinones, this named non-photochemical quenching (NPQ) will then change the Φ_{PSII} value in parallel to the electron harvesting resulting from the quinones. The convolution of the two phenomena (NPQ + electron diverting) due to exogenous quinones prevents Φ_{PSII} from being relevant to quantify the diverting effect from quinones.

3.3.2. Fraction of open centers

In this context, a second parameter can be obtained from the induction curves, namely **the percentage of open centers**, i.e the fraction of Q_A. Under such an oxidized state, PSII can undergo further charge separation (**Figure 2B**). This value should be sensitive to the harvesting effect of quinones which is expected to promote the re-oxidation of Q_A^- to Q_A and should therefore increase the open center fraction.[33, 34] In this view, the open center ratio thus corresponds to an electron extraction yield from Q_A^-. Moreover, it is important to note that the open center percentage considers the conversion of a photon at P680 into a photosynthetic electron while the PSII yield is related to the conversion of a photon at the chlorophyll antennae. The NPQ is involved at the level of these antennae, so it does not affect the value of the open center fraction.

Unfortunately, the way to derive the open center fraction is not unique and depends on the light capture mechanism considered in the data treatment.[42]

In the “puddle” case, the open center fraction is noted as **qP** and calculated according to:[42]

$$qP = \frac{F_{\max} - F_{stat}}{F_{\max} - F_0} \tag{2}$$

This is the way of working out that we had chosen in our previous studies in spite of different notations and corrections.[33, 34] The derivation of the equations used from the fluorescence measurements made the implicit assumption that the reaction centers were mutually independent. However, in the “lake” case, the open center fraction is thus noted as **qL** and calculated according to:[42]

$$qL = \frac{F_0}{F_{stat}} \times \frac{F_{\max} - F_{stat}}{F_{\max} - F_0} \tag{3}$$

To date, calculations considering the "lake" type mechanism and qL are considered more accurate due to the high connectivity of PSII units.[41, 42, 47] Therefore, qP is rather viewed as an approximation or indicator of the percentage of open centers. As a consequence, it is necessary in our case to revisit the fluorescence data by comparing the results obtained with the two mechanisms.

4. Fluorescence measurements of algae-quinones interactions – Results and Discussion

4.1.Data treatment and analyses

Using the same experimental fluorescence induction curves to calculate Φ_{PSII} have helped to display qL or qP as a function of quinone concentration (C_Q). The corresponding graphs (qL or qP = f(C_Q)) can be well fitted with a single rectangular hyperbola (3 parameters; $y = y_0 + Ax/(B+x)$; $R^2 > 0.99$; see an example in **Figure 4**). This is in agreement with a Michaelis-Menten like behaviour, i.e. a reduction reaction of exogenous quinones catalysed by PSII under illumination.[33, 34]

As a consequence, the maximum open center fraction under quinone addition ($(qL)_\infty$ or $(qP)_\infty$) can be extracted. This is a relevant parameter for analyzing the electron transfer between reduced PSII and quinones.[34] However, these values also cover the open center percentage in the absence of quinones, which has to be subtracted by the the initial open center fraction ($(qL)_0$ or $(qP)_0$ at $C_Q = 0$ mol.L^{-1}). The whole parameter indicating the effect of the quinones is therefore the constant D_L or D_P, according to:

$$D_L = (qL)_\infty - (qL)_0 \quad (4)$$

$$D_P = (qP)_\infty - (qP)_0 \quad (5)$$

The values were summarized in **Table 1**.

4.2.Discussion

As shown in the above data analysis, the PSII yield is not the most suitable parameter for studying photosynthetic electron extraction by exogenous quinones since it is both related to the electron harvesting by quinones and the quinone induced decrease in light perceived by photosynthetic chain (non-photochemical quenching). The open center ratio parameter (i.e. the electron extraction yield) is therefore preferable as it is not affected by NPQ. As a consequence, there is no clear correlation (see **Figure S2**) between the fraction of photons converted to electrons along the photosynthetic chain (Φ_{PSII}) and the fraction of harvested electrons by quinones (qP/qL)

As described above, there are two ways to determine the open center ratio parameter. The comparison between extracted D_L and D_P values is shown in **Figure 5A**, as the treatment

applied for the calculation of D_P is similar to that used in our previous work. It can be seen that the results of the two mechanisms are obviously different as expected. More interestingly, D_L and D_P values can be globally correlated (within the experimental error; R^2 = 0.98) even knowing that the values for the puddle mechanism are still higher than those for the lake mechanism. Of note, it was commonly accepted that the lake model is generally more relevant than the puddle model, as established in some excellent reviews.[39, 41, 42, 48, 49] or demonstrated for example in chloroplasts[50] or plants.[51] In other words, qL (from the lake mechanism) really stands for the fraction of open centers. Conversely, considering the puddle mechanism, the qP value is well related to PSII efficiency but is only an estimation of the open center ratio whose actual value is thus derived by the lake model. Furthermore, qP is often named as « photochemical quenching » and should be non-linearly related to qL.[41] This may seem contradictory to our results since a linear relationship was globally observed between D_L and D_P values. Indeed, the lack of linearity is readily observed when global qP and qL data are normalized (see 2,6-DCBQ for example in **Figure 4B**). It is clear that the difference between qL and qP is never constant, thus meaning that the D_L/D_P linear relationship is a singularity. As a consequence, the fact that the values of D_L and D_P appear to be linearly related could be a coincidence or a singularity biased by experimental uncertainties.

Furthermore, at high quinone concentration, photosynthetic electron extraction is limited by the charge transfer step (i.e. electron transfer between Q and Q_A^-) and not by the mass transfer from the solution to the thylakoid membrane by the quinone Q.[34] In this context, as displayed in **Figures 5B** and **5C**, D_L and D_P values were compared to the relevant thermodynamical values in aqueous medium, i.e. the standard redox potential involving the quinone and semi-quinone forms ($E°(Q^-/Q)$) or the formal redox potential involving the quinone and hydroquinone forms ($E°'(QH_2/Q)$ at pH 7). It can be seen that there is a global correlation between the open centre percentage and standard potential values, thus confirming that the intrinsic ability for a given quinone to be reduced is expectedly related to its efficiency to harvest photosynthetic electrons in our case. It can be seen that the accuracy of the correlation does not seem to depend on the chosen redox potential. Indeed, for $E°(Q/Q^-)$, regression coefficients were equal to R^2 = 0.90 and 0.83 for D_L and D_P respectively. For $E°'(Q/QH_2)$, R^2 = 0.92 and 0.85 were obtained for D_L and D_P respectively. Of note, the D_L and D_P values are obtained for constant values of open center fraction (i.e. a plateau at high quinone concentration). In this case, as already mentioned, D_L and D_P are directly related to the electron transfer between Q and Q_A^-. The globally linear relationship between these parameters and the

formal potentials (E° or E°') results by transitivity in a constant D_L/D_P ratio. Conversely, when the quinone concentration remains moderate, the open center percentage is never constant. The conditions of an intermediate regime (mass transport + electron transfer)[34] take place and there is then no reason for qL and qP to be proportional since the formal potentials by themselves cannot fully explain the situation.

The fact that the choice of the nature of the redox potential for making comparisons is not important has already been observed in our previous work involving photocurrents.[30] Thus, using an algal suspension in the presence of quinones and a polarized gold-ITO collecting electrode, the maximum photocurrent values measured were indifferently correlated to $E°(Q/Q^-)$ and $E°'(Q/QH_2)$. Conversely, Grattieri, Minteer and co-workers showed that the correlation was better when considering $E°(Q/Q^-)$ in the case of photosynthetic purple bacteria deposited on Toray carbon paper electrodes.[52] Such a result seems more consistent because the first electron transfer has to involve the Q/Q^- couple. It therefore suggests that the experimental configuration (suspension under stirring vs immobilisation) could play a role on the correlation by favouring/defavouring protonation reactions.

Finally, as shown from the apparent linear correlation between D_L and D_P, the light capture model plays a role on the efficiency values (**Table 1**). However, it does not affect the trend of the comparisons since the D_L/D_P ratio remains constant. Of note, in our previous works directly or indirectly involving fluorescence measurements,[28, 29, 33, 34] we have implicitly considered the puddle mechanism. As a consequence, the corresponding statements or conclusions remain valid.

5. Conclusion

In our previous fluorescence studies,[33] we evaluated the electron accepting effect of different quinones towards PSII in a suspension of *Chlamydomonas reinhardtii* algae. The data treatment implicitly involved the "puddle" light capture mechanism (i.e. without connectivity between centers) and enabled to define diverting parameters related to the maximum percentage of open centers in presence of quinones. In this work, we revisited our data with the most suitable mechanism ("lake"; with connectivity between centers). If the value of the diverting parameter is then modified (on average, D_P is 1.8 times larger than D_L), the trends do not change (i.e. the harvesting efficiency increases when E° increases) and show that our previous work

remains relevant. However, if the way of considering the light capture mechanism does not influence the conclusions of the "*Chlamydomonas reinhardtii*/quinones" tandem, this cannot be a general rule. Indeed, although the lake model is considered more consistent and close to the experimental data by the scientific community, the biological reality seems to be more complex and intermediate between the two visions that can be combined depending on the experimental conditions.[49, 53] Beyond the recent insights into the interactions between quinones and chlorophyll antennae,[45] this raises the question of the effect of connectivity between reaction centers on the production of electricity from whole photosynthetic systems (cyanobacteria, purple bacteria...) or isolated ones (thylakoid membranes, photosystems...). Because transient fluorescence rise measurements are a possible way to have more information on the light capture,[49] this paves the way for future coupled fluorescence-electrochemistry experiments for a simultaneous monitoring of the photocurrent production in relation to the light capture mechanism.

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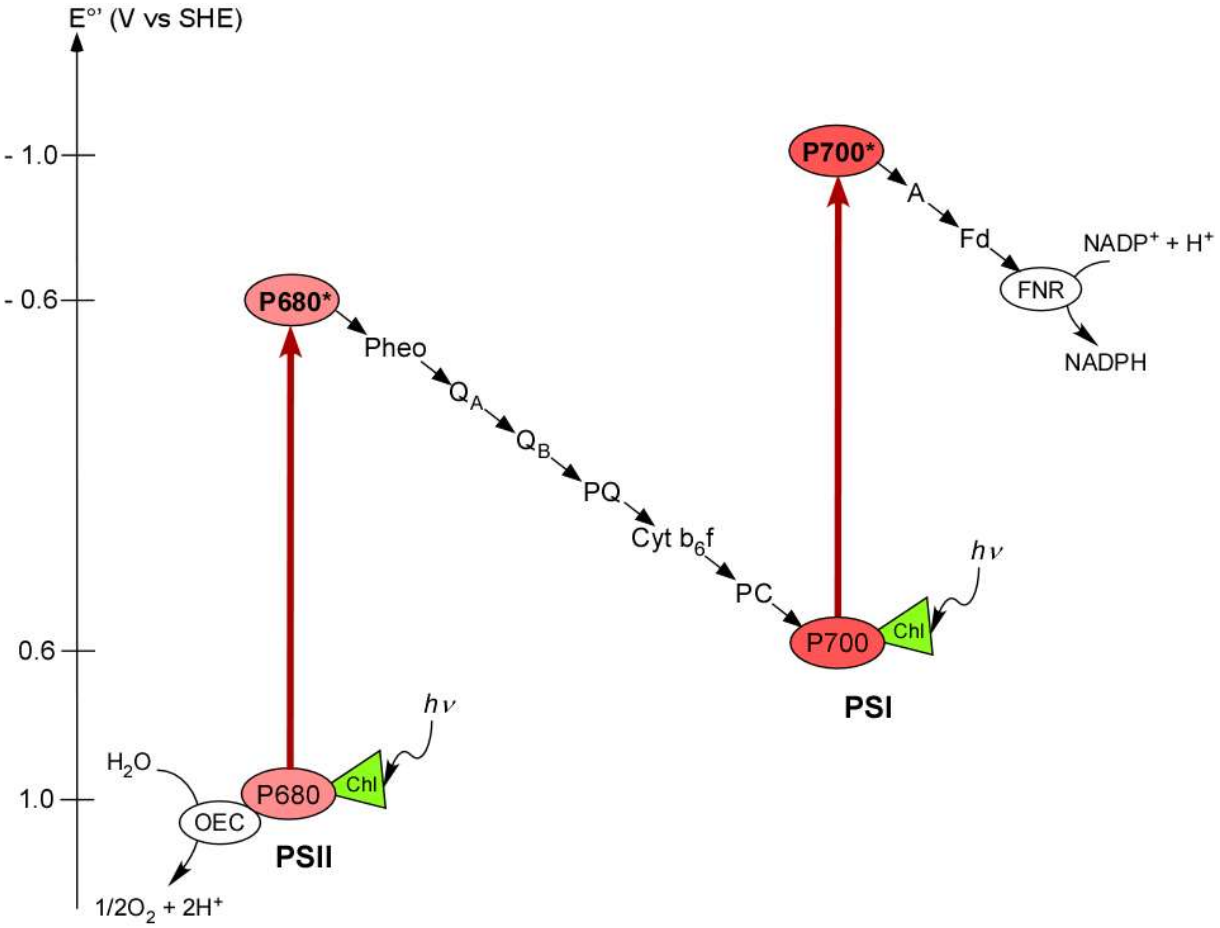
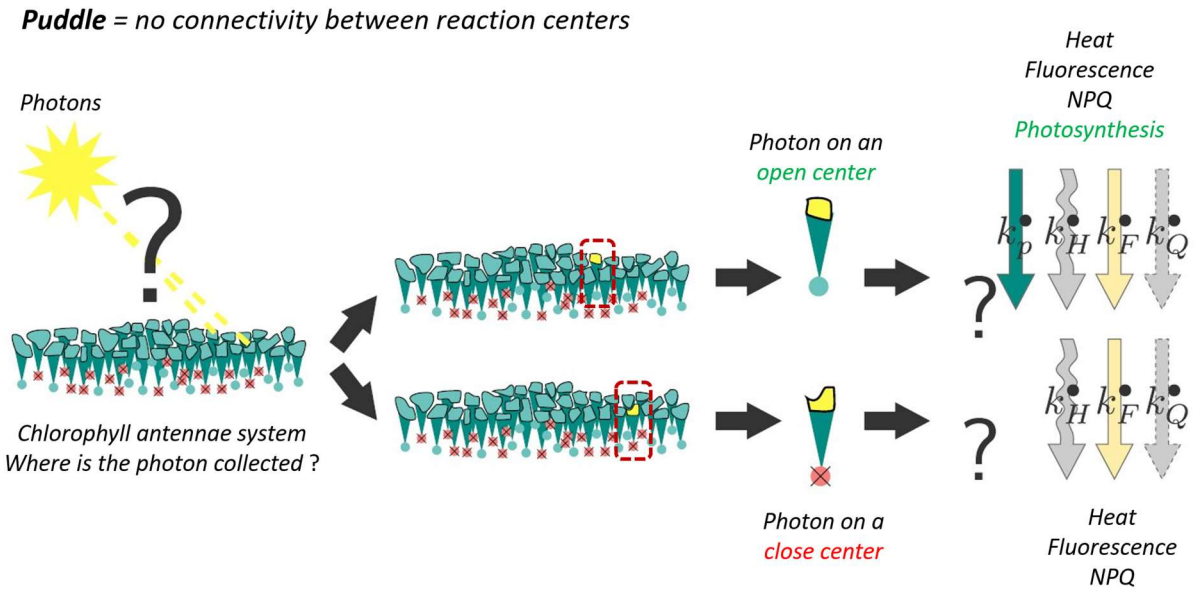
Scheme 1


E°' (V vs SHE)
- 1.0
- 0.6
0.6
1.0
P680*
Pheo
Q_A
Q_B
PQ
Cyt b_6f
PC
P700*
A
Fd
FNR
$NADP^+ + H^+$
NADPH
$h\nu$
P700
Chl
PSI
H_2O
P680
Chl
OEC
PSII
$1/2O_2 + 2H^+$

Scheme 2


Puddle = no connectivity between reaction centers
Photons
Chlorophyll antennae system
Where is the photon collected ?
Photon on an
open center
Photon on a
close center
Heat
Fluorescence
NPQ
Photosynthesis
k_p k_H k_F k_Q
k_H k_F k_Q
Heat
Fluorescence
NPQ

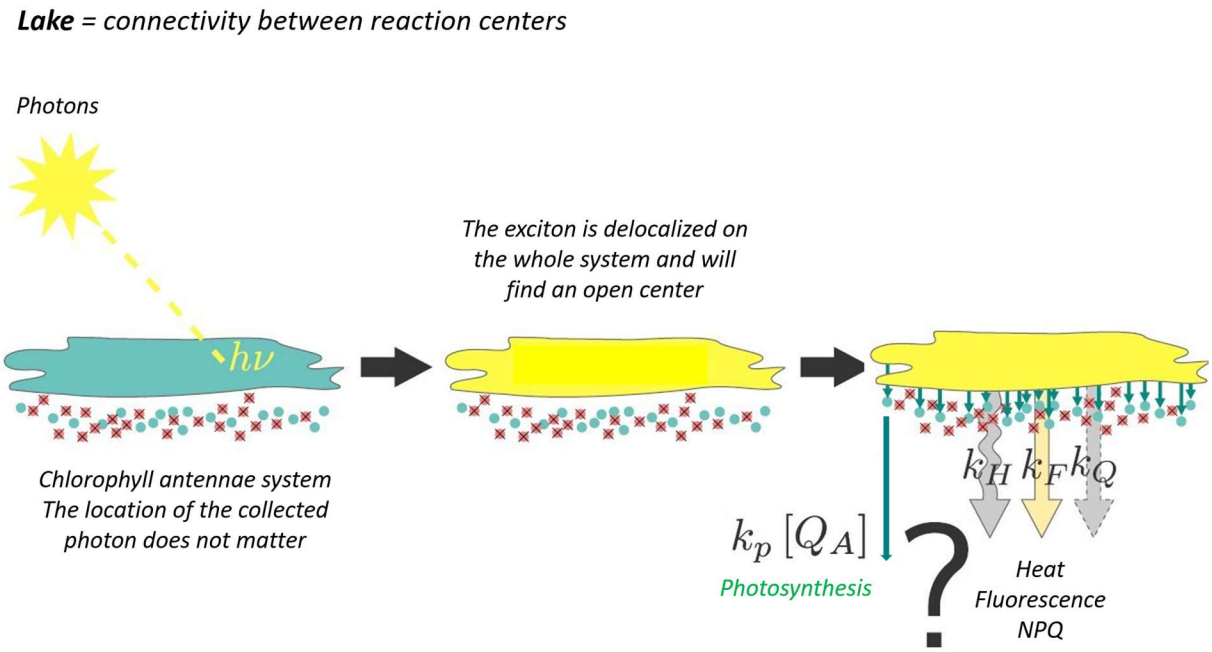
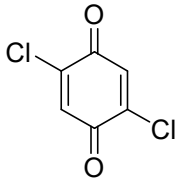

Lake = connectivity between reaction centers
Photons
$h\nu$
Chlorophyll antennae system
The location of the collected
photon does not matter
The exciton is delocalized on
the whole system and will
find an open center
$k_p\,[Q_A]$
Photosynthesis
k_H k_F k_Q
Heat
Fluorescence
NPQ

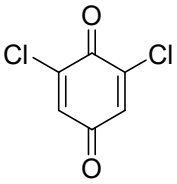
Figure 1

A)

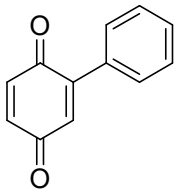
Quinones with electrowithdrawing groups



2,5-Dichlorobenzoquinone
(2,5-DCBQ)
$E°(Q^{-}/Q)$ = 230 mV vs SHE
$E°'(QH_2/Q)$ = 309 mV vs SHE

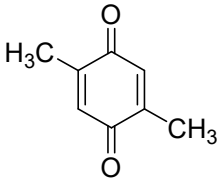


2,6-Dichlorobenzoquinone
(2,6-DCBQ)
$E°(Q^{-}/Q)$ = 221 mV vs SHE
$E°'(QH_2/Q)$ = 315 mV vs SHE

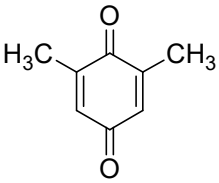


p-phenylbenzoquinone
(PPBQ)
$E°(Q^{-}/Q)$ = 62 mV vs SHE
$E°'(QH_2/Q)$ = 277 mV vs SHE

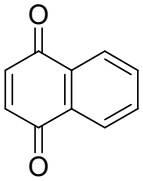
Quinones with electrodonating groups



2,5-Dimethylbenzoquinone
(2,5-DMBQ)
$E°(Q^{-}/Q)$ = -66 mV vs SHE
$E°'(QH_2/Q)$ = 180 mV vs SHE



2,6-Dimethylbenzoquinone
(2,6-DMBQ)
$E°(Q^{-}/Q)$ = -80 mV vs SHE
$E°'(QH_2/Q)$ = 174 mV vs SHE



1,4-Naphthoquinone
(NBQ)
$E°(Q^{-}/Q)$ = -140 mV vs SHE
$E°'(QH_2/Q)$ = 143 mV vs SHE

B)

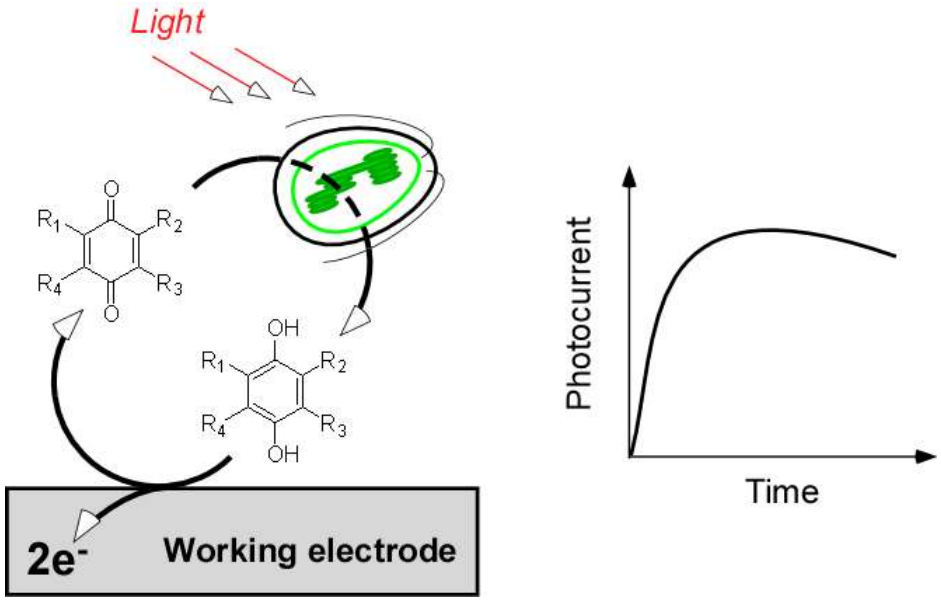
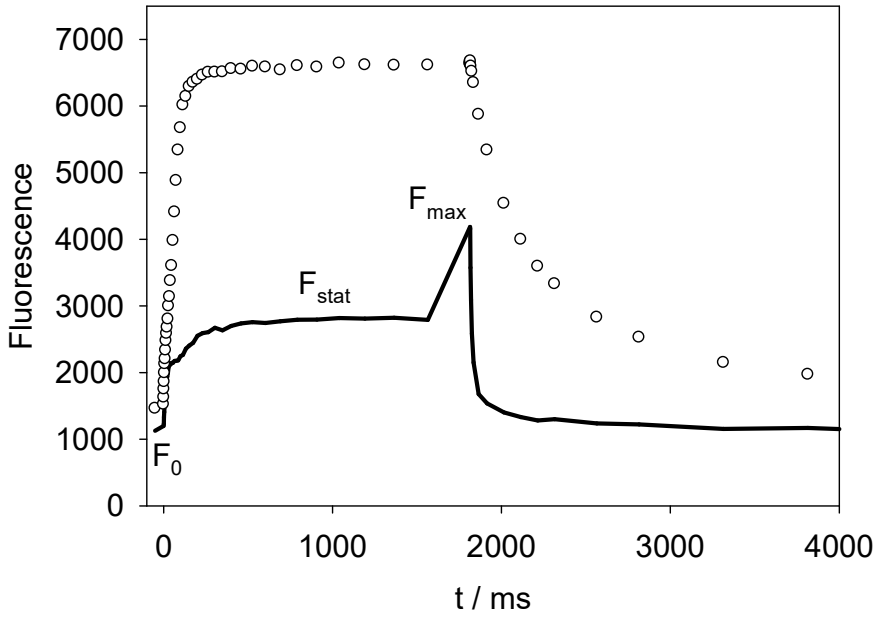


Figure 2

A)


7000
6000
5000
4000
3000
2000
1000
0
Fluorescence
F_max
F_stat
F_0
0
1000
2000
3000
4000
t / ms

B)

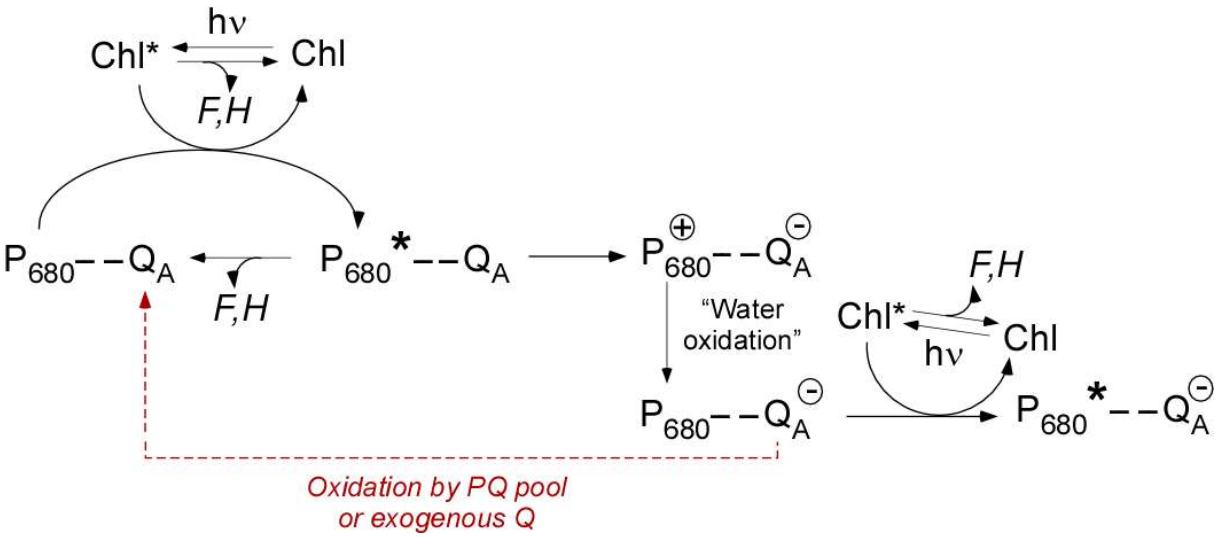
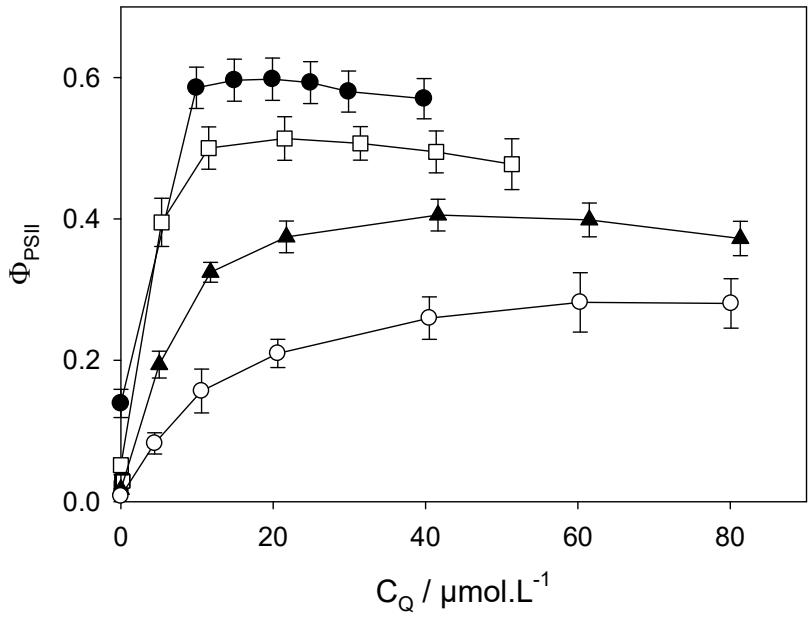

hν
Chl*
Chl
F,H
P680--QA
P680*--QA
F,H
P680+--QA-
"Water oxidation"
P680--QA-
F,H
Chl*
hν
Chl
P680*--QA-
Oxidation by PQ pool or exogenous Q

Figure 3

A)


0.6
0.4
0.2
0.0
ΦPSII
0
20
40
60
80
CQ / µmol.L-1

B)

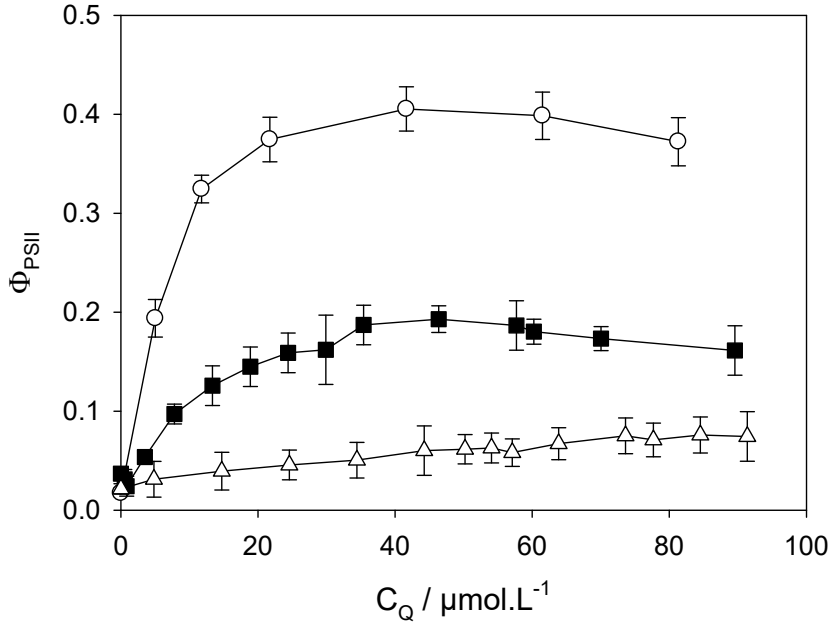
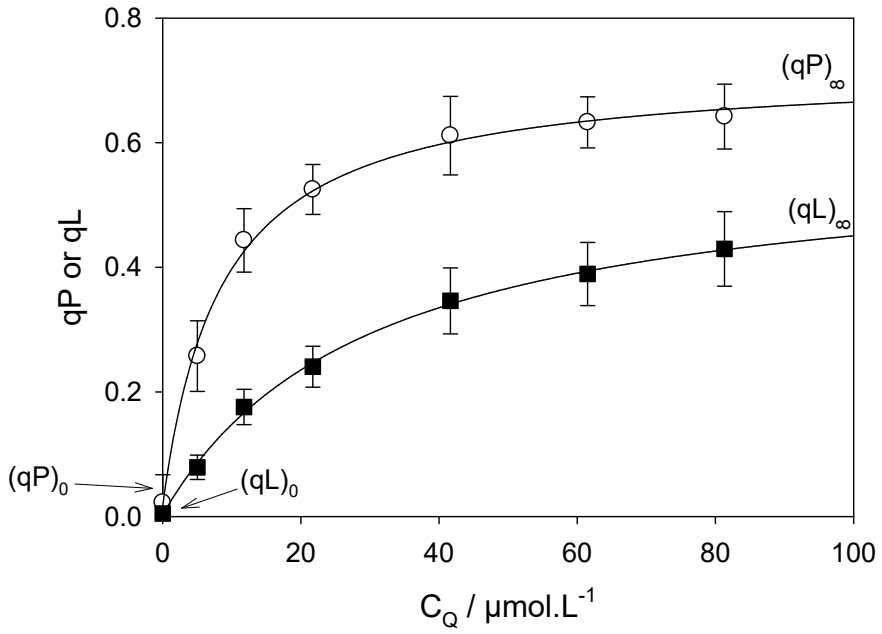

0.5
0.4
0.3
0.2
0.1
0.0
ΦPSII
0
20
40
60
80
100
CQ / µmol.L-1

Figure 4

A)


0.8
0.6
0.4
0.2
0.0
qP or qL
(qP)∞
(qL)∞
(qP)0
(qL)0
0
20
40
60
80
100
CQ / µmol.L-1

B)

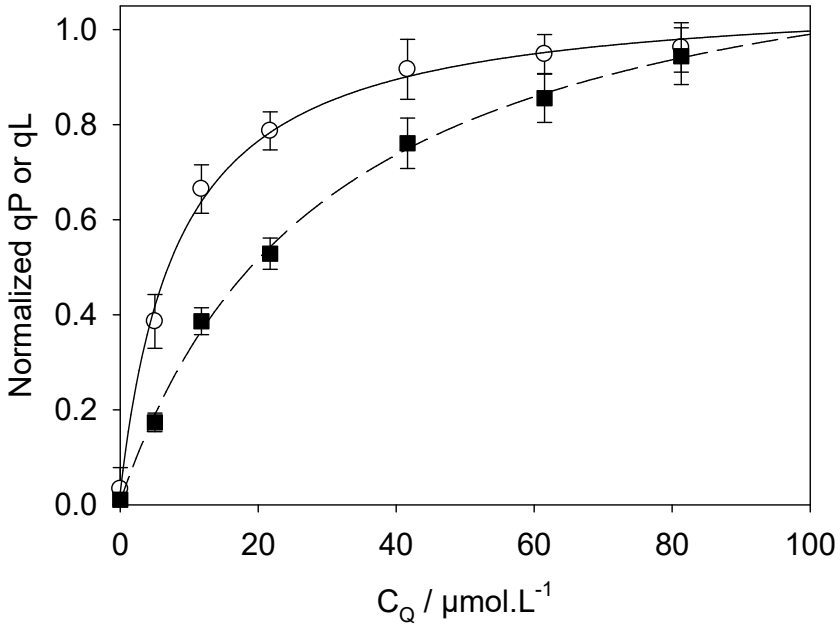
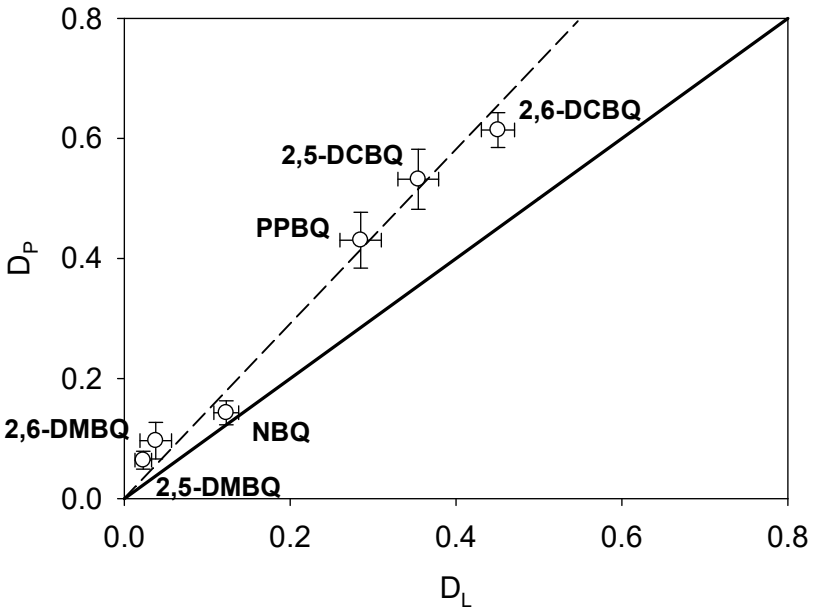
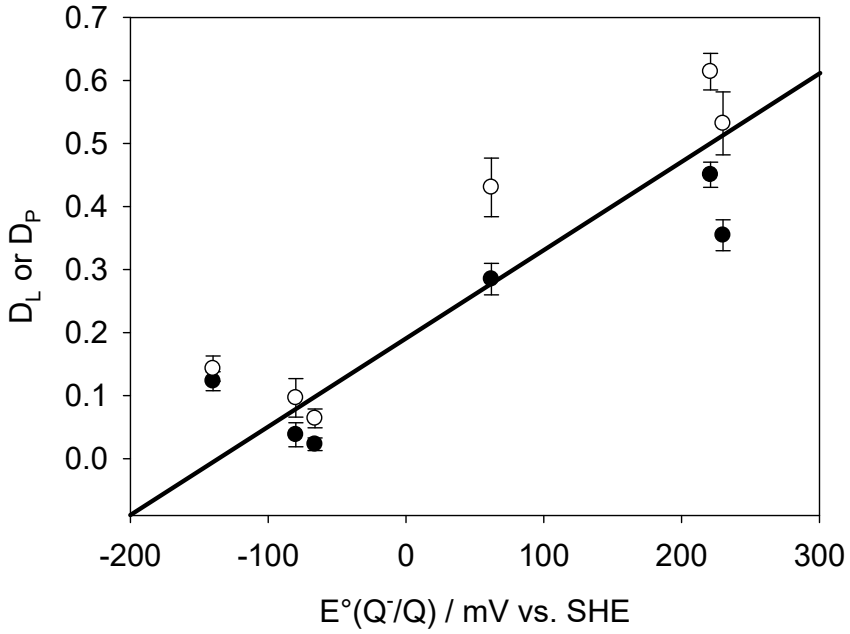

1.0
0.8
0.6
0.4
0.2
0.0
Normalized qP or qL
0
20
40
60
80
100
CQ / µmol.L-1

Figure 5

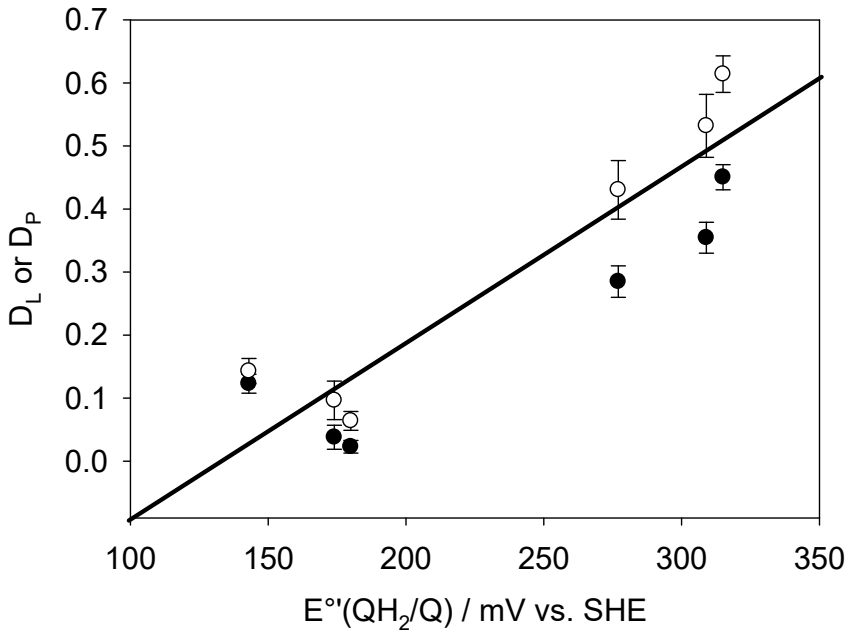
A)


0.8
0.6
0.4
0.2
0.0
D_P
0.0
0.2
0.4
0.6
0.8
D_L
2,6-DCBQ
2,5-DCBQ
PPBQ
NBQ
2,6-DMBQ
2,5-DMBQ

B)


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
D_L or D_P
-200
-100
0
100
200
300
E°(Q^-/Q) / mV vs. SHE

C)


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
D_L or D_P
100
150
200
250
300
350
E°'(QH_2/Q) / mV vs. SHE

Tables

Table 1. Harvesting efficiency values obtained for different quinones from fluorescence induction curves according to the mechanism of light capture by the algae (D_L for lake and D_P for puddle).

Quinone	D_L	D_P
2,6-DCBQ	0.45 ± 0.02	0.61 ± 0.03
PPBQ	0.29 ± 0.03	0.43 ± 0.05
2,5-DCBQ	0.36 ± 0.03	0.53 ± 0.05
2,6-DMBQ	0.04 ± 0.02	0.10 ± 0.03
2,5-DMBQ	0.02 ± 0.01	0.06 ± 0.02
NBQ	0.12 ± 0.02	0.14 ± 0.02

Scheme and Figure captions

Scheme 1. A) General Z-scheme of the different steps occurring along the photosynthetic chain located in thylakoid membranes. Light (hν) is captured by chlorophyll antennae (Chl) at the level of Photosystem II (PSII). It then promotes excitation of the P680 chlorophyll dimer which undergoes a charge separation. This leads to water oxidation by means of the Oxygen Evolving Complex (OEC) and the reduction of an embedded quinone Q_A into a Q_A^- form after a first step involving pheophytin (Pheo). This results in an electron flow through many electron transfer steps involving electron donors and acceptors (plastoquinone pool whose oxidized form (namely PQ) can be placed into the Q_B pocket; cytochrome b_6f complex (Cyt b_6f); plastocyanin (PC)). All these oxidoreduction steps are controlled by redox potential values (E°' at pH 7). Of note, the constant E°' decrease prevents electron transfer at the PSI level, which requires a renewed excitation at this stage (P700 chlorophyll dimer). Additional electron transfer pathways can thus occur involving the PSI acceptor (A), Ferredoxin (Fd) and Ferredoxin-$NADP^+$ reductase (FNR) that finally leads to the $NADP^+$ reduction into NADPH. The global H^+ gradient triggers ATP production used to reduce CO_2 by means of the Calvin cycle.

Scheme 2. Simplified view of the two light capture mechanisms considered in this work. A) "Puddle": the captured photon can be collected either by the chlorophyll antenna of a closed center (red cross) or by the one of an open center (blue circle). Four pathways can be defined by the following rate constants: $k^\bullet_P$ (electron transfer with Q_A^- or PQ pool), $k^\bullet_F$ (fluorescence emission), $k^\bullet_H$ (heat emission) and $k^\bullet_Q$ (non photochemical quenching). The place where a given photon interacts is therefore important for its fate ($k^\bullet_P$, $k^\bullet_F$, $k^\bullet_H$ and $k^\bullet_Q$ for an open center or only $k^\bullet_F$, $k^\bullet_H$ and $k^\bullet_Q$ for a closed center). B) "Lake": chlorophyll antennae are all connected. This means that a captured photon is delocalized on a "carpet" of chlorophylls. In other words, the exciton will always reach an open center, regardless of where it is collected. The different pathways can therefore be globally described by k_F, k_H and k_Q for the non-photosynthetic pathways and $k_P[Q_A]$ whether photosynthesis occurs (where $[Q_A]$ is the open center ratio).

Figure 1. A) Chemical structures of the quinones investigated in this work. Two redox potentials ($E°(Q^-/Q)$ and $E'°(QH_2/Q)$ at pH 7 are provided according to references mentioned in [30]. B) Principle of the photocurrent production from *Chlamydomonas reinhardtii* algae

suspension. Microalgae are illuminated in the presence of quinones (Q). Q is therefore reduced into its hydroquinone form (QH_2). The working electrode (gold, ITO or carbon; reference and auxiliary electrodes are not shown for more clarity) is polarized at a potential value leading to the QH_2 oxidation. It eventually leads to the recovery of the Q form and the concomitant photocurrent.

Figure 2. A) Representative fluorescence induction curves displaying initial (F_0), steady state (F_{stat}) and maximum (F_{max}) fluorescence levels. Solid line: *ΔpetA* cells (10^7 cells mL^{-1}) in presence of 2,6-DCBQ (C_Q = 30 µmol.L^{-1}); I° = 340 µE.m^{-2}.s^{-1}. F_{max} significantly increases because the supersaturating pulse transiently disables the electron harvesting by exogenous quinones. Please note that F_{max} is close to F_{stat} in case of absence of quinones (circles). Because the photosynthetic chain is impaired downstream of PSII in *ΔpetA* cells, endogenous electron flow remains very low. B) Simplified scheme of the different pathways involved within Photosystem II after light excitation. Excited chlorophylls can transfer their exciton to P680 or lead to heat or fluorescence emission (decay by means of non photochemical quenching is not shown for more clarity). Excited P680* can lead to charge separation and, after water oxidation, to the reduced form of the embedded Q_A (i.e. Q_A^-). The restored P680 can be excited again but a further charge separation cannot take place as long as Q_A^- (closed center) is not reoxidized to Q_A (open center). Such a reoxidation can occur by means of exogenous quinones (Q) or along the photosynthetic chain (by insertion of PQ within the Q_B pocket).

Figure 3. PSII photochemical efficiency in a *Chlamydomonas reinhardtii* algae suspension (10^7 cells.mL^{-1}; *ΔpetA* strain lacking the cytochrome b_6f complex). A) as a function of 2,6-DCBQ concentration for different light irradiances (black circles: 56 µE.m^{-2}.s^{-1} ; white squares : 135 µE.m^{-2}.s^{-1} ; black triangles: 340 µE.m^{-2}.s^{-1} ; white circles: 800 µE.m^{-2}.s^{-1}). B) for three quinones derivatives (white circles: 2,6-DCBQ; black squares: PPBQ; white triangles: 2,6-DMBQ) at I° = 340 µE.m^{-2}.s^{-1}. The quinone concentrations were corrected to take into account losses due to partition effects.[33, 34]

Figure 4. A) Example of open center ratio as a function of quinone concentration for the two mechanisms considered in this work (qP : white circles ; qL : black circles) with a suspension of

Chlamydomonas reinhardtii ΔPetA algae (10^7 cells mL^{-1}) under illumination ($I° = 340$ $\mu E.m^{-2}.s^{-1}$. with 2,6-DCBQ. B) Example of normalized open center ratio (by $(qL)_\infty$ or $(qP)_\infty$ values; see text) as a function of 2,6-DCBQ concentration.

Figure 5. A) Comparison of the D_L and D_P values extracted from fluorescence measurements (see text) for different quinones ($I° = 340$ $\mu E.m^{-2}.s^{-1}$). The solid line corresponds to the equality between D_L and D_P. The dashed line corresponds to the linear regression of the $D_P = f(D_L)$ curve ($R^2 = 0.98$). B) Quinone harvesting efficiency according lake and puddle mechanisms (i.e. D_L (black circles) and D_P (white circles)) as a function of $E°(Q^-/Q)$ values for different quinones. C) The same analysis than B) for $E°'(QH_2/Q)$ values.

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