Interrelated Roles of Chloride and Bicarbonate in Regulating Photosystem II Function in *Limnospira maxima*

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Efficient charge separation and electron transfer in Photosystem II (PSII) depend on small inorganic cofactors that maintain redox balance and catalytic stability. Chloride facilitates oxygen evolution by stabilizing the electrostatic and hydrogen-bonding network surrounding the water oxidizing complex, thereby supporting proper turnover and minimizing charge recombination. Bicarbonate, coordinated to the non-heme iron that bridges the primary and secondary quinones, plays a key role on the acceptor side by facilitating electron transfer and maintaining redox balance within the plastoquinone pool. While traditionally viewed as independent, previous studies suggest that chloride and bicarbonate may act cooperatively to coordinate proton and electron transfer across PSII. To examine this possible relationship, the hypercarbonate-requiring cyanobacterium Limnospira maxima was studied due to its high tolerance for dissolved inorganic carbon and halide substitution. This work investigates how bicarbonate depletion impacts PSII activity in bromide substituted cells, in comparison to the native chloride containing system, probing potential interdependencies between chloride and bicarbonate. In 77K fluorescence spectra, bromide substituted cells retain a higher PSII:PSI emission ratio and relatively elevated F685:F695 ratio, consistent with greater antenna association under depletion. Fast repetition rate fluorometry (FRR) fluorescence revealed a loss of stable PSII centers in bromide depleted samples. Q_A reoxidation kinetics showed fewer active centers overall, with the remaining centers transferring electrons rapidly to Q_B or the non-heme iron but unable to sustain downstream turnover. Cytochrome b₆f and plastocyanin measurements indicate enhanced PSI cyclic electron flow, suggesting compensatory energy balancing when linear flow through PSII is restricted. P700 oxidation signals further support stronger and faster PSI activity under depletion. Together, these studies indicate that chloride and bicarbonate work together to sustain PSII turnover and their combined depletion disrupts the balance of electron transfer across the photosynthetic apparatus in Limnospira maxima.

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