

Modelling Changes in the Carbon Chemistry of the Aquatic Media during Photosynthesis

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Abstract

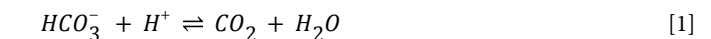
Mathematical modeling of systems requires a considerable knowledge about the subsystems, and the various rate processes and transfer coefficients that control the system. One such system involves changes in the carbon chemistry of the aquatic media during photosynthesis because inorganic carbon is a potentially limiting factor in the aquatic media. We used two artificial systems: an aquarium and a pond system with Hydrilla as the major photosynthetic organism to study the changes in the carbon chemistry and the carbon species taken up. The study depicts that carbon dioxide is the major molecular species taken up and in its absence; free carbon dioxide is released initially from the dissociation of bicarbonate ions rather than its direct use. The rate of entry cannot be accounted directly by diffusion alone because of the pH gradients in and out of the cell, and therefore carbon concentrating mechanisms and aquaporins are thought to be involved in the process. The study gives a clear picture of the amount of carbon dioxide available in the free form and the amount released from bicarbonate ions and used in photosynthesis, and can be accounted perfectly.

Keywords: Modelling; Carbon chemistry; Photosynthesis; Stroma; Diffusion

Introduction

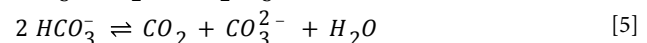
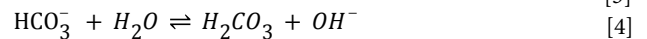
Photosynthesis requires net transport of inorganic carbon from the bulk media into the cell. At the site of carbon fixation is the chloroplast stroma which is surrounded by a membrane. CO₂ can freely cross the chlorophyll membrane by diffusion [1]. As CO₂ is removed from the bulk media, its concentration decreases and causes the relative concentration of bicarbonate and carbonate ions to change, and the pH to increase. In some cases the rate of diffusion cannot account for the observed rates of exchange across the membrane and diffusion through protein channels has been suggested as an alternative mechanism [2]. In any case this diffusion can be explained by Ficks law along a concentration gradient.

A conservative estimate of the rate of diffusion was given by Falkowski and Raven [1] to be about 2.6 μmol m⁻²s⁻¹ and is supported by the carbon pump, and the enzymes Rubisco and carbonic anhydrase aid in the process. Upon illumination of the chloroplast, the pH of the stroma rises from 7.0 to 8.0 because of the proton gradient produced through the photolysis of water. This increase in pH activates Rubisco which can fix 3-10 carbon dioxide molecules per second [3,4]. Ribulose-1,5-bisphosphate carboxylase/oxygenase, commonly known by the abbreviation RuBisCO, is an enzyme involved in the first major step of carbon fixation, a process by which atmospheric carbon dioxide is converted by plants to energy-rich molecules such as glucose. In chemical terms, it catalyzes the carboxylation of ribulose-1,5-bisphosphate. Once the free carbon dioxide in freshwater decreases below the level of utilization, the plants uses bicarbonate and carbonate ions as their source of carbon dioxide as follows:



One of the problems that we encountered during our studies on photosynthesis and respiration in polluted and unpolluted aquatic environments is the specific reaction releasing carbon dioxide during photosynthesis in the event when free carbon dioxide is unavailable.

Work on the modeling of changes in inorganic carbon due to photosynthesis and respiration has been done by King [5], Young and King [6], King and Novak [7], Novak and Brune [8], Leibr et al. [9], Golubiatnikov et al. [10], Heymans et al. [11], Xing et al. [12] and Mukherjee [13-18]. However, the question remains whether the plants use bicarbonate ions directly during a scarcity of free carbon dioxide or the bicarbonates release carbon dioxide during the process and has been the subject of considerable research [19,20]. Conventionally various equations have been formulated to explain this release during different carbon equilibrium as follows:



In 2002 we developed a model based on established chemical principles to define the changes in carbon speciation due to photosynthesis and respiration, and the addition and deposition of calcium carbonate. We prepared a database from our three year study on two simulated systems [14,15].

Using the model we calculated the changes in carbon speciation and pH equilibrium of the aquatic media due to the uptake of carbon dioxide. In the next step we have drawn inferences on whether bicarbonates are taken up in the absence of CO₂ or the bicarbonates

dissociate into carbonates and carbon dioxide which is then taken up for photosynthesis.

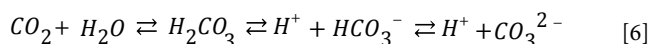
Materials and Methods

Chemical analysis of water samples was done using standard techniques [21]. The method of Culberson et al. [22] and Strickland and Parsons was used to calculate alkalinity by the pH method [23,24].

Values for total inorganic carbon, free carbon dioxide, carbonates and bicarbonates were calculated using the basic dissociation equation for polyprotic acids [9,24] and our mathematical model.

Field studies were done on aquatic systems (a ponds with a depth of 0.5 m) and laboratory simulation studies were conducted in an aquarium (dimensions: 0.5 × 0.5 × 1.5 m³), to calculate the effect of photosynthesis, respiration, and carbonate addition on the carbon speciation and hydrogen ion concentration, and compared with field data collected from a simulated freshwater aquatic system.

System design



Carbon dioxide reacts with water to form a weak acid known as carbonic acid which dissociates as follows:

The amount of CO₂ present as simple solution plus that in the form of carbonic acid is termed as free CO₂, while the amount present in the form of carbonates and bicarbonates is termed as bound carbon dioxide. If a strong acid is added the bound carbon dioxide is converted into the free form. The amount of acid required to accomplish this is a measure of the alkalinity.

Carbonic acid is a polyprotic acid that is, it has more than one ionizable proton, and the distribution of the different species is a function of the pH. It is thus possible to calculate the fraction of the total inorganic carbon (ΣC_t) that exists in a given form under a specific pH.

Processes which utilize carbon dioxide (such as photosynthesis) shift the equilibrium to the right increasing the pH. In contrast, processes releasing carbon dioxide (such as respiration) shifts the equilibrium to the left, decreasing the pH. The carbon balance and the pH may be altered by two other processes: addition of carbonates or bicarbonates or the deposition of calcium carbonate. The above four processes (photosynthesis, respiration, addition, and deposition) change the carbon budget which can be represented as follows:

$$\Sigma C_t = H_2CO_3 + HCO_3^- + CO_3^{2-} \quad [7]$$

Then the fractions of the various forms of carbon are as follows:

$$\alpha_0 = \frac{H_2CO_3}{\Sigma C_t}; \quad \alpha_1 = \frac{HCO_3^-}{\Sigma C_t}; \quad \alpha_2 = \frac{CO_3^{2-}}{\Sigma C_t}$$

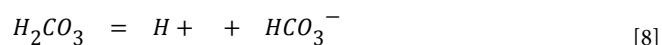
where $\alpha_0 + \alpha_1 + \alpha_2 = 1$

and α_0 = fraction of free carbon dioxide (Table 1)

α_1 = fraction of bicarbonates

α_2 = fraction of carbonates

Considering the two stage ionization of carbonic acid we have:



and the equilibrium constant

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7} \quad [9]$$



$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.8 \times 10^{-11} \quad [11]$$

and the equilibrium constant for this reaction is

$$HCO_3^- = \frac{K_1[H_2CO_3]}{[H^+]} \quad [12]$$

we can also express CO₃²⁻ in terms of [H₂CO₃] and [H⁺] as:

$$CO_3^{2-} = \frac{K_2[HCO_3^-]}{[H^+]} \quad [13]$$

Similarly, total inorganic carbon (ΣC_t) can be derived from alkalinity (A), H⁺ and the dissociation constants as follows

$$\Sigma C_t = \frac{A([H^+]^2 + K_1[H^+] + K_1K_2)}{K_1[H^+] + 2K_1K_2}$$

and equation 7 can also be expressed as:

$$\frac{d\Sigma C_t}{d[H^+]} = \frac{AK_1([H^+]^2 + 4K_2[H^+] + K_1K_2)}{(K_1[H^+] + 2K_1K_2)^2} + \frac{[H^+]^2 + K_1[H^+] + K_1K_2}{K_1[H^+] + 2K_1K_2} \times \frac{dA}{d[H^+]}$$

Photosynthesis and Respiration Addition and deposition of Carbonates

Thus using our system design we can evaluate the various carbon species using the H⁺ concentration and the first (K₁) and second (K₂) dissociation constants of carbonic acid. Similarly we can also calculate the rate of change of total carbon using equation 14.

In this paper we have used the data base and the model to explain the process that accounts for the changes in the freshwater aquatic system due to photosynthesis and respiration.

Results

Tables 1 and 3 gives the changes in the various species of carbon due to photosynthesis while Tables 2 and 4 have been derived from Tables 1 and 2 respectively. Using equation 6 we calculated the relative concentrations of all the inorganic carbon species and the rate of

change in inorganic carbon with respect to the change in H⁺ as shown below. The H⁺ concentration was similarly calculated from the relative concentrations of carbon dioxide (H₂CO₃), bicarbonate ions (HCO₃⁻) and k₁.

H ⁺ *10 ⁻⁸ moles l ⁻¹	ΣCt	CO ₂	HCO ₃ ⁻ mmoles l ⁻¹	CO ₃ ²⁻
1.6595	0.828398	0.030698	0.795399	0.002301
0.5495	0.803181	0.010048	0.78626	0.006868
0.537	0.802791	0.009816	0.785951	0.007025
0.5248	0.802403	0.009588	0.785629	0.007186
0.5129	0.802016	0.009366	0.785301	0.007349
0.5012	0.801631	0.009149	0.784964	0.007518
0.4786	0.800864	0.008729	0.784269	0.007865
0.4571	0.800101	0.008329	0.783544	0.008228
0.4467	0.799719	0.008135	0.783168	0.008416
0.4365	0.799339	0.007946	0.782785	0.008608
0.4169	0.798577	0.007581	0.781992	0.009004
1.2426	-0.029821	-0.023117	-0.013407	0.006703

Table 1: Showing the changes in hydrogen concentration and carbon speciation due to photosynthesis in an aquarium with an alkalinity of 0.8 meq l⁻¹ consisting of Hydrilla as producers.

ΔΣCt	ΔHCO ₃	ΔCO ₃ ²⁻	ΔCO ₂	Δ HCO ₃ / CO ₃ ²⁻	Total CO ₂ utilized
-0.025217	-0.009134	0.004567	-0.02065	2	0.025217
-0.00039	-0.000314	0.000157	-0.000232	2	0.000389
-0.000388	-0.000322	0.000161	-0.000228	2	0.000389
-0.000387	-0.000326	0.000163	-0.000222	2	0.000385
-0.000385	-0.000338	0.000169	-0.000217	2	0.000386
-0.000767	-0.000695	0.000347	-0.00042	2	0.000767
-0.000763	-0.000726	0.000363	-0.0004	2	0.000763
-0.000382	-0.000376	0.000188	-0.000194	2	0.000382
-0.00038	-0.000384	0.000192	-0.000189	2	0.000381
-0.000762	-0.000793	0.000396	-0.000365	2	0.000761
-0.02982	-0.013408	0.006703	-0.023117		0.02982

Table 2: The flux of various carbon species drawn from Table 1.

H ⁺ *10 ⁻⁸ moles l ⁻¹	ΣCt	HCO ₃ ⁻ m moles l ⁻¹	CO ₂	CO ₃ ²⁻
1.148	0.6134003	0.595025	0.015888	0.002488
1.047	0.611753	0.594549	0.014478	0.002725

0.8912	0.6091066	0.593606	0.012303	0.003196
0.537	0.6020932	0.589463	0.007362	0.005269
0.2754	0.5936092	0.579791	0.003714	0.010104
0.1412	0.5827542	0.561817	0.001845	0.019091
0.0912	0.5725803	0.542858	0.001151	0.028571
0.0871	0.5713107	0.540432	0.001095	0.029784
0.0759	0.5672387	0.532508	0.000939	0.033701
0.0525	0.5542279	0.507218	0.000619	0.046391
0.0447	0.5474434	0.493861	0.000513	0.053069
0.0269	0.5214059	0.442255	0.000277	0.078871
0.0295	0.5266762	0.452731	0.000311	0.073634
0.0229	0.5116335	0.422817	0.000225	0.088592
0.0209	0.5057517	0.411104	0.000199	0.094448
0.0214	0.5072415	0.414071	0.000206	0.092964
0.0162	0.4885925	0.376901	0.000142	0.111549
0.0151	0.483698	0.367138	0.000129	0.116431
0.0138	0.477057	0.353887	0.000114	0.123057
0.0098	0.4514034	0.302669	0.000069	0.148665
0.0182	0.496558	0.392784	0.000166	0.103608

Mean CO₂=0.008778

The potential changes from -56.4 mv to -180.06 mv=-123.66 mv=0.12366 v Limiting concentration of carbon dioxide (0.0025 mmoles or 2.5 μ moles)

Table 3: Showing the changes in hydrogen concentration and carbon speciation due to photosynthesis in a simulated pond system with an alkalinity of 0.6 meq l⁻¹ consisting of Hydrilla as producers.

(From Table 3; row 1 and 2) Initial pH: 7.94, final pH: 7.98 half average pH: 7.96; ΔH⁺=0.101 × 10⁻⁸; ΔΣCt=0.0016473

$$\frac{d \sum Ct}{dH^+} = \frac{0.6 \times 10^{-3} \times 4.3 \times 10^{-7} \left[(1.0965 \times 10^{-8}) + 4 \times 4.8 \times 10^{-11} \times 1.0965 \times 10^8 + 4.3 \times 4.7 \times 10^{-18} \right]}{\left[4.3 \times 10^{-7} \times 1.0965 \times 10^{-8} + 2 \times 4.3 \times 4.7 \times 10^{-18} \right]^2}$$

=0.000001647 moles or 0.001647 moles

For instance in Table 3; row 2 we have: HCO₃⁻=0.5945492,

H₂CO₃=0.014478, and k₁=4.3 × 10⁻⁷ then

$$[H^+] = \frac{k_1 \times [H_2CO_3]}{[HCO_3^-]} = \frac{4.3 \times 10^{-7} \times 0.014478}{0.594592} = 1.047 \times 10^{-8}$$

The specific growth rate was calculated from the equation of Young and King [6] as follows:

$$\mu_{\Delta t} = \frac{\Delta M / \Delta t}{m} = \frac{(M_t - M_0) / (t - t_0)}{\left(\frac{M_t + M_0}{2} \right)} \quad [15]$$

Where μ_{Δt}=specific growth rate during a time increment (hr⁻¹)

ΔM=biomass increment (inorganic carbon fixed)

M; t, t₀=boundary parameters of time increment

Δt=t-t₀=time increment (hr)

M=average standing crop biomass during the time increment

In the simulated pond system the alkalinity was 0.6 and the initial pH was 7.94. Photosynthesis started at 0630 hours and as light intensity increased, there was a continuous increase in photosynthesis and utilization of inorganic carbon. With the utilization of inorganic carbon there was a slow rise in pH (Figure 1). The total amount of inorganic carbon taken up from the bulk media was about 168.755 μ moles per liter. Photosynthesis stopped at about 1600 hours and respiratory processes became dominant.

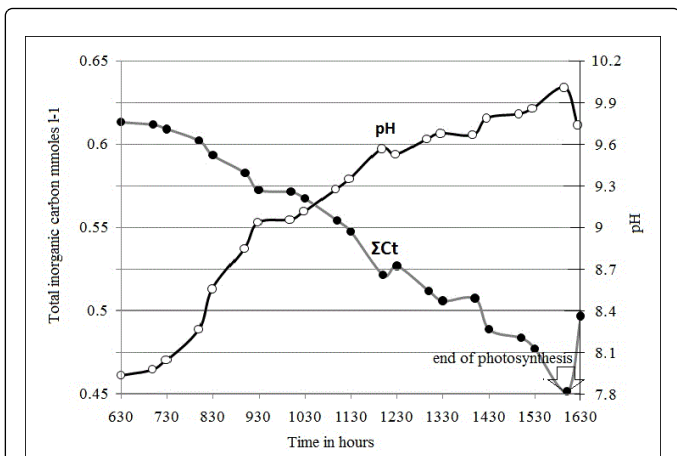


Figure 1: Changes in pH and total inorganic carbon in the simulated pond system.

In the initial stages when free carbon dioxide was available the average rate of dissociation of bicarbonate ions was about 8 μ moles per hour (Figure 2) but, as the carbon dioxide decreased below the limiting concentration (2.5 μ moles; Shameih [25]; King [5]) the dissociation of bicarbonate ions increased to about 45 μ moles per hour (5.6 times). With the change in the carbon equilibrium the pH increased to about 10.01 at the end of the day when photosynthesis stopped. The ratio of carbonates to bicarbonates increased from 0.004 to 0.5. At the limiting concentration of carbon dioxide this ratio was about 0.017. The mean specific growth rate was about 34.9 μ moles hr^{-1} (Figure 3).

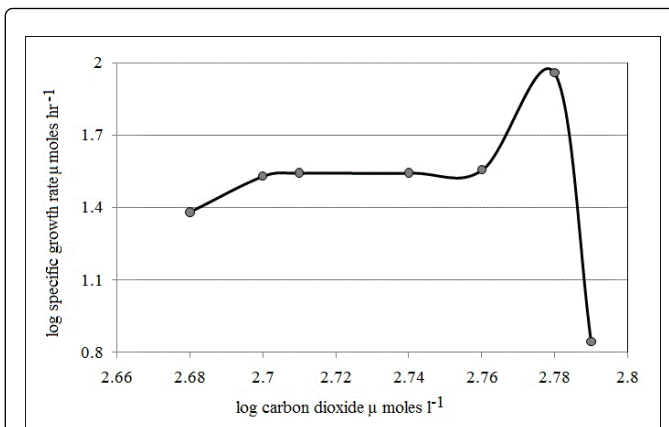


Figure 3: The specific growth rate in the simulated pond.

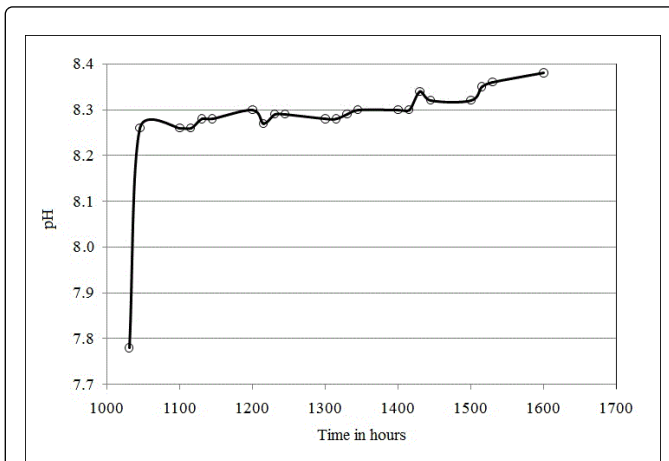


Figure 4: Changes in pH in the aquarium with photosynthesis.

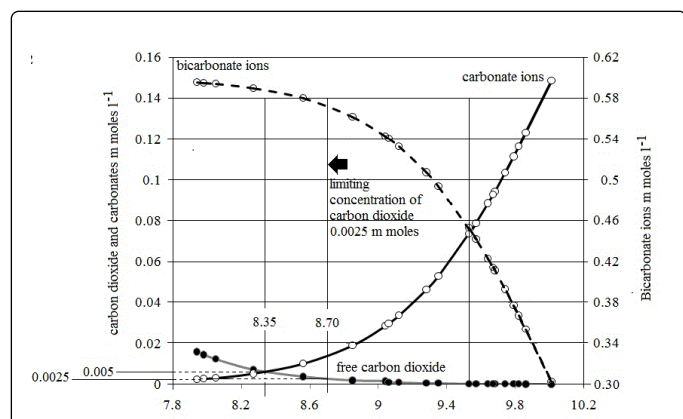


Figure 2: Showing the changes in the concentration of carbon dioxide, bicarbonates, carbonates and pH with photosynthesis, and the limiting concentration of free CO₂ in the simulated pond.

In the aquarium the alkalinity was 0.8 and an initial pH of 7.78. The system was started at 1030 hours and since the light intensity was constant the pH increased rapidly and reached an equilibrium position (Figure 4). The total amount of inorganic carbon taken up from the bulk media was about -29.821 μ moles per liter. We stopped the system at 1600 hours after which the respiratory processes became dominant. In this system the carbon dioxide did not reach limiting concentration (at the end of photosynthesis the concentration is 7.581 μ moles per liter). Maximum photosynthesis occurred at the start of the system using 25.217 μ moles (in the first fifteen minutes) while throughout the rest of the time photosynthesis used about 16 μ moles per liter per hour. The amount of carbon dioxide utilized throughout the rest of the day was low, so the rate of dissociation of bicarbonates was relatively low and the ratio of carbonates to bicarbonates increased from 0.003 to 0.012 (Figure 5).

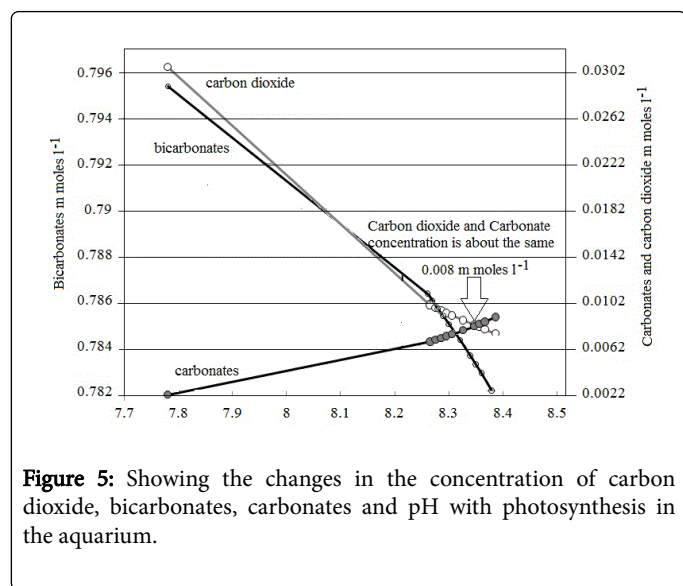


Figure 5: Showing the changes in the concentration of carbon dioxide, bicarbonates, carbonates and pH with photosynthesis in the aquarium.

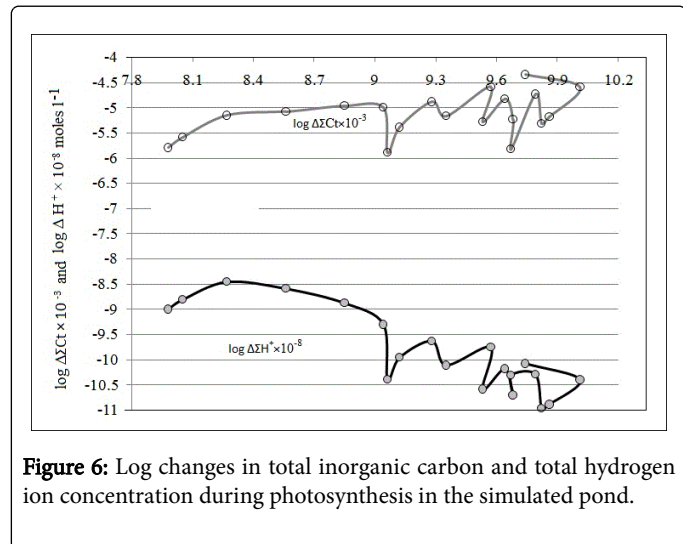


Figure 6: Log changes in total inorganic carbon and total hydrogen ion concentration during photosynthesis in the simulated pond.

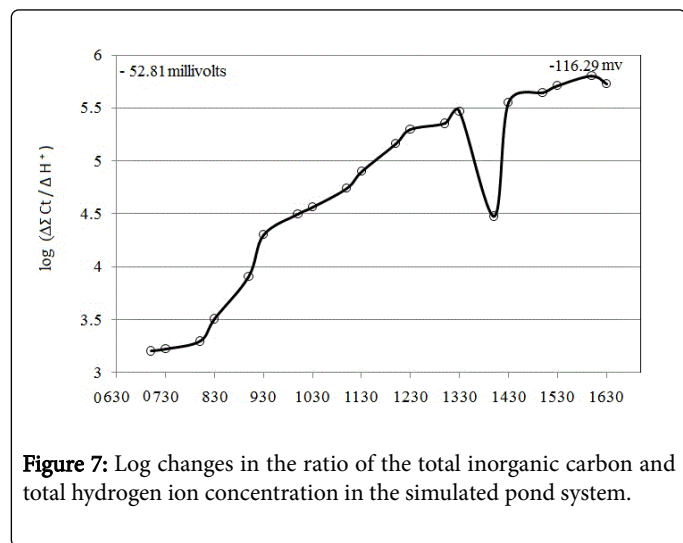
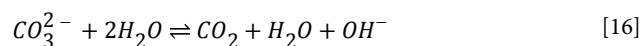


Figure 7: Log changes in the ratio of the total inorganic carbon and total hydrogen ion concentration in the simulated pond system.

The changes in total inorganic carbon and hydrogen ion during the photosynthetic process followed the same pattern (Figure 6) and the ratio of the change in inorganic carbon and hydrogen ion increased as photosynthesis proceeded (Figure 7).

The CO₂ flux from the bulk media into the Hydrilla leaves was about 2.3 μ moles m⁻² s⁻¹ (2.6 μ moles m⁻² s⁻¹; [1]) initiating a specific growth rate of about 34.88 μ moles hr⁻¹. The total amount of carbon utilized in the aquarium was about -29.82 μ moles while in the simulated pond system the total amount of carbon utilized was -168.755 μ moles. Based on the data given in Table 2 and 3, as the amount of free carbon dioxide decreases to limiting concentrations the bicarbonates dissociate to provide free carbon dioxide for photosynthesis as represented in equation 5. If bicarbonate ions were used directly then the concentration of the bicarbonate ions would have decreased and carbonate ions would have dissociated to buffer the pH. This would have decreased the concentration of carbonates, increasing the pH and hydroxide alkalinity considerably as follows:



However, in our studies we found the concentration of carbonates to increase confirming our view that two moles of bicarbonate ions dissociate to produce one mole of carbon dioxide and one mole of carbonate ion. The carbon dioxide released is used up in photosynthesis while the carbonates released, buffers the pH. Our results show that in the case of Hydrilla, carbon dioxide is the basic carbon molecule that is used in photosynthesis.

Discussion

Diffusion is the sole means by which inorganic carbon crosses the plant membranes. Only CO₂ can freely cross the plasmalemma or chloroplast envelope by diffusion in contrast to HCO₃⁻ and CO₃²⁻. The obvious mechanism is for the gas to dissolve in the membrane lipid phases, diffuse across the membrane, and dissolve back into the aqueous phase at the other side. In some cases the rate of diffusion by this mechanism cannot account for the observed rates of exchange across the plasmalemma, and CO₂ diffusion through protein channels have been suggested as an alternative mechanism [26]. Carbon concentrating mechanisms (CCM's and aquaporins) have also been suggested in order to account for the rate of influx of CO₂ [27]. In either case diffusion occurs from a high to a low concentration of the diffusing solute. The diffusion transport across a plane can be described by Ficks law:

$$J_{bc} = D \frac{dC}{dL} \quad [17]$$

Where:

J_{bc}=flux of the diffusing molecule through the plane (mol m⁻²s⁻¹)

C=diffusing molecule (mol m⁻³)

D=empirically derived diffusion coefficient (m² s⁻¹)

L=the boundary layer (m)

The concentration gradient is given by dC/dl and J_{bc} is given as

$$J_{bc} = \frac{D(C_b - C_c)}{L} \quad [18]$$

where

C_b=the bulk phase concentration of the diffusing molecule

And C_c =the concentration of the molecule inside the cell.

L =thickness of the membrane= 5×10^{-9} m

Taking into consideration the mean values we have: J_{bc} =flux of the diffusing molecule through the plane ($\text{mol m}^{-2}\text{s}^{-1}$)= $2.34 \mu\text{mol m}^{-2}$

Thus $C_b - C_c = 6.5 \mu\text{ moles m}^{-2}$ in the simulated pond and $2.28 \mu\text{ moles m}^{-2}$ in the aquarium when the concentration of CO_2 in the bulk media C_b is $8.78 \mu\text{ moles m}^{-3}$ and $10.9 \mu\text{ moles m}^{-3}$ respectively (Tables 2 and 4).

$s^{-1}/0.82 \mu\text{mol m}^{-2}\text{s}^{-1}$ (simulated pond/aquarium)

D =diffusion coefficient of $\text{CO}_2 = 1.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

$\Delta\Sigma\text{Ct}$	ΔHCO_3^- m moles l^{-1}	ΔCO_3^{2-}	ΔCO_2	$\Delta\text{HCO}_3^-/\text{CO}_3^{2-}$	Total CO_2 utilized
-0.00165	-0.000476	0.000237	-0.001409	2	0.001646
-0.00265	-0.000943	0.000471	-0.002175	2	0.002646
-0.00701	-0.004143	0.002073	-0.004941	2	0.007013
-0.00848	-0.009672	0.004835	-0.003648	2	0.008484
Limiting concentration of free carbon dioxide					
-0.01086	-0.017974	0.008987	-0.001869	2	0.010856
-0.01017	-0.018959	0.00948	-0.000694	2	0.010174
-0.00127	-0.002426	0.001213	-0.000056	2	0.001269
-0.00407	-0.007838	0.003917	-0.000156	2	0.004073
-0.01301	-0.025381	0.01269	-0.00032	2	0.013011
-0.00678	-0.013357	0.006678	-0.000106	2	0.006784
-0.02604	-0.051602	0.025802	-0.000236	2	0.026038
0.00527	0.010473	-0.005237	0.000034	2	0
-0.01504	-0.029914	0.014958	-0.000086	2	0.015043
-0.00588	-0.011713	0.005856	-0.000026	2	0.005882
0.001489	0.002967	-0.001484	0.00007	2	0
-0.01865	-0.037171	0.018586	-0.000064	2	0.01865
-0.00489	-0.009763	0.004882	-0.000013	2	0.004895
-0.00664	-0.013251	0.006626	-0.000015	2	0.00664
-0.02565	-0.051217	0.025608	-0.000045	2	0.02565
-0.162					
End of photosynthesis					
-0.162	-0.29236	0.146178	-0.015756		0.168755

$$\Delta\Sigma\text{Ct} = \Delta\text{HCO}_3^- + \Delta\text{CO}_2 - \Delta\text{CO}_3^{2-} = (-0.292360 - 0.015756) + 0.146178 = -0.161938.$$

Total CO_2 utilized = 0.168755 (168.755 $\mu\text{ moles}$)

Table 4: The flux of various carbon species drawn from Table 3.

Our experiment with Hydrilla in both the aquarium and the simulated pond shows that the major carbon component entering the plant is carbon dioxide formed by the dissociation of bicarbonate ions. Once CO_2 enters the system it is converted to bicarbonate ions by the enzyme carbonic anhydrase, and remains within the system due to its relatively low diffusibility (Figure 8). The bicarbonate is converted into carbon dioxide in the active centre (using carbonic anhydrase) and is utilized by Rubisco for the conversion of Ribulose 1,5-biphosphate to two molecules of 3-phosphoglycerate.

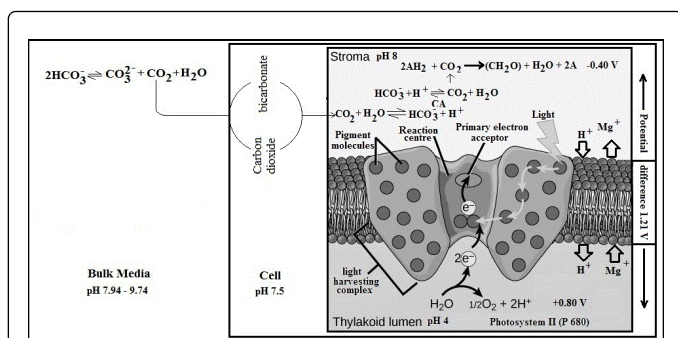


Figure 8: The entry of carbon dioxide and formation of carbohydrates during the process of photosynthesis. Carbon dioxide is converted rapidly into bicarbonates and trapped in the cell to prevent its diffusion back into the bulk media.

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