

EXCHANGE RATES OF O₂ AND CO₂ BETWEEN AN ALGAL CULTURE AND ATMOSPHERE

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Abstract—The mechanism of CO₂ and O₂ exchange between atmosphere and an algal mini-pond was examined by monitoring, with a novel microcomputer based system, pH, dissolved oxygen, turbidity, light intensity and temperature. The microcomputer based system was also used to monitor on-line the net oxygen production rate (OPR) and the gas exchange processes. The measured data support the assumption that the gas exchange is driven by the gradient of the partial pressure of the gases across the imaginary boundary layer (*z* layer). An analytical model based on this assumption was simulated by a computer and compared with the experimental data. The photosynthetic activity of a blue-green alga (*Spirulina platensis*) mini-pond as it is influenced by the CO₂ concentration in the growth medium is discussed. The overall photosynthetic process was studied by comparing the experimental data with a mathematical model, evaluating the effectiveness of alternative carbon sources.

Key words—gas exchange, oxygen, carbon dioxide, algal pond, *Spirulina platensis*, oxygen production rate

INTRODUCTION

It is well recognized that algal mass cultures have a great potential for producing various materials of industrial importance and for solving environmental problems (Round, 1973; Richmond *et al.*, 1981). Whereas the main interest in algal cultures has been in the past in single cell protein production (Round, 1973; Richmond *et al.*, 1981) and water treatment (Goldman *et al.*, 1981), recent developments suggest the possibility of extracting various biochemical products (Vonshak *et al.*, 1982), or utilizing algae as an alternative energy source.

Despite the differences between the various types of algae, the basic biotechnology of algal cultures has many common features, particularly the requirements for carbon, phosphorus, nitrogen and trace elements. Indeed, the feasibility of large scale production depends heavily on the optimal utilization of these feed materials. As the organic carbon produced via photosynthesis represents approximately half of the total biomass, its supply rate must be much higher than those of other nutrients, and hence the importance of studying alternative methods for feeding it to the system (Goldman *et al.*, 1972, 1974, 1981, 1982).

In most algal growth media, as in natural waters, the carbonate system constitutes the principal pH buffering system (Skirrow, 1975). Uptake of inorganic carbon through photosynthesis results in a change of the equilibrium conditions, resulting in a pH rise. These pH changes cause a redistribution of

various carbon species, which may have an adverse effect on the growth processes (Goldman *et al.*, 1974, 1981).

Several hypotheses have been proposed (Goldman *et al.*, 1972, 1974, 1982) about the form in which the carbon is assimilated by the algae and the importance of the diffusion process that transports CO₂ from the atmosphere to the medium has been discussed widely (Bollin, 1960; Quinn and Otto, 1979; Emerson, 1975). There are however a number of open questions concerning CO₂ exchange between the atmosphere and the medium, the answer to which may improve the technology of algal production.

Diffusion of CO₂ from normal atmosphere cannot keep pace with algal CO₂ fixation during intense algal growth; it is thus not uncommon to observe a rise in pH to over pH 10 in some natural waters and mass culture systems (Goldman *et al.*, 1981). Intense stirring may increase, to some degree, CO₂ transport from the atmosphere (Goldman *et al.*, 1981; Kanwisher, 1962; Liss, 1973), but the role of atmospheric contribution in intense algal growth is still not completely understood. In a recent paper Nishimuna *et al.* (1983) studied the exchange of oxygen and carbon dioxide algal blooms in a pond, and reported that during the production period, 60% of produced O₂ was lost to the atmosphere and 20% of the consumed TCO₂ (see Appendix) was supplied from the atmosphere. During the decomposition period, 80% of consumed O₂ was supplied from the atmosphere and 35% of produced TCO₂ was lost to the atmosphere.

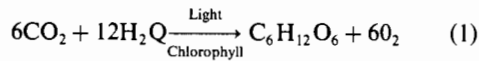
The objective of the present study was to investigate CO₂ and O₂ exchange between a laboratory algal pond and the atmosphere during normal

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growth. This was accomplished by fitting experimental data to a simple model which describes the gross process of carbon assimilation and O₂ evolution and takes into account gas exchange between the culture and the atmosphere. The rate of photosynthesis and the gas diffusion fluxes were determined by a previously developed on-line procedure (Ben-Yaakov *et al.*, 1985). The method is based on parameter estimation which is carried out after the system is perturbed from its dynamic equilibrium.

THEORETICAL CONSIDERATIONS

The photosynthetic process can be described by the following simplified equation:



which emphasizes the inherent relationship between CO₂ consumption and O₂ production rates (Riley and Chester, 1971). The real O₂/CO₂ quotient differs from one and its value depends on the average C:N:P ratio of the algae and the experimental conditions.

The exchange of O₂ and CO₂ between the gas and liquid phases, which is fundamental to the growth process, can be described by the Film Model which is generally used to describe gas exchange between gas and liquid phases (Danckwerts, 1970). It consists of an imaginary stagnant solution layer (z layer) separating the gas phase from the bulk solution, both of which are assumed to be well mixed. The exchange process between the two phases is thus assumed to be controlled by molecular diffusion of the dissolved gas through the z layer. In the case of CO₂ this simple model is complicated by the fact that CO₂ reacts with the water. The process might be dependent on the hydration kinetics as well as migration rates of a number of species such as HCO₃⁻ and CO₃²⁻ (Bollin, 1960; Quinn and Otto, 1979; Emerson, 1975; Kanwisher, 1962; Liss, 1973). However, for a well mixed solution (low z) the importance of the kinetics can be neglected (Ben-Yaakov and Guterman, 1983).

Assuming that the growth conditions of the culture do not change appreciably during a given experiment or set of experiments, net O₂ production rate OPR can be used as an indicator for the photosynthetic rate. Dissolved oxygen concentration in the culture can be described by the following differential equation:

$$\frac{d\text{DO}(t)}{dt} = -\frac{D_{\text{O}_2}}{zH} [\text{DO}(t) - \text{DO}(\text{atm})] + F_{ph} \quad (2)$$

The solution for O₂ concentration is an exponential function:

$$\text{DO}(t) = [\text{DO}(0) - A] \exp\left(-\frac{D_{\text{O}_2}}{zH} t\right) + A$$

$$A = \text{DO}(\text{atm}) + \frac{zH}{D_{\text{O}_2}} F_{ph} \quad (3)$$

which predicts an exponential increase in DO with a time constant $(D_{\text{O}_2}/zH)^{-1}$ and a final value A (Ben-Yaakov *et al.*, 1985). This final value may not be reached if the supersaturation level is high enough to permit gas bubble formation (Ben-Yaakov *et al.*, 1985; Horne, 1961). In this case the DO level will be limited by the critical value at which bubbles are formed. In other cases, the asymptotic value can be reached, but since z is unknown it is impossible to evaluate the photosynthetic rate from this final value [equation (3)]. Consequently, DO at a steady state is not a good measure of the photosynthetic rate. However, if the system is perturbed by a forced excitation that moves DO from its dynamic equilibrium value, DO will also follow an exponential path when returning to its quasi steady state value—this transient response can then be used to evaluate the parameters of interest (F_{ph}) and D_{O_2}/z by fitting the transient DO data to the model of equation (2)—the equation can be written as a linear equation of the form:

$$y = ax + b \quad (4)$$

where

$$y = d\text{DO}(t)/dt$$

$$a = -\frac{D_{\text{O}_2}}{zH}$$

$$b = F_{ph}$$

The variables x , y can be calculated from the DO(t) data sampled during the transient response and the parameters a and b can then be estimated by a linear least square algorithm (Ben-Yaakov *et al.*, 1985; Bevington, 1969; Raviv and Ben-Yaakov, 1982; Sorenson, 1980). Once the estimated a and b are obtained they can be used to estimate the values of F_{ph} and (D_{O_2}/z) . It should be noted that the proposed method yields an independent estimate for the gas exchange factor (D_{O_2}/z) which can then be used to calculate the estimated fluxes of both O₂ and CO₂. If the relationship between oxygen production and CO₂ consumption is known, F_{ph} can be used to estimate the net carbon consumption rate (CCR).

$$F_p C = Q F_{ph} \quad (5)$$

Considering that $(D_{\text{O}_2}/z) \cong (D_{\text{CO}_2}/z)$ (Ben-Yaakov and Guterman, 1983) the change in the concentration of inorganic CO₂ in the algal cultures can be described in a form similar to the one used for the dissolved oxygen concentration [equation (2)]:

$$\frac{dT\text{CO}_2}{dt} = -\frac{D_{\text{CO}_2} \cdot \alpha \text{CO}_2}{zH} \times [p\text{CO}_2(t) - p\text{CO}_2(\text{atm})] - F_p C \quad (6)$$

The partial pressure of CO₂ and the concentration of total CO₂, can be calculated from carbonate alkalinity and pH using the apparent constants of the

carbonate system (Skirrow, 1975):

$$p\text{CO}_2 = \frac{CA \cdot a_{\text{H}}^2}{K_1 \cdot \alpha \text{CO}_2 [a_{\text{H}} + 2K_2]} \quad (7)$$

$$T\text{CO}_2 = CA \cdot \left[\frac{a_{\text{H}} K_1 + K_1 K_2 + a_{\text{H}}^2}{a_{\text{H}} K_1 + 2K_1 K_2} \right] \quad (8)$$

The model assumes that the driving force of the CO₂ exchange processes is dependent, as in the case of O₂, on the partial pressure gradient across the *z* layer, and neglects all kinetics and migration effects. That is, the model assumes that the hydration and ionization rates effects are insignificant as compared to the overall time constant of the exchange process. In such a case the carbonate system in the bulk of solution can be considered to be in equilibrium at any instant.

Although equation (6) can theoretically be employed for estimating and $F_p C$, practical considerations suggest that simpler and better estimates can be obtained by utilizing the results for OPR and obtained from Equation (2):

$$\frac{dT\text{CO}_2}{dt} = - \frac{D_{\text{O}_2} \cdot \alpha \text{CO}_2}{zH} \times [p\text{CO}_2(t) - p\text{CO}_2(\text{atm})] - Q \cdot F_{ph} \quad (9)$$

in the present calculations Q was taken as (106/138)—this equation can then be used to determine the state of the carbonate system as well as the CO₂ exchange rates, at any time.

METHODS

The present study was carried out by the instrumentation described in detail elsewhere (Guterman and Ben-Yaakov, 1983) and, for the sake of brevity, only a general description is given here. The experimental assembly consists of a minipond (Fig. 1) that is submerged in a thermostatic bath which was in turn regulated by a dip type thermostat. The necessary stirring of the water (to prevent settling of algae) was provided by a motor-driven paddle. An independent

level control regulates water height (and volume) by automatically replenishing with deionized water the volume lost by evaporation.

The parameters measured in the present study were pH, dissolved oxygen (DO), optical density (OD), light intensity, and water and air temperatures. The electrode's signal was sent to a microcomputer via a general purpose interface/controller which has been previously described (Ben-Yaakov *et al.*, 1982). The interface comprises 16 high-impedance analog inputs, 16 digital input-output (I/O) lines, and 16 control relays. The interface/controller is connected to the microcomputer via one 8 bit I/O port plus an additional edge-sensitive input line. In the present study, we have used a Commodore model CBM3032 microcomputer which includes one free port of a Versatile Interface Adaptor (VIA) type 6522. Analog-to-digital conversion is obtained by first converting the analog signal to a proportional frequency signal and then counting the frequency pulses over a fixed period. The advantages of this conversion method are not only its low cost but also its ability to attenuate interfering noise by the inherent integration operation. The major disadvantage of the method is the low conversion rate, about one sample per second (depending on the required resolution). However, this was not proved to be a problem since the rate of change of the phenomenon under study is rather slow (time constants of hours).

Organism and growth conditions

Spirulina platensis was cultivated in a 7 l PVC mini-pond. Surface area of the mini-pond was about 1000 cm². Depth of solution was about 7 cm. The medium was gently stirred by a paddle type stirrer with an effective (solution immersed) paddle area of 25 cm² (for each of the two vanes).

The algae were grown in a Zarouk (Vonshak and Maske, 1982) solution at 35° with an average surface light intensity of about 2500 lux. The light source was an array of four fluorescent tubes (Cool White 18 W, Osram). The culture was harvested by dilution with fresh Zarouk solutions when an OD (*ca* 560 nm) of about 0.45 was reached. Dilution was carried out by adding the fresh feed solution and discarding the overflow.

Analytical methods

Dry weight, chlorophyll, PO₄ and NO₃ were measured on water samples taken from the culture twice a week. The

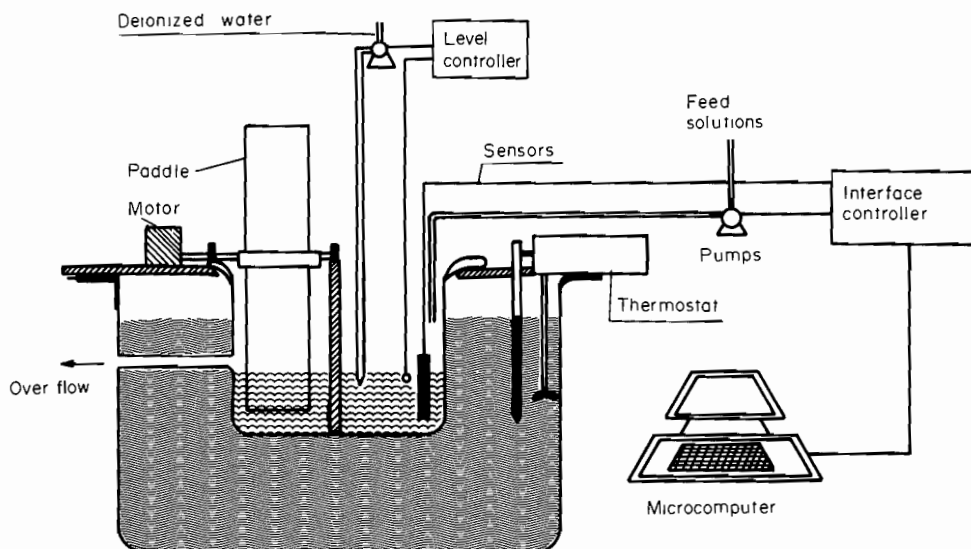


Fig. 1. Experimental assembly used.

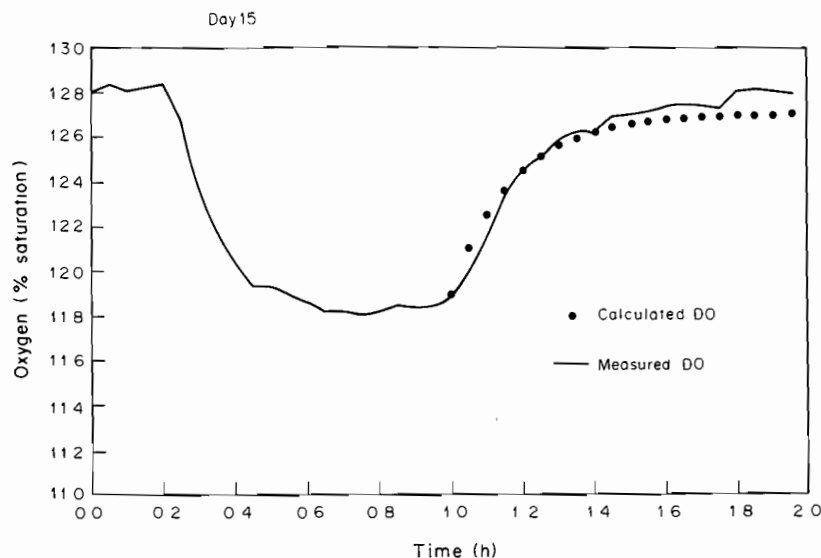


Fig. 2. Typical DO response in mini-pond to 45 min of air bubbling.

results of this measurement can be found elsewhere (Ben-Yaakov *et al.*, 1985).

Alkalinity of the medium was measured daily with an automatic titration system, described elsewhere (Ben-Yaakov *et al.*, 1982). The procedure employed follows that described earlier by Saas and Ben-Yaakov (1977).

DO perturbation

Application of the algorithm for estimation of OPR (F_{ph}) was made possible by monitoring the transient in DO level. The perturbation was obtained by bubbling air through the mini-pond solution and hence accelerating the rate at which O_2 was released from the solution to the atmosphere (Ben-Yaakov *et al.*, 1985), for the perturbation time (*ca* 45 min).

Data processing

Was carried out off line on the recorded data. However, there is no objective problem in carrying out all the analysis

including the algorithm F_{ph} estimation, and the carbonate calculation, on-line. All data processing programs were written in BASIC and the analysis was performed on a microcomputer system similar to the one used for this monitoring operation (Ben-Yaakov *et al.*, 1985).

RESULTS

The experiments were conducted for a period of 54 days, a complete data report can be found elsewhere (Ben-Yaakov *et al.*, 1985). A typical response of the system to the perturbation caused by forced air bubbling is depicted in Fig. 2. Air bubbles, which were induced for about 45 min, lower the DO level

Table 1. Operational parameter of algal mini pond as estimated by proposed model from on-line data. r^2 is the model fitting correlation [equation (4)]. \pm limits are $\pm 20\sigma$ as estimated from the t distribution

Day	$D_{O_2}/z\uparrow$ ($cm\ min^{-1}$)	OPR \uparrow ($\mu mol\ l^{-1}\ min^{-1}$)	OD (560 nm)	pH	Correlation coefficient r^2	Dissolved oxygen	
						Calculated (% saturation)	Measured
2	0.333 \pm 0.052	3.06 \pm 0.446	0.276	9.83	0.8951	131	133
3	0.353 \pm 0.023	3.13 \pm 0.196	0.322	9.85	0.9791	129.9	130
5	0.438 \pm 0.094	3.50 \pm 0.725	0.39	9.92	0.8221	126.9	127
7	0.436 \pm 0.077	3.40 \pm 0.571	0.434	9.88	0.8708	126.3	128
9*	0.606 \pm 0.060	4.07 \pm 0.376	0.28	9.32	0.9787	122.6	128
10	0.600 \pm 0.070	3.40 \pm 0.365	0.29	9.47	0.9708	119.1	125
11	0.605 \pm 0.059	2.89 \pm 0.270	0.322	9.63	0.9588	116.1	115
12	0.571 \pm 0.150	5.31 \pm 0.437	0.35	9.73	0.7633	131.3	135
14	0.396 \pm 0.039	3.39 \pm 0.306	0.41	9.83	0.9979	128.9	125
15	0.639 \pm 0.096	4.83 \pm 0.745	0.35	9.57	0.9456	125.8	127
18	0.585 \pm 0.084	4.87 \pm 0.683	0.443	9.87	0.9112	128.0	128
19	0.406 \pm 0.045	3.27 \pm 0.341	0.305	9.43	0.9459	127.2	130
24	0.758 \pm 0.096	5.47 \pm 0.685	0.385	9.96	0.9289	124.3	125
26	0.421 \pm 0.081	3.57 \pm 0.628	0.275	9.69	0.9246	128.5	125
30	0.307 \pm 0.080	2.55 \pm 0.635	0.15	9.52	0.7548	127.9	127
31	0.451 \pm 0.075	3.76 \pm 0.618	0.18	9.63	0.8822	128.0	127
34	0.432 \pm 0.072	3.62 \pm 0.586	0.29	9.89	0.9418	128.2	128
35	0.355 \pm 0.047	3.13 \pm 0.399	0.285	9.95	0.9219	129.7	130
38	0.230 \pm 0.075	1.73 \pm 0.516	0.37	9.43	0.8673	125.3	123
39*	0.507 \pm 0.027	1.71 \pm 0.086	0.2	9.27	0.9868	111.3	112
44	0.656 \pm 0.033	1.73 \pm 0.165	0.32	9.6	0.9834	118.9	118

*After dilution with Zarouk medium.

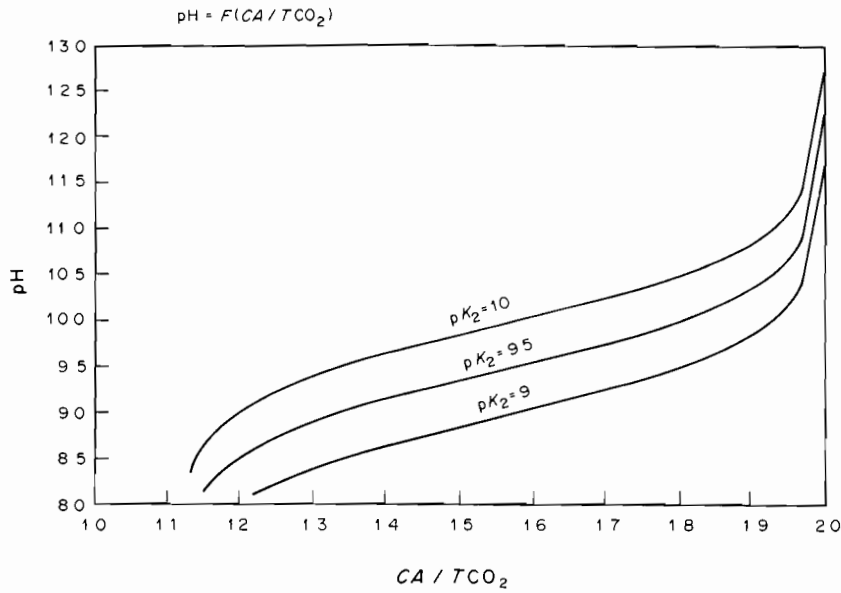


Fig. 3. Model calculated pH as a function of carbonate alkalinity and total carbonate for different values of pK_2 .

from 128% to about 118%. When the bubbling was stopped, the DO increase toward the steady state level. The OPR (F_{ph}) and the gas exchange coefficient equation (2) were evaluated for each air bubbling experiment for the period of investigation. Part of these results as well as other pertinent data that were collected during this study are given in Table 1, a complete listing of results and a thorough discussion of the method can be found elsewhere (Ben-Yaakov *et al.*, 1985).

A simulation of the "free" system response (when the forced air bubbling was removed), using the estimated values of F_{ph} and (D_{O_2}/z) is given in Fig. 2.

The estimated (D_{O_2}/z) values were in the range of 0.3–0.6 cm min^{-1} which implies that the film thickness (z) was in the range 21.2–42.4 μm and the O₂ time constant was about 10–22 min. The question of kinetic enhancement can thus be excluded in the present case (Bollin, 1960; Quinn and Otto, 1979; Emerson, 1975; Kanwicher, 1962; Liss, 1973; Ben-Yaakov and Guterman, 1983). This supports our previous assumption that the only CO₂ flux that should be considered in this case is the one directly associated with the molecular diffusion which is linearly proportional to the $p\text{CO}_2$ gradient across the z layer.

Table 2. Comparison of measured and simulated pH by proposed model

Day	Alkalinity (m-equiv l ⁻¹)	Time period (h)	pH Initial	pH final	
				Calculated	Measured
2	108.1	20	9.83	9.95	9.89
3	106.4	20	9.85	9.97	9.92
5	104.9	22	9.92	10.08	9.95
7	115.6	20	9.88	9.33	10.00
8	107.4	20	9.90	10.01	9.96
9*	122.0	20	9.32	9.50	9.50
10	159.0	20	9.47	9.59	9.63
11	161.0	20	9.63	9.72	9.75
12	159.0	24	9.73	9.80	9.85
14	173.0	22	9.83	9.92	9.91
15	170.8	45	9.57	9.85	9.84
18	170.6	21	9.87	10.00	9.94
19	192.0	44	9.43	9.63	9.77
24	195.0	24	9.96	10.120	10.05
26	213.0	22	9.69	9.77	9.80
30	203.0	13	9.52	9.57	9.63
31	156.0	25	9.63	9.76	9.80
34	158.0	44	9.89	10.05	10.12
35	153.0	45	9.95	10.17	10.04
38	153.0	24	9.43	9.68	9.50
39	160.0	3	9.68	9.69	9.70
39*	194.0	10	9.27	9.34	9.50
44	182.0	22	9.60	9.67	9.80

*After dilution with Zarouk medium.

As stated earlier, the pH increase in the solution is caused by consumption of inorganic carbon. The relationship between TCO_2 and pH can be derived from equation (8) in the form of a second order equation:

$$a_H^2 + b a_H + c = 0 \quad (10)$$

where

$$b = K_1' - \left[1 - \frac{TCO_2}{CA} \right]$$

$$c = K_1' K_2' \left[1 - 2 \frac{TCO_2}{CA} \right].$$

It is thus clear that the ratio of TCO_2/CA is the master variable that controls pH, and that the apparent constants of the carbonic acid (K_1', K_2') determine the state of the carbonate system. As $K_1 = 10^{-6}$, equation (8) can be approximated by:

$$TCO_2 = CA \left[\frac{a_H + K_2'}{a_H + 2K_2'} \right] \quad (11)$$

from which

$$pH = pK_2' - \log \left[\frac{x}{1-x} - 1 \right] \quad (12)$$

where

$$x = TCO_2/CA.$$

This equation is valid for a pH range above pH 8. Examination of equation (12) reveals that the pH is equal to pK_2' when $x = 0.666$ and that as the pK_2' value increases the buffer effect is greater (Fig. 3.) The behavior of the carbonate system can be simulated using equation (6) to calculate the change in TCO_2 and equation (12) to calculate pH. Simulations were

performed using the data available in Table 1. Initial pH, OPR and time period were the value given in the data, and the final calculated and measured pH were compared. The results of these simulations as well as other pertinent data are given in Table 2. Compatibility of the model calculated and measured pH is exemplified in Fig. 4. The reasonably good agreement suggests that the model can be used to simulate the evolution of the dissolved carbonate system along the growth process.

DISCUSSION

Notwithstanding the questions of the form of carbon which is used for assimilation by the algae, and ecological restrictions to eliminate undesired species (Richmond *et al.*, 1981), the present model can be used for estimating the contribution of the atmospheric CO_2 flux to be required carbon supply. Since the concentration of CO_2 in the atmosphere is only 330 ppm the transport gradient is always small and CO_2 diffusion is relatively ineffective unless very turbulent mixing is employed. The fluxes were studied by two simulation runs, one for 200 m-equiv (Fig. 5) and the other for 20 m-equiv (Fig. 6) carbon alkalinity (CA). The values of (D/z) and OPR were the same as in day 15 of the experiment (Tables 1 and 2). The graphs depict the diffusion fluxes between solution and atmosphere in units of percent net carbon consumption rate (FpC). It is observed that for $CA = 200$ m-equiv (Fig. 5) the atmospheric flux is negative for pH values up to pH 9.9. This implies that the CO_2 diffusion is from the solution to the atmosphere. For higher pH levels there is a net contribution reaching about 20% at pH = 11.

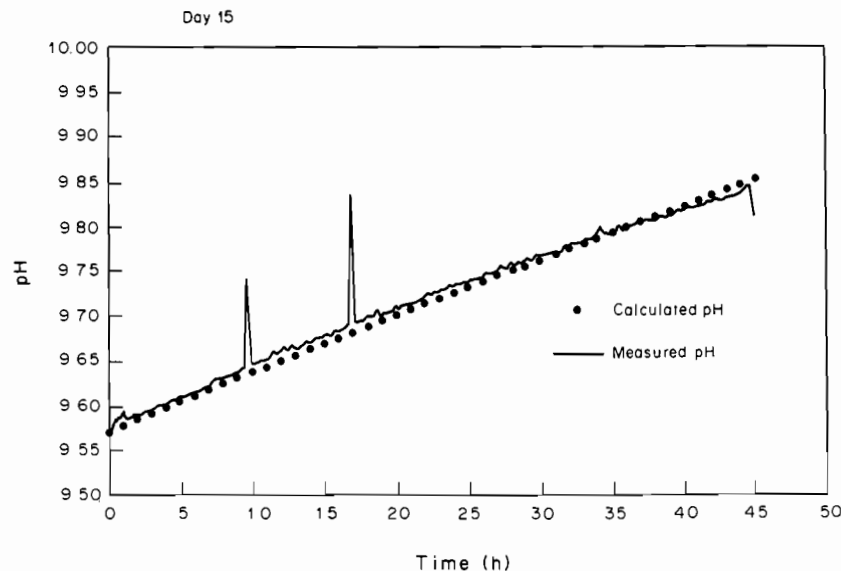


Fig. 4. A comparison between the measured and model calculated pH for the system under study based on the data of Tables 1 and 2 (Day 15).

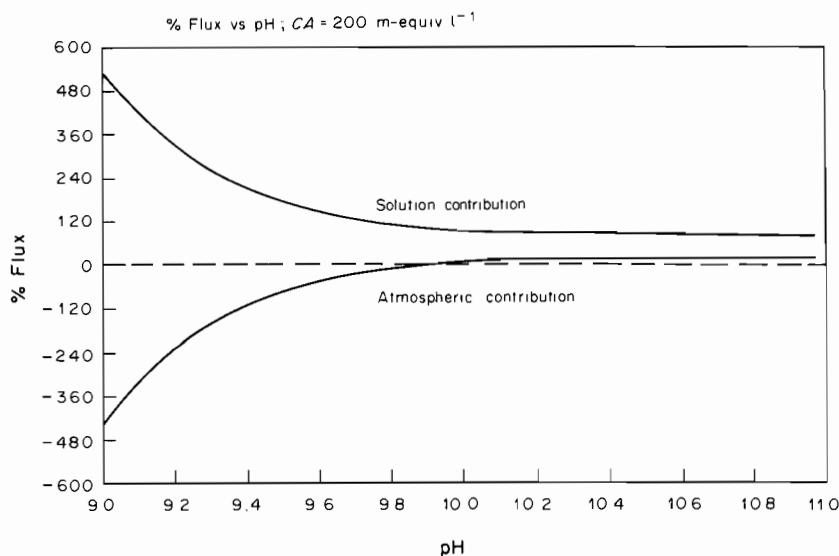


Fig. 5. Model estimated atmospheric and solution carbon contribution as percent of net photosynthetic range vs pH, for CA = 200 m-equiv l⁻¹—other parameters are those of Day 15 (Tables 1 and 2).

In the case of CA = 20 m-equiv (Fig. 6) there is no atmospheric contribution of CO₂ up to pH = 9.2. For pH greater than that the contribution of the atmospheric flux is positive, about 20% for pH = 11. Hence, the use of lower levels of alkalinity appears to be the more rational way of CO₂ utilization. However, as the CA decreases the buffer capacity of the carbonate system is reduced, as can be inferred from the time that it takes the system to reach the same pH (Figs 7 and 8). It takes about 27 h to reach pH 11 for CA = 20 m-equiv compared to 227 h for CA = 200 m-equiv. Hence, if low CA is used it will be necessary to provide an inorganic carbon supply earlier.

Assuming a constant growth condition, and that the total carbon produced via photosynthesis is about a half of the total biomass, the increment of biomass growth (T_b) can be calculated by:

$$T_b = K \int_{t_0}^{t_1} F_{ph} dt \quad (13)$$

where K is a constant. The total atmospheric contribution to the biomass (T_a) can be obtained by integrating the atmospheric flux, then:

$$T_a = K \int_{t_0}^{t_1} - \frac{D_{CO_2, CO_2}}{zH} [pCO_2(t) - pCO_2(atm)] dt. \quad (14)$$

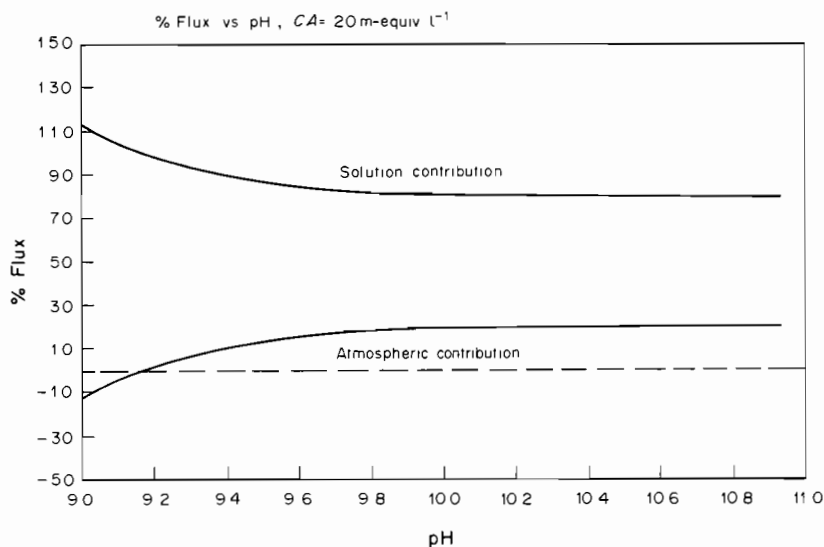


Fig. 6. Model estimated atmospheric and solution carbon contribution as percent of the net photosynthetic rate vs pH, for CA = 20 m-equiv l⁻¹—other parameters are those of Day 15 (Tables 1 and 2).

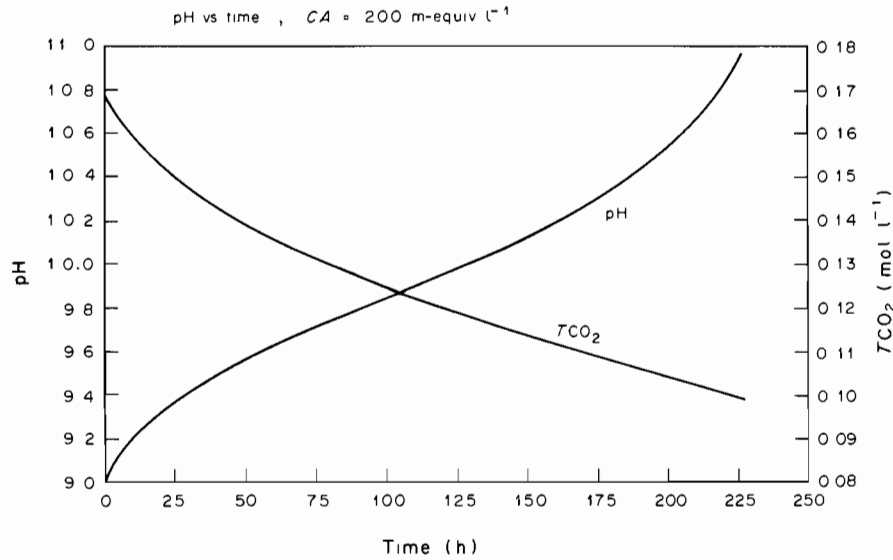


Fig. 7. Simulated pH and TCO₂ variation as a function of time. Parameters are the same as Fig. 5.

The value of T_o should be calculated of course only for positive atmospheric fluxes, so that only the atmospheric contribution is considered and not the wasting effects, which result when the $p\text{CO}_2$ pressure in the medium is higher than the atmospheric CO₂ pressure (Figs 7 and 8). This calculation was carried out for the two cases as before (CA = 20 and 200 m-equiv l⁻¹). The calculation revealed that atmospheric contribution in the first case (CA = 200 m-equiv l⁻¹) was about 7% compared to about 16% for CA = 20 m-equiv l⁻¹. This appears to confirm our earlier suggestion about the rationality of using lower levels of CA.

Considering the fact that the time constant of the DO response to a perturbation is small enough, one

can assume that there almost always exists a steady state condition, then from equation (2):

$$F_{ph} = \frac{D_{O_2} \cdot \alpha_{O_2}}{zH} \Delta p_{O_2}. \quad (15)$$

The final supersaturation level of dissolved oxygen will be thus given by:

$$p_{O_2}(\infty) = p_{O_2}(\text{atm}) + \frac{zH}{D_{O_2} \cdot \alpha_{O_2}} \cdot F_{ph}. \quad (16)$$

Using this equation, the expected supersaturation level can be calculated (Table 1) independently.

Assuming that steady state condition is also feasible for CO₂, i.e. that atmospheric CO₂ is the only carbon source, then from equation (6)

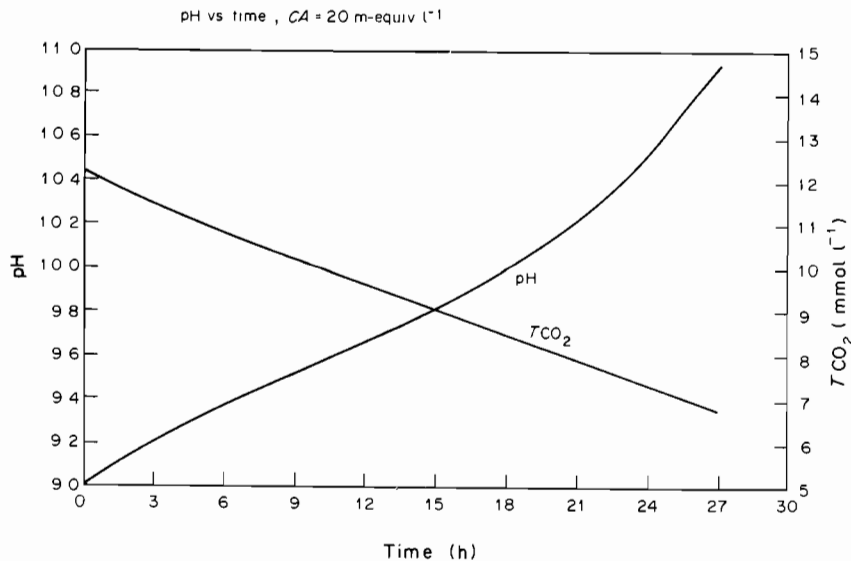


Fig. 8. Simulated pH and TCO₂ variation as a function of time. Parameters are the same as Fig. 6.

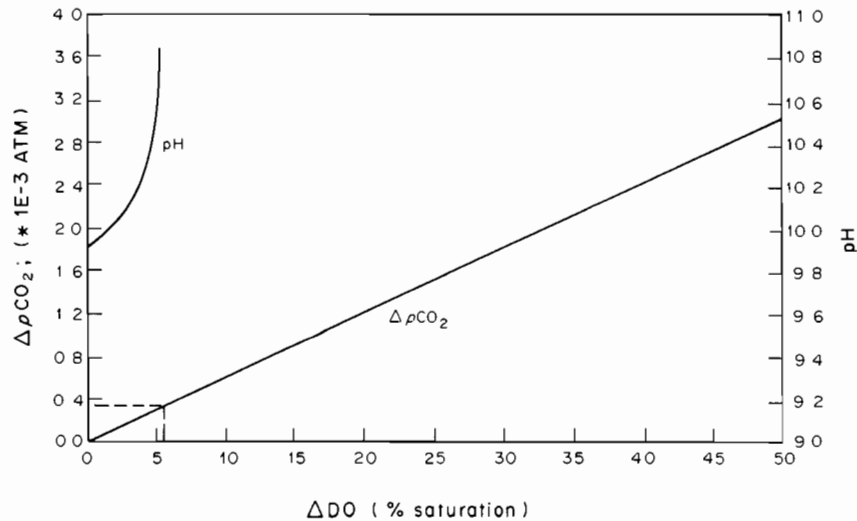


Fig. 9. Model estimate of $\Delta p\text{CO}_2$ and pH for an assumed equilibrium condition in the system in which the atmosphere is the only carbon source. CA = 200 m-equiv. Other parameters are the same as used before.

($d\text{TCO}_2/dt = 0$):

$$F_p C = \frac{D_{\text{CO}_2} \cdot \alpha_{\text{CO}_2}}{zH} \Delta p\text{CO}_2 \quad (17)$$

which implies

$$p\text{CO}_2 = Q \frac{\alpha_{\text{O}_2}}{\alpha_{\text{CO}_2}} p\text{O}_2. \quad (18)$$

Hence, knowing the DO level, in solution one should be able to calculate $p\text{CO}_2$ in the medium, required to utilize atmospheric carbon supply exclusively. It should be noted that this equilibrium relationship is independent of the gas exchange features (D/z), which are about equal for the two gases.

The relationships of equation (18) (Fig. 9) are valid of course for positive $p\text{CO}_2$ levels. The lower limit ($\Delta p\text{CO}_2 = 0$) is obtained when $p\text{CO}_2$ is equal to $p\text{CO}_2$ (atm) (Fig. 9), [assuming $p\text{CO}_2$ (atm) = 330 ppm]. Hence, for DO supersaturation of only up to about 105% it might be possible to provide adequate supply of carbon via atmospheric CO₂. This condition can be met, however, for rather low photosynthetic rate conditions, a conclusion which supports previous studies of low rates of algal growth (Round, 1973; Goldman *et al.*, 1972, 1974, 1981). For higher values of O₂ supersaturation which is a result of a high assimilation rate, equilibrium condition cannot be reached since atmospheric contribution to the total carbon supply cannot be sufficient. Atmospheric CO₂ contribution can be enhanced by a higher rate of stirring (lower D/z) which will in turn also lower the degree of DO supersaturation.

It can be concluded that for intense algal growth the atmospheric flux of CO₂ is an insufficient source of inorganic carbon. Mixing can enhance CO₂ transport from the atmosphere, but due to the very low atmospheric concentration of CO₂, the transport gradient is always small, as compared to the oxygen

gradient. This conclusion is valid despite the fact that CO₂ solubility is greater than that of O₂. Although the results of this work are strictly valid for the culture system and growth conditions of this system and cannot be readily extrapolated to large-scale mass culture systems, some general conclusions can nevertheless be obtained. First, the atmospheric flux is insufficient as a single source of inorganic carbon, and secondly, the conditions of high CA level result in a waste of inorganic carbon. Thirdly, the pH level is a function of the master variable TCO_2/CA following an explicit relationship. And finally it was demonstrated that although for low photosynthetic rate it is possible to reach a condition of steady state in the system, it is physically impossible to reach an equilibrium under intensive growth conditions. It is concluded that the present approach can provide a new and better insight into the biological process of algal cultures, helping to optimize algal growth systems.

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APPENDIX

a_{H} = activity of hydrogen ion

CA = carbonate alkalinity

DO(atm) = dissolved oxygen concentration at the surface film

D_{CO_2} = molecular diffusion coefficient of CO₂

F_{ph} = net oxygen production rate (OPR)

F_{pC} = net carbon consumption rate

H = height of the mini-pond

K_1 = first apparent constant of carbonic acid

K_2 = second apparent constant of carbonic acid

p_{CO_2} = partial pressure of CO₂(g) (atm)

p_{O_2} = partial pressure of O₂(g) (atm)

Q = the quotient of CO₂ consumption to O₂ production

TCO_2 = concentration of total CO₂ (mol cm⁻³)

z = the thickness of the solution boundary layer

α_{CO_2} = solubility of CO₂(g) (mol cm⁻³ atm⁻¹)

α_{O_2} = solubility of O₂(g) (mol cm⁻³ atm⁻¹)

$\Delta p_{\text{CO}_2} = [p_{\text{CO}_2}(t) - p_{\text{CO}_2}(\text{atm})]$

$\Delta p_{\text{O}_2} = [p_{\text{O}_2}(t) - p_{\text{O}_2}(\text{atm})]$.