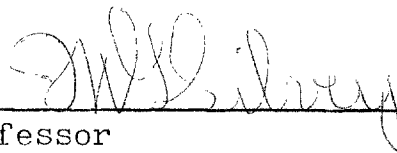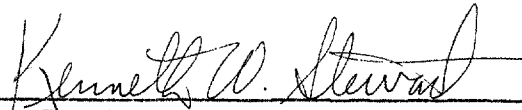A COMPARISON OF THE CARBON DIOXIDE AND OXYGEN RATE

OF CHANGE METHODS FOR MEASURING

PRIMARY PRODUCTIVITY

APPROVED:

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Major Professor

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Minor Professor

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Director of the Department of Biology

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Dean of the Graduate School

A COMPARISON OF THE CARBON DIOXIDE AND OXYGEN RATE

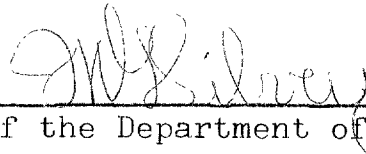OF CHANGE METHODS FOR MEASURING

PRIMARY PRODUCTIVITY

THESIS

Presented to the Graduate Council of the

North Texas State University in Partial

Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

By

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CHAPTER I

INTRODUCTION

Limnologists and oceanographers have long been interested
in the biological parameters of the various waters making up
the hydrosphere. Paramount among these has been the investi-
gation of the production of organic matter in aquatic envi-
ronments. Such work has been referred to as primary production,
primary productivity, and bioactivity (Ryther, 1956; Ohle,
1956; Odum, 1959; Westlake, 1965). The definitions for these
terms have become increasingly specific as the amount of work
on the subject becomes more voluminous. Westlake (1965) de-
fined primary productivity and closely related terms such as
biomass, primary production, standing crop, crop, and yield
as they are currently used today. Use of the term primary
productivity has varied considerably, even in recent works.
For example, primary productivity was measured as milligrams
per liter ash free dry weight of suspended material in a paper
by Jackson and Dence (1958). Westlake (1965) agreed with the
Odum (1959) definition of primary productivity as being "the
rate at which energy is stored by photosynthetic and chemo-
synthetic activity of producer organism (chiefly green plants)

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in the form of organic substances which can be used as food materials." The key word in the above definition is rate, as this word permits the expression of organic production as a function of time. Using the simplified equation representing photosynthesis,

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2 \qquad (1)$$
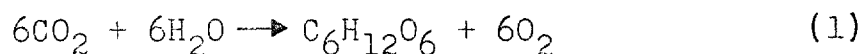
it is evident that the speed with which this chemical reaction occurs is directly related to the amount of organic material produced in a certain unit of time. Each of the components in the above equation varies with aquatic situations. However, the equation in which they participate provides a stoichiometric relationship for them, such that, if the rate at which one component changes is known, the velocity of the total photosynthetic reaction can be calculated in terms of that particular changing component.

Winkler (1888) provided what has become a standard titrametric method for measuring dissolved oxygen. However, it was not until 1927 that the light and dark bottle method for measuring the rate of change of dissolved oxygen was developed (Gaarder and Gran, 1927). The basis for this method is the fact that phytoplankton in a sealed, black bottle are solely engaged in the consumption of dissolved oxygen, while the phytoplankton in a sealed, clear bottle can both produce

and consume dissolved oxygen by means of their photosynthetic and respiratory mechanisms. Therefore, if the dissolved oxygen concentration is known at the beginning of the time period (usually twenty-four hours), the reduction of dissolved oxygen in the dark bottle at the end of the time period is due to respiration. The increase in dissolved oxygen in the light bottle is a measure of net primary productivity or that rate of production of oxygen in excess of the amount needed for respiration. Total or gross primary productivity can then be calculated by adding the values for net primary productivity and respiration. The light and dark bottle method has found wide application among limnologists and oceanographers, and is particularly reliable when phytoplankton constitute the greater portion of the community being measured for primary productivity (Smayda, 1957; McFarland, 1963; Goldman and Wetzel, 1963).

Sargent and Austin (1949) developed another method for measuring the rate of change of oxygen; it was subsequently modified and used in a study of the primary productivity of silver Springs, Florida, in 1953 and 1954, and Eniwetok Atoll, in 1955 (Odum and Odum, 1955). The basis for this method is the change in the dissolved oxygen content of water flowing over attached primary producers, where the motion of the

water is that of a stream or the result of tidal action.
Simultaneous oxygen measurements made at two stations with
water flowing between them show an increase during the day,
demonstrating photosynthetic production or primary productivity.
The dissolved oxygen decrease between the two stations at night
represents respiration. When the difference in dissolved
oxygen between the two stations is measured at intervals over
a twenty-four hour period and the resulting data graphed as
milligrams per liter dissolved oxygen against time in hours,
a curve is formed. The rate of change curve is the total
primary productivity between the two sampling stations for
the daily cycle (Odum, 1956). Using a single sampling station
(as is used in a standing body of water), the rate of change
of dissolved oxygen is found by first graphing the dissolved
oxygen determined at various intervals of time over a twenty-
four hour period to form a curve. The rate at which the curve
changes is the rate at which the dissolved oxygen changes.
Mathematically speaking, the curve which expresses the rate
of dissolved oxygen change is the first derivative of the
dissolved oxygen curve.

A more thorough explanation of the theory behind the rate
of change method for measuring primary productivity is best
accomplished graphically: see Figure 1.
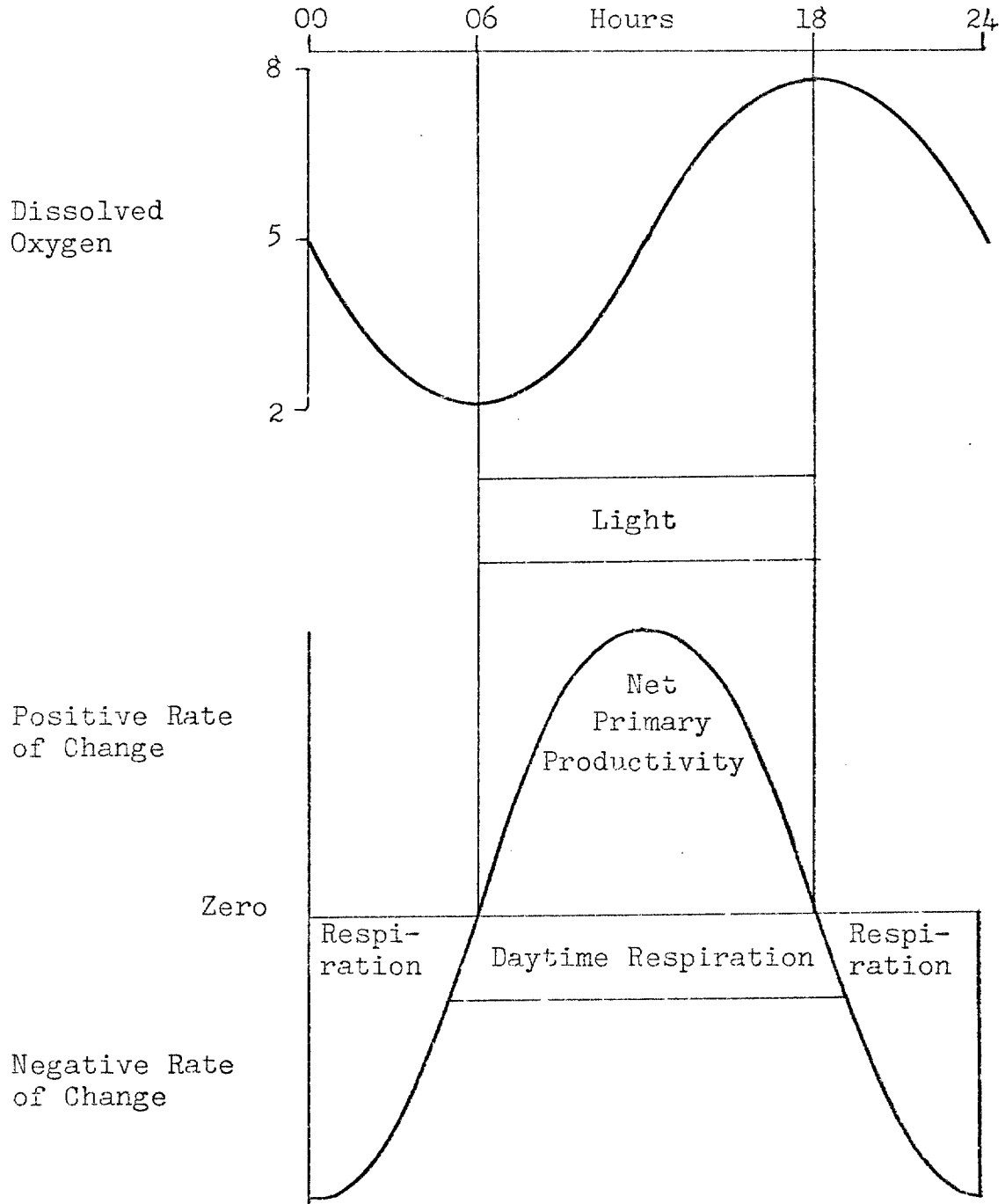
Fig. 1.   Theoretical change and rate of change curves.

The upper graph describes the change in dissolved oxygen over the sampling period. The lower graph depicts the change of the slope of the upper graph. In other words, the lower graph is the rate of change of dissolved oxygen for the sampling period. Both curves are a direct result of the variation in light intensity from dawn to sunset. Thus, any increase in dissolved oxygen or positive rate of change reflects photosynthesis and any decrease in dissolved oxygen or negative rate of change characterizes respiration. The dissolved oxygen measured in the water during the day can be considered an excess of the amount needed for daytime respiration. Therefore, the area enclosed by the positive portion of the rate of change curve and the zero rate of change axis symbolizes the amount of photosynthesis or net primary productivity which caused the observed change in dissolved oxygen. The greater the increase in dissolved oxygen, the higher the positive portion of the rate of change curve and consequently, the greater the net primary productivity. Gross or total primary productivity is the sum of net primary productivity and daytime respiration. The amount of respiration during the night can be accurately measured from the area enclosed by the zero rate of change axis and the negative portion of the rate of change curve. Daytime respiration, however, is not expressed

on the rate of change graph. An estimation of the area which
describes daytime respiration is made by choosing a predawn
and postsunset point on the rate of change curve below the
zero rate of change axis and connecting the points with a
straight line. The area enclosed by the curve and the line
connecting the predawn and postsunset points represents that
amount of oxygen produced by the primary producers that is
both used in respiration and responsible for the increase of
dissolved oxygen in the water. Due to the variability of dis-
solved oxygen curves and the difficulty of obtaining a mathe-
matical equation to describe them, graphic methods are employed
to acquire the first derivative as well as the areas under
the curves. A more detailed account of the operations in-
volved in the diurnal method is given by Odum and Hoskin (1958).

The rate of change of carbon dioxide, as well as that
of oxygen can be used to determine primary productivity. His-
torically, the carbon dioxide content of water has been used
for many years as an indicator of biological activity. Ellms
and Beneker (1901) reviewed the three oldest and most estab-
lished volumetric methods for determining the amount of carbon
dioxide in water known at that time. In addition, they cited
a method developed by Leeds (1891) as being the simplest and
most direct for the determination of the carbon dioxide

content of water. Methods describing the use of pH and carbon

dioxide concentration for the study of photosynthesis and

respiration began to appear in this country with the works

of Haas (1916), Osterhout (1918), Osterhout and Haas (1919),

and Osterhout (1919). Such simple techniques as growing

algae in media containing colorimetric pH indicator established

methods using pH and carbon dioxide for the study of biologi-

cal activity. More work using the pH-carbon dioxide rela-

tionship to examine photosynthesis and respiration was done

in the 1920's (Greenfield and Baker, 1920; Wells, 1922;

Shelford, 1923; Atkins, 1922, 1923, and 1924).

Verduin (1951) modified the method of Osterhout and

Haas (1919) by using a pH meter instead of colorimetric pH

indicators, and calculated the carbon dioxide removal or

evolution by the use of equilibrium equations from Moore (1939).

Verduin later used pH measurements again (Verduin, 1956a) to

determine photosynthetic and respiratory rates, but determined

the relationship between pH and the carbon dioxide content of

the water by differential titration of the water with 0.01 N

sodium hydroxide solution. The resulting pH changes were

used to interpret carbon dioxide changes by the theoretical

reaction of the strong base with carbonic acid. This method

was used again by Verduin and others for studies of

phytoplankton photosynthesis and respiration (Verduin, 1956b, 1960; McQuate, 1956; Fry and Stahl, 1958; Meqard, 1961). Beyers and Odum (1959), however, described errors in the use of strong acids and bases for determining the pH-carbon dioxide relationship in a natural water system and suggested the use of carbon dioxide saturated distilled water as a titrant for natural water artifically stripped of its free carbon dioxide. Verduin (1960a) defended his technique, but gained an immediate rebuttal by Beyers and Odum (1960). Lyman (1961) also attacked Verduin's method of interpreting carbon dioxide changes from pH changes due to the titration of the water with strong acid or base. Verduin (1961) replied that his method was valid and capable of 95% accuracy.

Odum (1957a, 1957b) had previously used the rate of change of carbon dioxide in water in conjunction with his diurnal oxygen method for measuring primary productivity. The relationship between free carbon dioxide in the water and pH was determined by sodium hydroxide titration using phenolphthalein indicator. The most recent method for measuring primary productivity using the pH change of the water with a known pH-carbon dioxide relationship was developed by Beyers, Larimer, Odum, Parker, and Armstrong (1963). Previous suggestions for establishing the pH-carbon dioxide relationship and using

the carbon dioxide rate of change, form the basis of the above method.

The purpose of this study was to demonstrate the variability of oxygen and carbon dioxide rate of change methods for measuring primary productivity and respiration in an aquatic environment.

CHAPTER II

METHODS

The body of water used in this study was Garza-Little Elm Reservoir, located in Denton County, Texas. A total of four diurnal analyses for oxygen and carbon dioxide rate of change was made from August to December, 1968. Specific dates were diurnal #1, August 14-15; #2, September 4-5; #3, September 19-20; #4, December 9-10. The method used for measuring primary productivity by the carbon dioxide rate of change was a modification of Beyers et al. (1963). A modification of the diurnal oxygen method (Odum and Hoskin, 1958) was used for the oxygen rate of change measurement.

A vital facility used in this study was a mobile laboratory complete with a 110-volt gasoline driven generator, refrigerator, butane stove, florescent lighting, and ample work space. Two sampling stations were used for the four diurnals. They were located at points on the lake over depths of six and ten meters. Every two hours samples were taken at the surface, and at two and four meters in depth at both stations. In addition, six and eight meter samples were taken at the ten-meter station.

Oxygen samples were fixed according to the azide modification of the Winkler method described in Standard Methods (1965) and titrated with 0.025 N sodium thiosulfate immediately upon return to the mobile laboratory. The permanganate modification of the Winkler method was used as a check against the azide modification to determine any possible errors due to excessive amounts of iron in the water.

Because of the accuracy needed in the determination of pH, 500-ml samples of water were collected in plastic bottles and brought back to the mobile laboratory, where the pH of the water was immediately recorded, using a Fisher Accumet model 210 pH meter connected to a constant voltage regulator. A Tonometer, for use in titration with carbon-dioxide-saturated distilled water, was constructed from a 50-ml burret and a 600-ml cylindrical separatory funnel. The amount of time used to saturate the distilled water with carbon dioxide in the rotating cylindrical separatory funnel was 45 minutes. The same amount of time was used to strip 300-ml of lake water with nitrogen bubbled through an air stone at the bottom of a 500-ml graduated cylinder. The stripped water was slowly mixed with a magnetic stirrer, while it was titrated with 0.5-ml increments of the carbon-dioxide-saturated distilled water. The tip of the burret was kept at the surface of the

stripped lake water throughout the titration. The time be-
tween the addition of the 0.5-ml increments of carbon-dioxide-
saturated distilled water and the recording of the pH measure-
ment was 15 seconds. The titrant was added so that pH values
on either side of the pH range of the lake water were obtained.
Titrations with carbon-dioxide-saturated distilled water were
performed approximately every six hours during the sampling
period, for a total of four titrations.

Because primary productivity measurements are given in
terms of surface area (so that bodies of water may be compared
with fields, forests, deserts, and the like), it is necessary
to think in terms of the productivity taking place below one
square meter of the water surface. The primary productivity
of the square meter of water surface is the primary productiv-
ity of the column of water one meter square and as tall as
the depth of water located beneath it. The dissolved oxygen
in this column is derived from photosynthesis and atmospheric
diffusion. The significant amount of dissolved carbon dioxide
is the result of the respiration of the aquatic community.
Extreme mixing, caused by horizontal and vertical currents,
generated by density differences and wind, distributes these
gases throughout the water column. An average value of dis-
solved oxygen or carbon dioxide for the water column was found

by assigning dissolved gas concentrations to each meter depth,
taking the sum, and dividing by the depth of the particular
water column. In other words, the dissolved gas concentra-
tions in samples below one meter are representative of the
dissolved gas in the cubic meter of water above and below
that particular sample. A sample at two meters establishes
the amount of dissolved gas in the second and third cubic
meters of the water column. This method was used for all
samples below the surface except the deepest samples. At
both sampling stations, the deepest sample was taken two
meters above the bottom. The dissolved gas content of the
deepest sample, then, was representative not only of the
cubic meter above it, but also the two meters below it, or
a total of three cubic meters of water. In accordance with
the previous discussion, the value for a dissolved gas in
the surface sample was multiplied by one and the value of
the deepest sample was multiplied by three. Intervening
values for dissolved oxygen or carbon dioxide were multiplied
by two. The sum of these products was divided by the depth
of the water column to obtain the average dissolved oxygen
or carbon dioxide concentration for the water column.

The average dissolved oxygen values for each sampling
period were plotted on millimeter graph paper against time

in hours, see example, Figure 2. The upper graph is the
change in dissolved oxygen over the sampling period. The
rate of change curve (bottom graph) is then derived by graph-
ically determining the slope of the line between the dissolved
oxygen values on the upper graph and dividing by the number
of hours between the sampling periods. This value is the
rate of change of the dissolved oxygen from one sampling time
to the next in milligrams of oxygen per liter or grams of
oxygen per cubic meter. The points for the rate of change
curve were placed on the horizontal axis halfway between the
times of the sampling periods. For example, the rate of change
value for dissolved oxygen between 2 p.m. and 4 p.m. was placed
on the horizontal axis at 3 p.m. As stated previously, oxygen
may also diffuse in or out of the water and effect the rate
of change. To compensate for this effect, the temperature
and dissolved oxygen data for the surface water of each sta-
tion were used with a nomogram to determine the percentage of
saturation of the surface water for each sampling period.
The values for percentage of saturation were graphed using
the same horizontal axis as the previous graphs, see middle
graph, Figure 2. Predawn and postsunset points on the rate
of change graph were established with the use of pyrhelio-
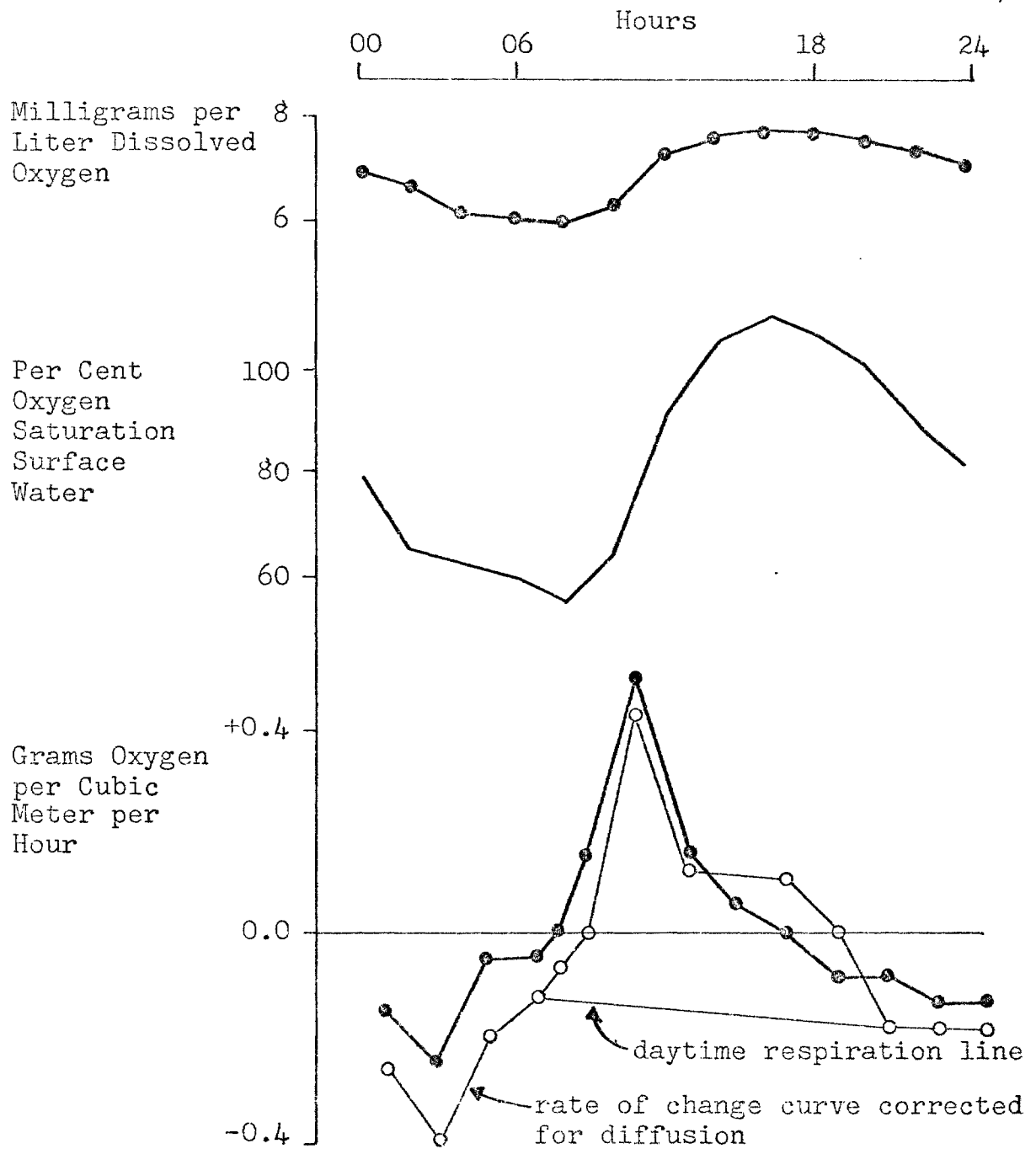meter tracings taken during the sampling period. The same

Fig. 2. Example of graphic method for oxygen rate of change method.

predawn and postsunset points were established on the satura-
tion percentage curve. Together, the values of these four
points were used to establish a diffusion constant with the
use of the following equation,

$$k = (q_m - q_e)/(S_m - S_e) \times 100 \qquad (2)$$

where k is the diffusion constant; q_m is the predawn rate of
change; q_e is the postsunset rate of change; S_m is the predawn
saturation percentage; S_e is the postsunset saturation per-
centage. The diffusion constant (k) was multiplied by the
saturation percentage deficit for each point on the rate of
change curve. Each rate of change point was then adjusted by
the addition or subtraction of the product. If the saturation
percentage was below 100%, the product was subtracted. If the
saturation percentage was above 100%, the product was added.
Thus, a rate of change curve corrected for diffusion was formed.
The above method differs slightly in operation, but gives the
same results as the calculations described by Odum (1958). The
line connecting the predawn and postsunset points, called the
daytime community respiration line, on the corrected rate of
change curve, completes the perimeter of the area describing
gross primary productivity. The direct connection of the
predawn and postsunset points differed from Odum's 1958

technique of averaging the nighttime rate of change points
and drawing a horizontal line under the curve at that value.
However, the connection of the predawn and postsunset points
has become the acceptable way of approximating daytime res-
piration in work after 1958 (Davis, 1968).

Determinations of areas depicting gross primary produc-
tivity and respiration were made with a planimeter. The area
in square centimeters was converted to grams oxygen per cubic
meter for the sampling period by using the factor 0.2 $g/m^3/cm^2$,
which was obtained from the product of the values of one centi-
meter on the horizontal and vertical axes of the rate of change
curve.

The carbon dioxide concentration of the lake water was
derived from pH determinations and the relationship between
pH and dissolved carbon dioxide was established by using the
instructions of Beyers, et al. (1963). A table for the deter-
mination of the amount of carbon dioxide present in the
distilled water for a given temperature and barometric pres-
sure was given by Beyers et al. (1963) as well as the deriva-
tion of the equation for the change in carbon dioxide as a
function of the carbon dioxide added by titration. Hence, a
0.5-ml increment of carbon dioxide saturated water released
a known amount of carbon dioxide into the lake water, which

had been previously stripped of its free carbon dioxide. The

pH of the lake water resulting from the addition of titrant

was placed on the vertical axis of a graph. The product of

the millimoles of carbon dioxide present in the increment

which caused the pH change and a dilution factor was placed

along the horizontal axis. The resulting curve demonstrated

the relationship between the carbon dioxide content of the

water and its pH. The four curves which were generated in

this fashion during the sampling period were averaged and

the pH of the water at each depth was converted to carbon

dioxide in millimoles per liter. The average concentration

of carbon dioxide in the water column was determined as pre-

viously discussed. The change in carbon dioxide was graphed,

the rate of change determined (Figure 3), the areas described

by the curve computed, and the conversion of the areas to

grams of carbon dioxide per cubic meter was calculated in

exactly the same way as the oxygen rate of change method.

Carbon dioxide is about 200 times more soluble in water than

oxygen (Hutchinson, 1957) and the partial pressure of carbon

dioxide gas in the air is negligible when compared to the

respiration rates in this study (Park, et al., 1958). These

facts permitted any corrections in carbon dioxide concentration
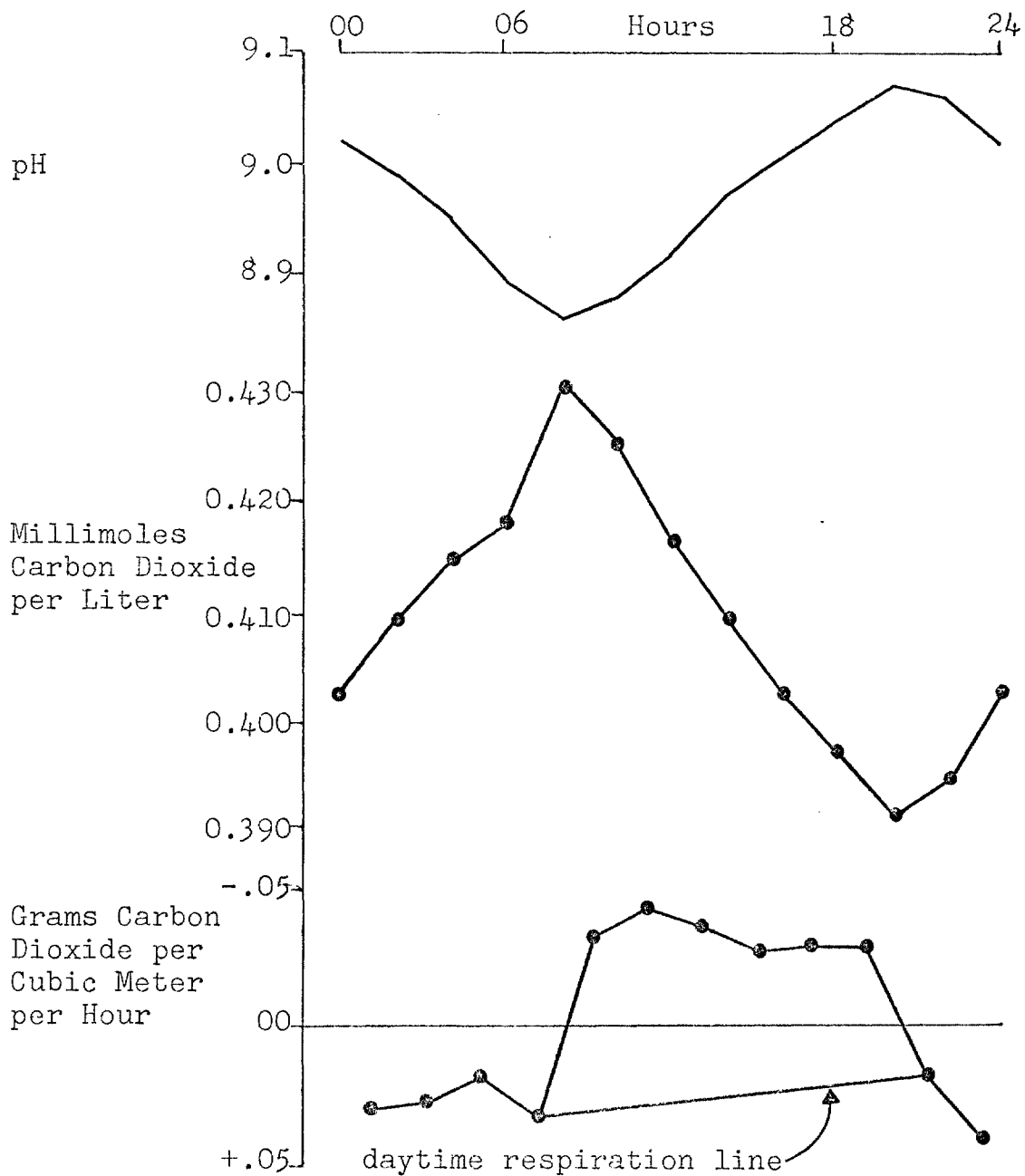
Fig. 3. Example of graphic method for carbon dioxide rate of change method.

due to atmospheric diffusion to be ignored as insignificant in the illustration of the rate of change graph.

The primary productivity and respiration estimates calculated from the diurnal rate of oxygen and carbon dioxide change were converted to a common unit termed grams of glucose-carbon. The conversion was accomplished by multiplying the oxygen values by 0.375 and the carbon dioxide values by 0.273. This method of conversion was used by Ryther and Vaccaro (1954) in their comparison of productivity measurements using the light and dark bottle method and the radioactive isotope (carbon-14) method. A comparison was also made of the ratios of productivity to respiration (P/R) in order to examine the characteristics of the community typified by the two methods.

CHAPTER III

RESULTS

The calculations of gross primary productivity and community respiration from oxygen and carbon dioxide rates of change are given in Tables 1 and 2, respectively. In addition, gross primary productivity and community respiration in terms of a common unit, glucose-carbon, are given in Tables 3 and 4. Table 5 compares the quotients of the data from Tables 1 and 2. This comparison is necessary so that the relative trends of gross primary productivity and community respiration at each station may be examined in addition to the specific values which produced the quotients.

Initial calculations of gross primary productivity and community respiration by the oxygen rate of change method showed the reservoir to suffer from gross pollution such as might be caused by the presence of raw sewage. Respiration was always well above primary productivity (Odum, 1956). This was known not to be the case from observations of the sampling sites. However, when the influence of the diffusion constant was eliminated from the calculations, the values for gross primary productivity and community respiration conformed

much more closely to similar estimates made on other south-
west reservoirs (Davis, 1968). Correction of the initial
calculations demonstrated that the fluctuation of dissolved
oxygen was not significantly affected by atmospheric diffu-
sion at the depth sampled (B. J. Copeland, personal com-
munication).

TABLE 1. Gross primary productivity in grams (oxygen or car-
bon dioxide) per square meter per day as calculated
from oxygen and carbon dioxide rate of change
for 6m and 10m columns of water

Diurnal	Oxygen		Carbon Dioxide	
Number	10m	6m	10m	6m
1	18.7	12.8	94.0	67.0
2	18.7	10.2	45.2	52.8
3	5.3	8.0	50.4	35.3
4	4.0	5.1	19.5	20.8

TABLE 2. Community respiration in grams (oxygen or carbon
dioxide) per square meter per day as calculated from
oxygen and carbon dioxide rate of change
for 6m and 10m columns of water

Diurnal	Oxygen		Carbon Dioxide	
Number	10m	6m	10m	6m
1	11.8	8.7	50.2	48.0
2	7.5	4.8	48.0	19.2
3	2.5	3.2	20.0	14.6
4	5.5	3.6	59.6	9.6

TABLE 3. Grams of glucose-carbon derived from oxygen and
carbon dioxide gross primary productivity measurements
for 6m and 10 columns of water

Diurnal	Oxygen		Carbon Dioxide	
Number	10m	6m	10m	6m
1	7.0	4.8	25.0	18.3
2	7.0	3.8	13.0	14.0
3	2.0	3.0	14.0	9.6
4	1.5	1.9	5.3	5.7

TABLE 4. Grams of glucose-carbon derived from oxygen and
carbon dioxide community respiration measurements
for 6m and 10m columns of water

Diurnal	Oxygen		Carbon Dioxide	
Number	10m	6m	10m	6m
1	4.4	3.3	13.7	13.1
2	2.8	1.8	13.0	5.2
3	0.9	1.2	5.5	4.0
4	2.1	1.4	16.0	2.6

TABLE 5. Productivity-respiration ratios (P/R) for 10m and
6m water columns as derived from the
oxygen and carbon dioxide rate
of change methods

Diurnal	Oxygen		Carbon Dioxide	
Number	10m	6m	10m	6m
1	1.6	1.5	1.8	1.4
2	2.5	2.1	0.9	2.7
3	2.1	2.5	2.5	2.4
4	0.7	1.4	0.3	2.1

CHAPTER IV

DISCUSSION

All measurements of primary productivity and respiration
rates in a body of water are affected by climatic conditions
as well as by the dissolved and suspended materials in it.
Primary productivity is dependent upon light and nutrients
present in the water, while respiration is dependent upon the
concentration of organic matter in the water (Odum, 1956).
Hence, a bright sunny day produces greater productivity rates
than a cloudy day. Water containing a greater amount of dis-
solved inorganics is more productive than water with a lower
dissolved inorganic content. The presence of organic material,
such as sewage, in the water produces values indicating very
little primary productivity, but tremendous community respi-
ration. An increase in wind increases wave action and sub-
sequently increases the rate of exchange of dissolved gases
between the atmosphere and water. This diffusion may or may
not be important depending upon the depth of the water and
its phytoplankton population, as mentioned previously. Tem-
perature is also an important factor controlling the solu-
bility of gases in the water. Rain can increase significantly

the amount of dissolved carbon dioxide in water and give incorrect values for both primary productivity and respiration when determined by the carbon dioxide rate of change method (Park et al., 1958).

The comparison between the carbon dioxide and oxygen rate of change methods for measuring primary productivity and community respiration is also a comparison of chemical and instrumental determinations. Chemical fixation and titrametric analysis with a color indicator was used to determine the amount of dissolved oxygen present in the water. A pH meter was the necessary instrument not only for determination of the change in pH of the water over the sampling period, but also for the determination of the pH-carbon dioxide relationship.

The Winkler analysis for dissolved oxygen has an accuracy of ± 2 mg/l and is, therefore, best suited to situations in which the diurnal dissolved oxygen fluctuation is large. The dissolved oxygen concentrations are used to calculate primary productivity and community respiration by a method which has basically two weak operations. They are the estimation of daytime respiration and the modification of the diurnal curve by a diffusion constant. Whether or not the area representing daytime respiration is a true estimation

of what actually occurs in the reservoir is never known.

There must be, however, a small section of the area repre-

senting gross primary productivity in the negative rate of

change portion of the graph in order for the term gross

primary productivity to be properly defined (Westlake, 1965).

Thus, the estimation of daytime respiration is accomplished

as easily as possible by the connection of the predawn and

postsunset points. Diffusion of gases through the air-water

interface is dependent upon the various climatic situations

which occur over the sampling period. Individual measure-

ments of each factor influencing diffusion over the sampling

period is a task so monumental as to subordinate drastically

the major investigation of primary productivity and respira-

tion. Hence, an estimate of the diffusion occuring during

the sampling period must be used. As stated previously, the

significance of this diffusion constant must be determined

by the depth of the water as well as by the effect of the

diffusion constant on the productivity-respiration ratios.

The estimates of primary productivity and community

respiration by the carbon dioxide rate of change method should

be similar to those calculated by the oxygen method. Both

methods employ the determination of daytime respiration in

the same manner. Another similarity, which is unique to this

particular study, is that both rate of change curves were
not influenced by a diffusion constant. The carbon dioxide
rate of change method never uses a diffusion constant and
the diffusion constant for the oxygen method was disregarded,
both for reasons given earlier. The estimates for gross
primary productivity and community respiration, however, are
not in agreement. The carbon dioxide rate of change values
are much greater than those calculated from the oxygen method.

The carbon dioxide rate of change method is derived from
a measure of the pH of the water which is the result of the
dissociation of carbonic acid (the form which carbon dioxide
assumes when dissolved in water) as follows:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{3}$$
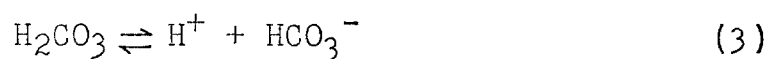
The first dissociation constant for carbonic acid is 4.3×10^{-7}.
The uptake of bicarbonate ion by the phytoplankton during
photosynthesis shifts the equilibrium to the right and the
hydrogen ion concentration increases causing a decrease in pH.
A buffer system present in the water would alter this relation-
ship and cause a smaller pH change than would be the case if
there were no buffer system present at all. The smaller the
diurnal pH fluctuation, the smaller the change of carbon
dioxide, no matter what the relationship. The decreased rate

of change of carbon dioxide produces lower primary productivity and respiration estimates. A buffer system cannot account for the observed data. The increased estimates of primary productivity and respiration calculated from the carbon dioxide rate of change could be caused by a fluctuation in pH greater than would be accounted for by simple carbonic acid dissociation. A substance or substances which exist in the water and provide a wide range of pH values over that which would normally be produced by carbonic acid alone could be responsible for the observed data. Among the largest group of substances which are present in natural water systems are the soluble organics produced by organisms in the water. Lee and Hoadley (1967) report that the relative portion of soluble organics in the sea is fifty times the amount of phytoplankton. The work on extracellular products of algae is voluminous and I shall refer here only to those works which have a direct bearing on my specific problem (Tolbert and Zill, 1956 and 1957; Lewin, 1957; Fogg, 1958, 1963; Pritchard, Griffin, and Whittingham, 1962; Miller, Meyer, and Tanner, 1963; Nalewajko, Chowdhuri, and Fogg, 1963; Fogg and Nalewajko, 1964; Helleburst, 1965; Watt, 1966; Watt and Fogg, 1966). These authors agree that the most abundant extracellular product is glycolic acid ($HOCH_2COOH$). Hence, glycolic acid is

used as a specific example of the possible effects which the general class of extracellular organic materials may have on the pH-carbon dioxide rate of change method.

Tolbert and Zill (1957) postulate a Donnan equilibrium occuring between intracellular and extracellular bicarbonate ion and intracellular and extracellular glycolate ion as follows:

$$\frac{(HOCH_2COO^- \text{ in cell})}{(HOCH_2COO^- \text{ in water})} = \frac{(HCO_3^- \text{ in cell})}{(HCO_3^- \text{ in water})} \tag{4}$$

A resulting shift of bicarbonate ion across the cell membrane results in a shift of glycolate in the opposite direction. If such a system existed during the sampling period, the net effect of photosynthesis would be to replace carbonic acid in the water with glycolic acid. Glycolic acid has a dissociation constant which is over 300 times that of carbonic acid. This would cause an increase in the hydrogen ion concentration and a lowering of pH during photosynthesis which would be greater than that caused by carbonic acid alone. The reverse is true for respiration. The more soluble compound, glycolic acid, is replaced by a less soluble compound, carbonic acid. The equilibrium in equation 3 is then shifted more to the left because of the increased amount of hydrogen

ions available from glycolic acid and the lower solubility of carbonic acid. The result is a decrease in hydrogen ion concentration and an increase in pH. This decrease in hydrogen ion concentration is greater than would be the case if glycolic acid were not present. The total effect of the soluble organic, then, is to increase the diurnal pH fluctuation over the fluctuation caused exclusively by the addition and removal of bicarbonate ion. This permits one possible explanation of the extremely high primary productivity and respiration estimates as being the result of the increased pH fluctuation due to glycolic acid or similar soluble extracellular compounds in the water.

The productivity-respiration ratios (P/R) seem to support the above hypothesis. Although the values for primary productivity and respiration as calculated from pH-carbon dioxide data are considerably above those calculated from oxygen determinations, the P/R ratios of the pH-carbon dioxide values are within 0.6 P/R unit of the respective values for oxygen determined P/R ratios for 75% of the data.

CHAPTER V

CONCLUSION

The use of the rate of change of dissolved gases in the water for measuring primary productivity must take into account parameters of the environment and operations used in the calculations which may adversely affect either the true rate of change, the resulting mathematical value, or both. The chemical fixation of dissolved oxygen is an old and well established method which has undergone modifications making it applicable for all but extremely polluted aquatic environments. The calculations using the change in dissolved oxygen are basically sound in theory, but suffer from two weak operations in practice; the estimation of daytime respiration and the correction of dissolved oxygen due to diffusion. The correction for diffusion is probably the more erroneous of the two. Even after its calculation and incorporation into the estimation of primary productivity and respiration, values for these parameters may have obvious errors in comparison with similar measurements in other ecosystems of the same type. This situation may be corrected by the complete elimination of the diffusion constant from the calculations.

The rate of change of carbon dioxide, as determined from diurnal pH readings, is not influenced by diffusion and has basically the same graphic calculations as the diurnal oxygen method (including the estimation of daytime respiration). The pH-carbon dioxide relationship is established by the change in pH of stripped water to which increments of carbon dioxide are added. This accounts for the diurnal pH fluctuation due to dissolved carbon dioxide, but not for any variation in the pH which might be caused by the effect of soluble organic components present in the water and acting in association with the dissolved carbon dioxide.

The diurnal oxygen method is best suited for field studies. The diurnal carbon dioxide is less suited to field studies due to the instrumentation necessary and the reliance upon hydrogen ion concentration, which may be affected by factors other than the change of dissolved carbon dioxide.

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