ANALYSIS OF DIURNAL OXYGEN CURVES FOR THE ESSAY OF REAERATION RATES AND METABOLISM IN POLLUTED MARINE BAYS

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ANALYSIS OF DIURNAL OXYGEN CURVES FOR THE ESSAY OF REAERATION RATES AND METABOLISM IN POLLUTED MARINE BAYS

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Many of the biological and chemical events in marine estuaries are supplied with energy through a daily pulse of photosynthetic and respiratory metabolism. Both of these types of metabolism are interdependent chemically, linked through physical patterns of circulation. Such systems containing photosynthesis, circulation, and community respiration are termed ecosystems.

Estuarine ecosystems are of an import-export type in which the relative amounts of inflow and outgo of organic matter and raw materials control the nature of metabolism. Imports of organic matter favor respiration whereas imports of regenerated inorganic raw materials stimulate photosynthesis.

When man modifies the estuaries by adding substances or changing rates of circulation, he profoundly affects the entire metabolism and the relative amounts of photosynthesis and respiration. Consequently measurements of the overall photosynthesis and community respiration are a principal means for the estimation of overall pollution effect. Since the metabolic uptake and release of particular chemical elements bears a definite relationship to the overall carbon synthesis and regeneration, metabolic rate measurements may also be used to obtain rates of cycling of elements for predicting fates of radioactive pollution.

In this paper some methods for the assay of total estuarine metabolism developed in non-polluted waters are extended to some polluted estuarine waters. The amount of total metabolism in the ecosystem, the relative role of photosynthesis and respiration, the role of export and import of organic matter, and the exchange of gases with the atmosphere are readily measured for characterizing some pollution types. Several distinct types of pollution metabolism are described.

METHODS

Diurnal measurements of dissolved oxygen and carbon-dioxide by the pH method are made in estuarine waters every three hours with various replications and other special means for estimating overall representive of large

* With the research assistance of Mr. Gonzalo Garza.

estuarine areas and large water masses. Then hourly rate of change graphs are constructed for oxygen and carbon-dioxide. From these curves are estimated rates of gross photosynthesis, total community respiration, and gaseous exchange with the atmosphere. The details of the methods, assumptions, variations, and applications to estuarine waters are given in previous publications (Odum, 1956; Odum and Hoskin, 1958; Park, Hood, and Odum, 1958; and Beyers and Odum, 1959).

Some of the results of previous studies may be summarized as follows for unpolluted estuaries.

CONCLUSIONS FROM PREVIOUS STUDIES

1. Gross photosynthesis and total community respiratory metabolism generally range from 1 to 60 gm / M^2 / day oxygen.

2. In shallow systems less then 3 meters in depth, bottom respiratory metabolism is usually greater in magnitude than the metabolism of the water with its plankton. In very shallow waters less than 0.5 M in depth, bottom photosynthesis and respiration may exceed metabolism in the water by 100 times.

3. High metabolic rates are associated with high circulation rates.

4. The reaeration constant for estuaries and streams is about 1-2 gm oxygen / M^2 / hr for 0.2 atmosphere oxygen gradient between water and air. Lower values are found in still and partly stratified waters. Higher values are found where currents are large and wave action great.

5. In some environments metabolic estimates from carbon-dioxide data are much larger than estimates from oxygen curves on a similar molar basis. This discrepancy may be due to nighttime anaerobic metabolism followed by aerobic daytime recovery.

6. Because of the small partial pressure of carbon-dioxide in the atmosphere of the order of 0.0003 atmospheres, diffusion of carbon-dioxide from air into the water is very slow. On the other hand the diffusion of carbon-dioxide out from a supersaturated system may be as rapid as diffusion of oxygen. A diurnal fluctuation from supersaturation to undersaturation may pump out carbon-dioxide.

7. Total community respiration closely follows total photosynthesis during the rise and fall of metabolism during a year in stabilized systems. consumers are regulated so that their life cycles and energy requirements are in phase with the pulse of energy from the sun or from import.

8. Streams and estuaries receiving large river flow have an excess of respiration over photosynthesis apparently due to the rate of import of organic matter from the land run-off. Loss of photosynthesis with increasing turbidity of systems receiving runoff is partly compensated for by extra importations or organic matter associated with turbidity. Systems with large import may have higher total respiratory metabolism than fertile photosynthetic systems.

9. Coral reefs and shallow grass flats are among the most fertile marine communities.

10. Because of uncertainties about the reality of measurements in bottles and because of the large role of current and bottom metabolism in estuaries, where applicable the diurnal measurements in free water are preferable to measurements of BOD and bottle metabolism.

11. The diurnal curve methods cannot be easily used in many estuaries where there are complexities of vertical stratification and changing tidal currents, which prevent the observer from readily obtaining average values for whole water masses. Many estimates of metabolic rate from diurnal curves tend to be underestimates.

In most of the studies carried out so far, measurements have been made by observers in the field in small boats at all times of day and night. Some recent measurements have been taken with a pilot model of a buoy developed by Joe Glover and George Creedle which take samples in glass stoppered bottles in a refrigerated chamber every 3 hours. The buoy contains a storage battery, a timer, and solenoid switches for allowing bottles to fill by gravity through valves opened at time intervals. Samples are removed from the buoy at the end of a 24 hour period for Winkler analysis or pH determination. First preliminary tests comparing measurements in the buoy with those outside the buoy indicate satisfactory agreement in waters where bottom metabolism is dominant. The buoy is manufactured by Texas Scientific Equipment Corporation Box 4367, Austin 51, Texas.

DIURNAL OXYGEN CURVES FROM POLLUTED WATERS

In Figures 1 and 2 are shown two extreme examples of the diurnal oxygen graphs for some waters known to be highly influenced by pollution. In each figures are curves of per cent saturation, oxygen rate of change, and corrected oxygen rate of change where the gaseous exchange with the atmosphere has been subtracted. In the corrected graph oxygen believed to be diffusing out is restored and oxygen believed to be diffusing in is removed. The corrected rate of change graph is the oxygen rate of change that might have been obtained if the bay were covered with a plastic layer.

A CASE OF LARGE EXCESS OF PHOTOSYNTHESIS OVER RESPIRATION

In the Oso Bay near Corpus Christi, Texas (Figure 1), treated effluent from domestic sewage provides a rich nutrient medium to a shallow enclosed bay. Large algal growths develop along the lateral mud flats causing a local problem with odors in residential districts nearby. The summer diurnal curve of oxygen analyzed in Figure 1 is distinctive. The oxygen remained over saturation the entire day and night indicating great excess of photosynthesis (P) over respiration (R). Such ratios of P and R do occur in nature in non-polluted waters in northern waters in the spring of the year, but such great imbalance of P and R has not often been found in non-polluted Texas waters.

The metabolic condition of the estuary is similar to that in algal cultures of sewage where cells are maintained in rapid growth and high P/R ratio by

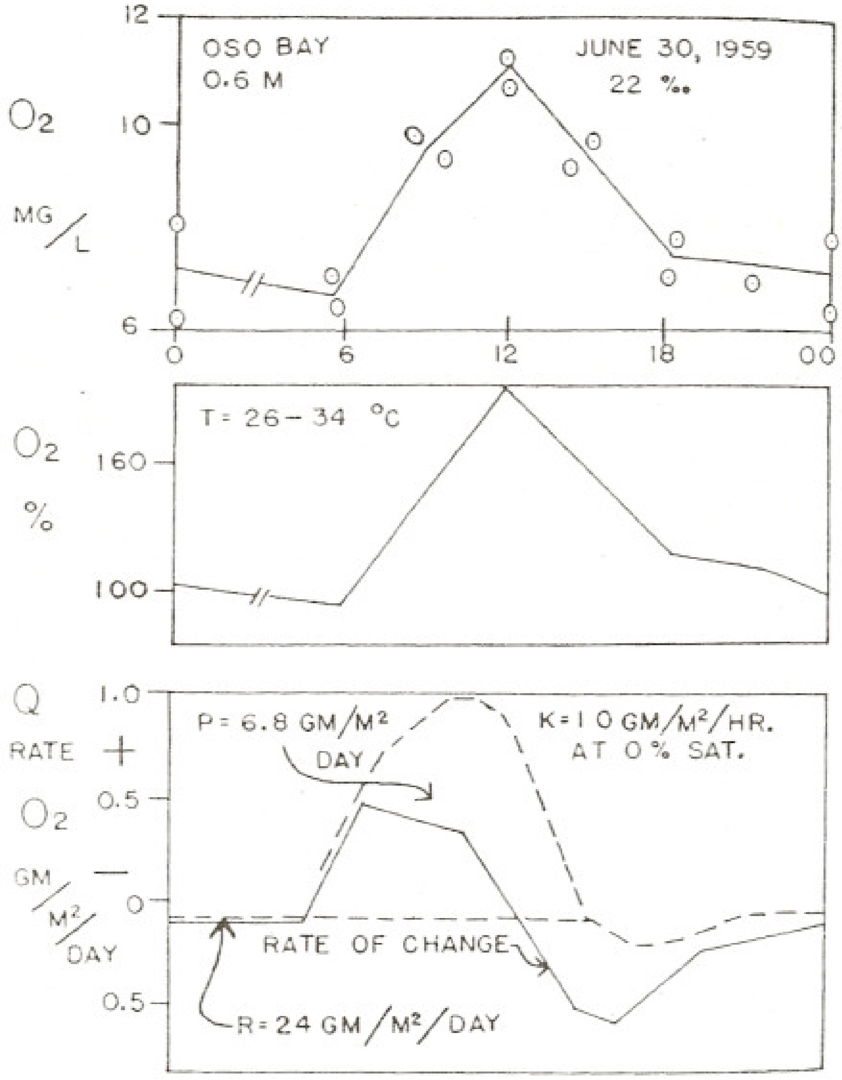

Fig. 1.

Diurnal Curves of Oxygen, per cent oxygen saturation and rate of change of oxygen in a bay receiving treated sewage effluent (Oso Bay near Corpus Christi, Texas). The dashed curve is the diffusion corrected curve as calculated with an aeration coefficient computed with the formula

$$K = \frac{Q_1 - Q_2}{S_1 - S_2} \, 100$$

where Q is the rate of change at a time at night and S is the saturation deficit in per cent at the same time of night. The amount of dotted area is computed as the total gross photosynthesis of the system. The excess of photosynthesis over respiration and the resulting algal problem are a pollution resulting from over fertilization.

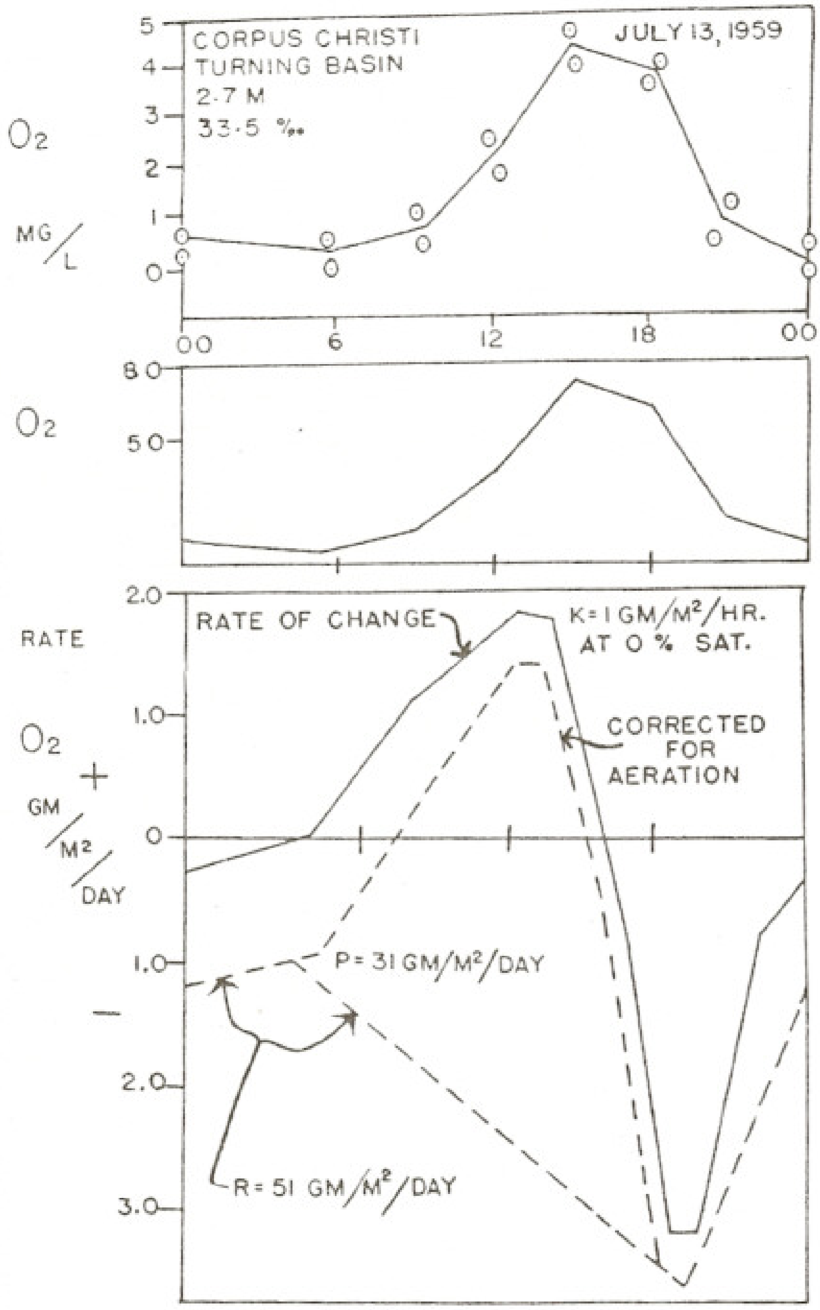

Fig. 2.

Diurnal curves of oxygen, per cent oxygen saturation, and rate of change of oxygen in a bay receiving multiple organic effluents. The dashed curve has been calculated from the rate of oxygen change curve using an aeration coefficient believed to be maximal possible (from other data). The residual curve (dashed) indicates the course of night respiration. Morning and evening respiration have been connected with a straight line to outline the hypothetical distribution of daytime community respiration used in computations. The great excess of respiration over photosynthesis and the resulting anaerobic conditions are a pollution resulting from excess organic import.

frequent renewal and turnover of medium (Ludwig, Oswald, Gotaas and Lynch, 1951). Equally high values of photosynthesis are found in many non-polluted Texas bays, in tropical grass flats and reefs in Puerto Rico, and in other naturally fertile waters.

In the Oso there is little water exchanges with other bays and there are changeable temperature and salinity conditions which interfere with colonization by ordinary marine consumers. Thus the production by algae is not consumed as readily as normally but remains to be deposited on the mud flats as a nuisance. Respiration did not balance photosynthesis in the central water area. If such conditions persist one might recommend measures for allowing re-entry of normal consumer food chains with more fishing as a beneficial by-product and less odoriferous, microbiological consumption on the margins. Considerable insight as well as quantitative estimation of rates are thus provided by the diurnal analysis of such a pollution situation.

Application of the formula for reaeration constant derived from simultaneous equations as described earlier (Odum and Hoskin, 1958) yielded K = 0.90 gm/M^2/H for 0% saturation. The formula may be used wherever it may be assumed that respiration is fairly constant.

A CASE OF LARGE EXCESS OF RESPIRATION OVER PHOTOSYNTHESIS

In the boat harbor of Corpus Christi, Texas, there are a great many sources of organic matter entering the water from municipal and industrial sources. Imports also include nutrients capable of stimulating photosynthesis. In Figure 2 is shown the diurnal oxygen curve in the surface waters of a portion of the upper end of the harbor.

In the ship harbor, in contrast to the curve from the Oso Bay, oxygen is undersaturated throughout the day and night indicating a great excess of R over P. In this case oxygen is entering the water at all times, but more rapidly at night. There is a strong pulse of photosynthesis during the day which is as large as that in most ordinary bays. Unlike most nearby bays, however, there is a very great total respiration (35 gm/M^2/day). The analysis provides an estimate of the actual in situ metabolism without the complexities of bottles, dilutions, and assumptions. In waters of Corpus Christi Bay outside of the polluted basin, metabolic values were much less (about 3 gm/M^2/day) as estimated with a similar diurnal curve analysis.

DIURNAL VARIATION OF RESPIRATION

In the analysis of Figure 2, the usual procedure of determing the reaeration coefficient from the diurnal using computations with simultaneous equations was not carried out, because it was obvious that there was a very great change of respiration rate during the night Instead, a reasonable value for reaeration in an enclosed harbor was assumed from previously published studies as 0.8 gm oxygen/M^2/hr at 100% saturation deficit. Because of the relatively deep water (2.7 M) the diffusion correction was relatively small. A dashed line was drawn sunrise and sunset points to indicate the possible daytime course of respiration rate.

Although it is fully realized that respiration of plants, microorganisms and animals varies markedly with the time of day, data are not yet adequate to generalize for ordinary bays as to the relative magnitudes at different times of day. Thus in previous publications constant night respiration was assumed as a first approximation in order to permit computation of reaeration rates. In curves of carbon-dioxide where diffusion is minor, considerable variation of carbon-dioxide metabolism was noted during the course of the night (Park, Hood, and Odum, 1959). In Silver Springs (Odum, 1957) some increased respiration was observed in late evening in comparison to that at dawn.

In environments low in oxygen like that in Figure 2 the variation of community respiration can be recognized readily as the oxygen concentration drops below one mg/liter. Many studies have shown that when oxygen falls below one mg/liter, metabolism of consumers is diminished. For a whole system it is obvious that oxygen metabolism must cease when the system runs out of oxygen. In Figure 2 it is clear that oxygen has become limiting after dark and respiration diminished. Anaerobic respiration undoubtedly proceeds at night to be partially equilibrated in the following day. Accelerated oxygen respiration in the morning thus may counteract photosynthesis.

Such oscillatory systems cannot support consumers but only specialized species capable of alternating aerobic and anaerobic metabolism.

The overall effect of photosynthesis coincident with the great respiration is to change the form of organic matter. Organic pollutants are replaced almost as fast as they are oxidized. The curve in Figure 2 is not unlike some in sewage lagoons. The diurnal curve provides an hourly picture.

TOXICITY CASE

In neither Figure 1 nor Figure 2 was photosynthesis or respiration diminished by a pollution situation although the two were less in balance than usual in nearby non-polluted waters. Where a pollution is directly toxic to biota, it may be expected that there will be little appreciable diurnal oxygen curve. Thus if light, nutrient, and organic matter levels are high but metabolism is not, some toxic type pollution may be recognized. So far this toxic type pollution has not been encountered in our studies of the estuarine waters of south Texas.

DIURNAL CURVE ANALYSES AT OTHER POLLUTION SITES

Two curves brought to us by Mr. Bill Renfrow of the Texas Game and Fish Commission on a marine bay, Clear Lake on Galveston Bay when analyzed had metabolism values not dissimilar to those in Figure 2. At Seabrook on August 18-19, 1958, at 28-32 deg. C, and salinity 14.6 PPT gross photosynthesis was 5.3 $gm/M^2/day$ and total respiration 8.2 $gm/M^2/day$. In water 1 M deep the reaeration coefficient was 0.2 $gm/M^2/hr/0.2$ atmosphere saturation deficit. The oxygen was below saturation all day indicating the excess of respiration over photosynthesis over a day span. On June 26-27, 1958, in salinity 7 to 10 PPT photosynthesis was 7.9 $gm/M^2/day$ and respiration was in excess at 16.1 $gm/M^2/day$. Reaeration was calculated at 1.4 $gm/M^2/hr/0.2$ atmosphere saturation deficit.

In the Mission River at its estuarine end on Copano Bay there is a discharge of a saline river water much affected by underground brines released by oil wells (bleedwater). The stream at times is rich in algae as might be expected where waters are stimulated with nutrient influx. The situation is complicated by municipal waste effluents and small runoff in dry years. A diurnal curve analysis by Mr. Charles Hoskin at two stations August 8-9, 1957 resulted in metabolic values from 8 to 16 $gm/M^2/day$ with respiration in excess of photosynthesis and all curves undersaturated throughout the day. Such patterns are not unusual where there are land drainages. Man's role in contributing to the moderately high metabolism is likely to be complex in this river system.

One of the most detailed applications of the diurnal oxygen studies to partially polluted waters was made by Mr. Charles Hoskin in his masters thesis (Hoskin, 1959) on the Neuse River in North Carolina. Hoskin found all stations with an excess of respiration over photosynthesis. Some of his stations were unaffected by man, draining forest lands. Others were heavily polluted with very large metabolic rates. The runoff of organic matter from agricultural fields and deforested lands increases respiratory metabolism of many streams. Such runoff is a type of pollution due to man's activity.

It is thus not easy to separate metabolic effects of pollution from some kinds of natural influxes, for natural metabolic systems exist of the types found in pollution. For example, diurnal curves made in the swamp waters of North Carolina such as in Singletary Lake, Bladen County, North Carolina (C. M. Hoskin, March 15-16, 1957) have only respiration and diffusion without photosynthetic pulse. The source of organic matter is the brown swamp substances which color the lake waters. Respiration of 2.2 $gm/M^2/day$ is due to a natural organic matter import. Nutrients are very low and photosynthesis was not measurable.

Thus measurements of bay metabolism indicate that the types of metabolism which result from organic pollution fall within the range of extreme metabolic conditions known in nature. The range of metabolic values in estuaries is similar to those in streams.

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