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Measurement in a Marine Environment Using Low Cost Sensors of Temperature and Dissolved Oxygen[1]

ABSTRACT: Continuous records of physical parameters of the marine environment are difficult as well as expensive to obtain. This paper describes preliminary results of an investigative program with the purpose of developing low cost time integrating measurement and averaging devices for water temperature and dissolved oxygen.

Measurements were made in an estuarine area of the Chesapeake Bay over two week periods. With chemical thermometers average water temperature for the two week period was found to be equal to average water temperature measured with thermocouples plus or minus 1.0 C. The slow diffusion of oxygen through the semipermiable sides of plastic bottles permitted the use of water filled bottles to obtain averaged oxygen measurements.

Oxygen measurements for two week averaging times using 500 ml polyethylene bottles were found to vary from conventionally measured and averaged dissolved oxygen by about 1.8 mg/l.

Introduction

Variability is a common characteristic of natural environments. Frequently, the greater detail in which an ecosystem is examined the greater is the variability in the measured parameters. Each variable has many degrees of freedom in which change may occur, but to simplify analysis it is often advantageous to reduce the complexity of the experimental design by restricting this freedom. A convenient dimension to restrict is the time dimension through the use of integrating or time averaging devices.

Some desirable characteristics of sensors for open water areas are resistance to corrosion, resistance to organisms, reliability when wet or dry and expendibility or low cost if the devices are lost. Most electrical devices do not possess all of those characteristics. In addition, because of the spatial variability in the marine environment it is often necessary to make measurements at many locations. In order to monitor the natural environment on a scale required for ecosystem studies in regions of encroaching population and development, accurate low cost sensors are needed. Temperature is known to be an important controlling and sometimes lethal factor in determining biological activity. Water-dissolved oxygen, unlike temperature, is strongly affected by the biota. These parameters are therefore important physical characteristics of the environment because of their relationship to the biota and were measured by averaging devices in the work described here.

Dissolved oxygen (DO) concentration in water and water temperature vary in a complex way in response to solar radiation intensity, wind, precipitation, tidal cycles and biological activity. Point measurements at any time will generally be non-representative of average conditions of the environment. For example, in the Rhode River the authors have measured daily variation of oxygen in excess of 13 mg/l.

Methodology

CHEMICALLY MEASURED TEMPERATURES

Inversion of sucrose in aqueous solutions of acid was studied in the middle 1800's in investigations concerned with reaction velocity. The reaction was followed by observation of the change of light polarization effect by the solution.

Pallmann et al. (1940) pointed out the usefulness of the sucrose inversion reaction for determination of average temperature. The relationship between reaction velocity (k) and temperature (T) is explained by the van't Hoff-Arrhenius law;

$$\log k = C_1 - (C_2/T) \qquad (1)$$

When the constants C_1 and C_2 are known, the average temperature T may be determined from the change of sucrose concentration. The change in concentration of sucrose is measured by the change in optical polarizing angle of the solution.

$$k = (1/tH^+) \log (R_0 - R_{00} / R_t - R_{00}) \qquad (2)$$

t is the time of exposure of the thermometer in days, H^+ is the acid supplied hydrogen ion concentration, R_0 is the optical polarizing angle of the sucrose solution initially, R_t is the polarizing angle of the solution after the exposure time t and R_{00} is the polarizing angle of the solution after all sucrose is inverted to glucose and fructose in the solution. Combining equation 1 and 2:

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$$T = \frac{-C_2}{pH - C_1 - \log t + \log (\log (R_0 - R_{00}) - \log (R_t - R_{00}))} \quad (3)$$

In practice the sucrose solution is prepared in the laboratory, put into small bottles and frozen until put into field use. After field collection they are refrozen on dry ice and stored until final laboratory analysis. Schmitz and Volkert (1954) found this temperature measurement technique useful in rivers. Lee (1969) refined the measurement techniques used to derive temperature from the sugar inversion reaction and applied the chemical thermometer in soil temperature studies. Measurements by Godshall (1972) in the Patuxent River of Maryland determined the usefulness of the thermometer in estuarine areas in spite of the attendant marine growth there. Godshall found that accuracy of the temperatures derived from these chemical thermometers was sufficient to define vertical depth profiles of temperature over the 20 feet of river depth considered. Comparison of the chemical thermometer measurements to conventionally measured and recorded temperatures indicated a difference of about ±0.5 C while the error of temperature measurement in comparison of one chemical thermometer to another was about ±0.1 C.

June 3 through October 26, 1972 a field test of the integrators was carried out in the Rhode River estuary (Fig. 1). At each of the four test sites chemical thermometers and dissolved oxygen measurement bottles were anchored to provide two-weekly averaged observations at the river bottom, at mid-depth and on the surface. Spot measurements of temperature, salinity and dissolved oxygen were made at each site at the end of each two-week period and a continuous record at mid-depth was taken by a U.S. Geological Survey monitor mounted on the Smithsonian Institution's Chesapeake Bay Center pier.

The averaged temperature data from the chemical thermometers along with the monitor temperature record at site 2 are graphed on Fig. 2. Considering the difference in averaging periods, the monitor and chemically measured temperatures are very similar (±1.0 C).

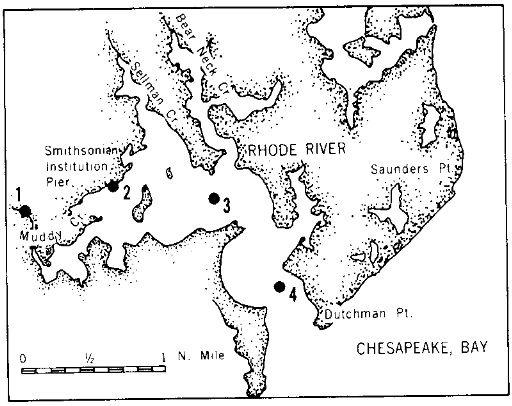

Fig. 1. Rhode River oxygen-temperature measurement sites.

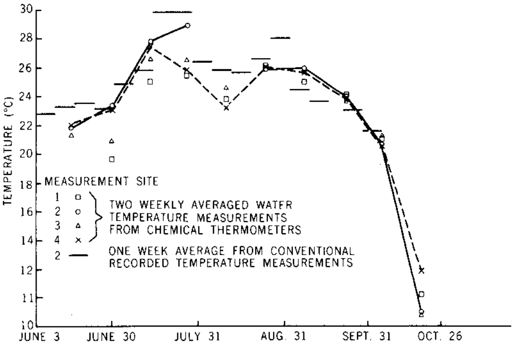

Fig. 2. Mid-depth temperature measurements in Rhode River area of the Chesapeake Bay Center for Environmental Studies, 1972.

MEASUREMENT OF DISSOLVED OXYGEN

Many plastics may act as semipermeable barriers, permeable to gas but not to water. Slack (1971) investigated the use of water filled plastic containers of various sizes, wall thickness, and of different kinds of plastic for measurement of dissolved oxygen in water. The speed at which oxygen diffused through the walls of Slack's containers varied considerably from one type of container to another. In application, the container is filled with biota-free water of about the same salinity and dissolved oxygen concentration as that of the measurement site and the water is treated with a disinfectant (1 or 2 percent solution of formalin). The containers were then placed in the river at the measurement sites and wiped clean each week.

A difference in dissolved oxygen concentration from inside to outside of the container is amortized by oxygen diffusion through the walls of the container. The time involved in reaching an equilibrium is cogent for smoothing the natural variations of oxygen in the environment. In general, the smaller the area of the diffusion barrier in relation to the volume of water in the container and the thicker the barrier the slower the diffusion processes. In addition the rate of diffusion through the sides of the bottle seems to be proportional to the difference in oxygen concentration across the sides of the bottle. The thicker the sides of the bottle the greater the difference between inside the bottle oxygen concentration and outside concentration when the diffusion rate becomes very slow. Five-hundred ml polyethylene round bottles with wall thickness of about 1.6 mm produced an approximate equilibrium of about 1.8 mg/liter oxygen concentration difference across the bottle walls after two weeks. These bottles were tested in the laboratory by placing the water filled bottles in a tank of water sealed from the air by oil. Nitrogen gas was bubbled through the tank for three weeks in order to drive the oxygen from the tank and bottles. After depletion of oxygen in the bottles, (amount of dissolved oxygen 6% of saturation) the bottles were transferred to a tank of oxygen saturated water into which air was bubbled. During subsequent days single bottles were withdrawn from the tank and the oxygen concentration in the bottle was determined by titration. Each measurement was subtracted from the oxygen saturation concentration in the tank and these differences are graphed on Fig. 3 with the corresponding time the bottle was in the tank. This test was conducted with both new and used bottles. The smoothness of the curve on Fig. 3 indicated that the diffusion characteristics of each bottle were about the same. It is evident that the plastic of the bottles was unaffected by previous exposure.

DO measurements at the Rhode River observation sites (Fig. 1) are graphed on Fig. 4. Hurricane Agnes (June 22-23) produced a great influx of fresh water into the observation area. This storm was followed by a four week period of high temperature with little wind. Evidently stratification of the water and high bio-chemical oxygen demand produced the decreased DO indicated in the graph during August. The relatively high DO concentrations measured at site 1 can be attributed to the cooler, nearly fresh, streamwater found there. During autumn gradual cooling and stronger winds produced equal DO concentrations throughout the measurement area.

Erroneous results were obtained with some of the oxygen bottles that were floating at the surface in open water. A dockside test, Table 1, confirmed the open water errors. Slack (1971) reported that the effect of increased temperature was increased rate of diffusion through the plastic bottles used in his measurements. Presumably the higher temperature of our sun exposed bottles caused a depletion of oxygen in the bottles.

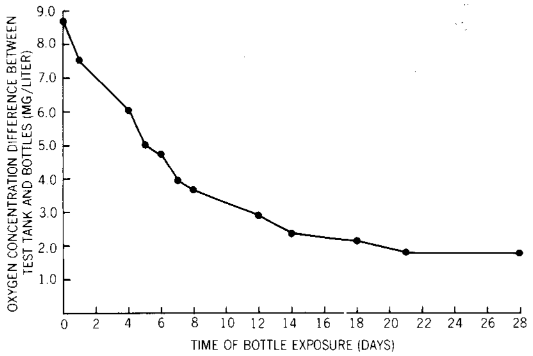

Fig. 3. Test of dissolved oxygen diffusion rate into 500 ML round polyethylene bottles.

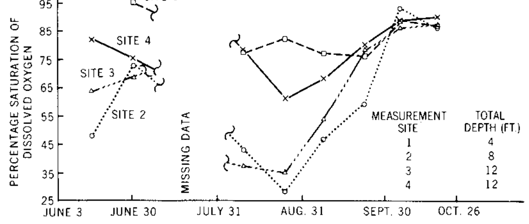

Fig. 4. Bottle smoothed bottom measurements of percentage saturation of dissolved oxygen in Rhode River area of Chesapeake Bay Center for Environmental Studies, 1972.

TABLE 1. Comparison of DO bottles floating at surface, sun shaded and sun exposed.

	Shaded Bottles		Unshaded Bottles	
Av. D.O.	Surface	At 15cm	Surface	At 15cm
mg/l	5.60	5.66	2.80	4.76
Range[1]	(5.3-5.9)	(5.1-6.1)	(2.6-3.1)	(4.7-4.8)

[1] Three bottles used for each test.

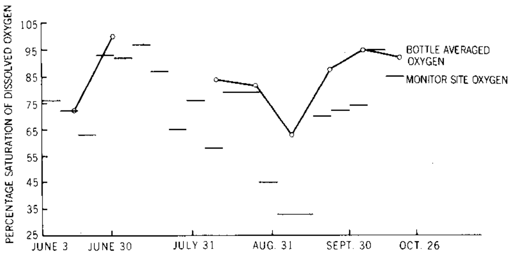

Fig. 5. Comparison of weekly averages of percentage saturation of oxygen measured at the monitor site with two weekly, bottle averaged, % saturation measurements from mid-depth.

At mid-depth the two weekly bottle averaged DO measurements are compared with weekly averaged DO measurements from the monitor on the Smithsonian Institution's pier (Fig. 5).

Conclusions

The need for inexpensive measuring devices is great. The chemical temperature measuring device is reliable and this work indicates the DO measuring bottle can be also useful in aquatic studies. The oxygen bottles chosen for this test were too thick walled resulting in too slow an equilibrium time. A thinner walled bottle would be expected to work better. In addition, it was found that because the sun effect on the bottles was great near the surface of the water, the measurement bottles are probably best used at depths greater than 1 meter. Although the thick walls of the bottles inhibited equalization of DO within and outside of the bottles, all measurements are consistent, relative to each other. An inequality of DO across the bottle walls of about 1.8 mg/l estimated from the laboratory test, is about the same as the difference between the bottle measured DO at site 2 and conventionally measured and averaged DO at that site.

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