SUPERSATURATION OF ATMOSPHERIC GASES IN THE COASTAL WATERS OF THE GULF OF MAINE

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ABSTRACT

Year round observations of dissolved oxygen in 1964–67 regularly revealed supersaturation of 120 to 150 percent during the spring and summer. Seasonal variations took the form of a sinusoidal cycle that showed definite phase relations to temperature. Comparisons with data for offshore dissolved oxygen showed that in general the coastal waters were more highly supersaturated.

Nitrogen measurements made in conjunction with those of oxygen led to the conclusion that oxygen supersaturation was usually due to photosynthesis, but occasionally supersaturation of both gases indicated some physical cause.

Supersaturation of oxygen in marine waters, particularly in coastal areas, is not uncommon, and references to it are numerous in the literature. Its effect on marine life has apparently not been investigated, nor are there adequate records for comparison with observed fluctuations in distribution or abundance of organisms.

The coastal waters of the Gulf of Maine support several fisheries, chief among which are those for lobsters (*Homarus americanus* M. Edw.) and for Atlantic herring (*Clupea harengus harengus* L.). The herring fishery in particular suffers from irregular periods of poor catches due to unfavorable distribution (hence, lack of availability) as well as to low abundance. The causes for these irregularities in availability are not known.

To seek possible relations between herring distribution and hydrography, the Bureau of Commercial Fisheries Biological Laboratory in Boothbay Harbor, Maine, is investigating several aspects of the hydrography of coastal waters. Interest in dissolved oxygen stemmed primarily from an outbreak of gas disease in the laboratory aquaria in June 1964. At that time the sea water in these aquaria effervesced with tiny bubbles; several herring died from gas disease and many more showed the typical symptoms—disorientation, exophthalmia (popeye), and bubbles in the fins and lateral line organs. This disease is frequently a result of supersaturation caused by defects in the water pumping system. Careful inspection of our system, however, revealed no defects. Furthermore, Winkler tests of water taken directly from the harbor as well as that supplied through the pumping system showed substantial supersaturation of oxygen. Whether the supersaturation was due to excessive dissolved air, or to oxygen only, was not determined at the time as no equipment was then available at the laboratory for measuring nitrogen. Routine measurements of dissolved oxygen began in the early summer of 1964, but nitrogen measurements were not undertaken until 1965.

Although some data on dissolved oxygen have been published for the Gulf of Maine (Gran and Braarud, 1935; Rakestraw, 1933; Colton, Marak, Nickerson, and Stoddard, 1968), these records are limited to short periods during a few years and cover mainly the open waters of the Gulf rather than the inshore regions. Only occasional measurements have heretofore been made in the coastal waters.

METHODS

Water samples for oxygen analysis were not taken according to a regular schedule, but were spaced to provide a fair coverage of each month. Samples were taken three to five times per week in spring and summer and about once a week in fall and winter. The most conveniently and frequently sampled source was the water pumped into the laboratory from a depth which varied accord-

Published August 1968.

ing to tide from about 3 to 6 m. The harbor water was sampled directly with a dissolved oxygen sampling bottle[1] at a depth of 2 m. at the same time the pumped water was sampled, except that during the first winter only one sample was taken each month.

For the first 6 months, samples were analyzed with a polarographic dissolved oxygen meter, but this method proved somewhat unreliable at low temperatures. After the first winter, all determinations were made by the unmodified Winkler procedure. Because the Winkler method has several sources of error, the routine technique was periodically checked on standards of water saturated with air under controlled conditions. The errors averaged about ±0.1 p.p.m.; I did not consider them serious for the purpose of this study. Solubility data for oxygen were obtained from the tables of Green (1965).

Measurements of dissolved nitrogen were not made during the first year (1964). In 1965 a few determinations were made with a manometric Van Slyke apparatus, and in 1966 and 1967 periodic nitrogen determinations were made according to the micro-gasometric method of Scholander, Van Dam, Claff, and Kanwisher (1955). Solubility data for nitrogen were obtained from the tables of Rakestraw and Emmel (1938).

The amount of dissolved oxygen sometimes varied considerably during the day. This fluctuation reflects in part the diurnal cycle of oxygen sometimes called the "oxygen pulse." To obtain comparable measurements from day to day, samples were taken in the afternoon, when concentrations of dissolved oxygen were approaching their maximum. Tides also caused some variation that was reflected as irregularities in the seasonal trends.

OBSERVATIONS IN 1964

The highest oxygen concentration in the laboratory water during 1964 was 12.7 p.p.m. on June 23; the saturation was 153 percent. At the same time, the oxygen in the surface water at Boothbay Harbor was 10.8 p.p.m. and the saturation was 131 percent. Daily maxima of 130 to 140 percent saturation were frequent during June, but thereafter during the summer the levels decreased and fluctuated between 110 and 120 percent saturation.

[1] Type recommended by A.P.H.A. Standard Methods of Water Analysis.

Samples taken elsewhere along the coast in July ranged from 107 to 115 percent saturation in Casco Bay, 100 to 104 percent saturation in Penobscot Bay, and 102 to 112 percent saturation along the eastern Maine coast. Unfortunately, these measurements were not made until after the extremely high values of dissolved oxygen at Boothbay Harbor had diminished; hence, they may be lower than would have been observed earlier in the year.

OBSERVATIONS IN 1965

Oxygen measurements were discontinued toward the end of 1964, but were resumed in January 1965. The water remained close to 100 percent saturation during the winter, but in mid-March the first of a series of peaks in both concentration and saturation appeared; concentration reached 13.5 p.p.m. and saturation 120 percent. The second major peak was in early May when the concentration was 13.5 p.p.m. and saturation over 130 percent. At that time dissolved nitrogen was also high (in excess of 120 percent saturation) for a few days. Thereafter, the concentration of dissolved oxygen decreased slowly and irregularly until the end of July, but because of rising temperature the saturation remained between 120 and 130 percent. Except for a few days in May, dissolved nitrogen, whenever measured, was close to 100 percent saturation.

Winds can sometimes produce dramatic changes in the amounts of dissolved oxygen. A precipitous decrease in dissolved oxygen took place after a strong northwest wind on August 28 and 29; the concentration dropped to 7.3 p.p.m. and saturation to less than 90 percent, but rose shortly to levels as high as before. A second northwest wind-storm on September 26 again dropped the oxygen to below 100 percent saturation where, except for a slight rise during October, it remained for the rest of the year.

For localities other than Boothbay Harbor, saturations in June were 114 to 119 percent in Casco Bay and 117 to 127 percent along the eastern Maine coast.

OBSERVATIONS IN 1966

Saturation of oxygen began to rise above 100 percent late in January. Three major peaks occurred during the spring. In the laboratory water supply these reached 128 percent in late March, 128 percent again in mid-April and 137 percent in

mid-May. The May peak was the highest for the year (13.6 p.p.m., 137 percent saturation) in the laboratory supply water, but the harbor surface did not reach its annual maximum until June 8 (12.3 p.p.m., 133 percent saturation). Thereafter the dissolved oxygen in both water sources decreased irregularly throughout the summer, although the highest average for August was in 1966. Throughout the fall and winter, saturation was usually between 90 and 100 percent.

OBSERVATIONS IN 1967

The dissolved oxygen remained near or below saturation through February, but the concentration reached a record high for the period of study: 14.8 p.p.m. on March 27. Despite the relatively low temperature, saturation reached 130 percent at this time. The next major peak appeared during the third week in May, when the concentration reached 13.5 p.p.m. and saturation 135 percent. Values for pumped water and harbor surface water differed only slightly. As in the 2 preceding years, dissolved nitrogen rose to about 120 percent saturation for a few days in May.

By the end of June the supersaturation of oxygen declined markedly, and the July average was the lowest for that month in the 4-year period. In general, oxygen supersaturation was lower during the whole summer of 1967 than in the 3 preceding years. This drop may have indicated a long-term downward trend, or could have been due to an unusual amount of cloudy or foggy weather.

ANNUAL TRENDS AND COMPARISON WITH OFFSHORE WATERS

The seasonal and annual trends in temperature and in oxygen concentration, percentage saturation of oxygen, and temperature are shown in figure 1. The values shown are averages of all afternoon measurements made each month. They can be considered to be the monthly means of daily maxima.

A study of the figure reveals several points of interest. Both concentration and saturation show a cyclic pattern that bears some relation to temperature. Oxygen concentration tends to be highest when the water temperature is low, but the peaks lag the temperature minima by about a month. Percentage saturation is highest during periods of rising temperatures. The probable reasons for these phase relations are that oxygen is more soluble at low temperatures but the peak of oxygen production by photosynthesis occurs later than the time of minimum temperatures. Maximum concentrations, therefore, occur when the interaction of high solubility and maximum production is optimal. Maximum saturation is similarly the result of optimal interaction between high production and low solubility. Saturation is further increased when the rate of warming outpaces the rate at which the dissolved gas can come into equilibrium with the atmosphere.

The supersaturation of oxygen appeared to be somewhat higher at Boothbay Harbor that at other localities along the coast, although the number of samples taken elsewhere may not have been sufficient to provide a fair comparison. Values for coastal waters were generally higher in 1965 and 1966 than those observed for comparable periods in offshore waters during the *Albatross IV* cruises (Colton et al., 1968). In 1965 no offshore samples exceeded 120 percent saturation in May and June, and in 1966 only 3 percent of all samples from the top 20 m. in the open Gulf of Maine were greater than 120 percent. At Boothbay Harbor during the comparable period of both years, 78 percent of the samples in 1965 and 82 percent in 1966 exceeded 120 percent saturation. Elsewhere along the coast during a comparable period, 14 percent of the samples in 1965 and 43 percent of those in 1966 showed over 120 percent saturation.

CAUSATIVE FACTORS

Oxygen supersaturation in the sea can result from several processes, of which two have major significance. The most important is probably the actual increase in oxygen concentration resulting from photosynthesis; the other is a change in the physical properties of the water which affects the solubility of gases. Air that diffuses into water from the atmosphere at the sea surface can produce 100 percent saturation of oxygen and nitrogen at the ambient temperature, salinity and barometric pressure; if these physical properties change rapidly, the water can become at least temporarily supersaturated. Rapid warming of saturated water, or the mixing of warm and cold saturated water results in supersaturation until the gases are able to once again achieve equilibrium with the atmosphere.

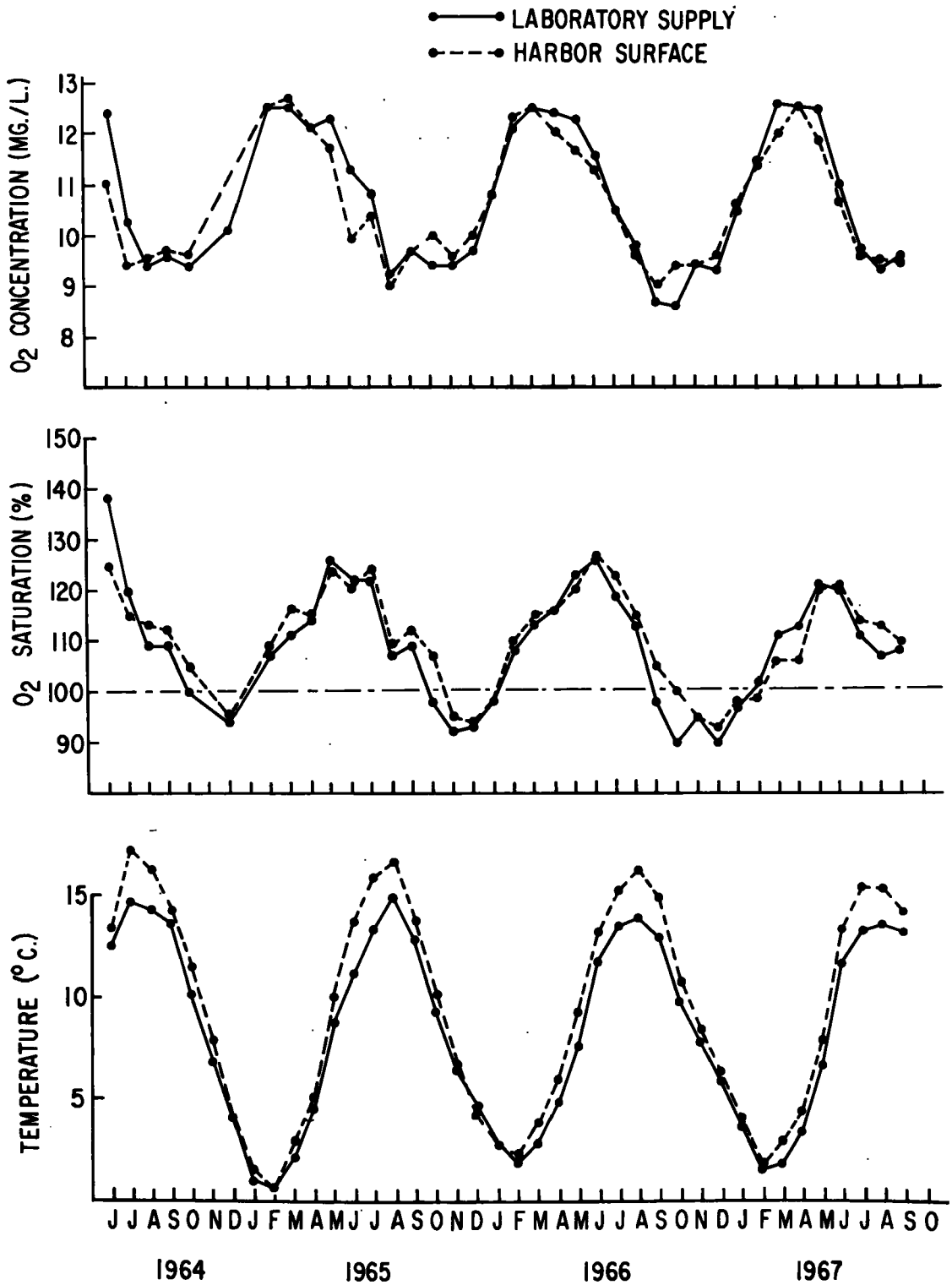

FIGURE 1.—Monthly means of daily maximum concentration and percentage saturation of dissolved oxygen and corresponding mean water temperatures at Boothbay Harbor, Maine, 1964–67.

TABLE 1.—*Percentage saturation of nitrogen and concentrations of oxygen in excess of saturation according to source, calculated from observed nitrogen and oxygen concentrations. P: photosynthetic oxygen, A: atmospheric oxygen. Entries for each month are given chronologically but the dates for each entry do not correspond exactly from year to year; approximate time of month is indicated by the position of each entry in a column.*

Year	1965			1966			1967		
Month	N_2 saturation	Excess O_2		N_2 saturation	Excess O_2		N_2 saturation	Excess O_2	
		P	A		P	A		P	A
	Percent	*Ml./l.*		*Percent*	*Ml./l.*		*Percent*	*Ml./l.*	
March				102	0.15	0.15			
				98	.75	None	109	0.10	0.75
April	98	None	None						
	104	0.80	0.30						
	113	None	.65				104	None	.27
	109	.55	.70	100	1.75	None	113	None	.70
	105	.25	.30	108	None	.45	110	.55	.80
				113	None	.60			
May	106	1.20	.30	106	1.50	.45			
	127	None	1.80	109	1.75	.50			
	127	.60	1.90	116	1.60	1.15			
				116	.95	1.20	117	1.05	1.25
				112	1.30	.80			
				114	1.20	.95	121	None	1.45
	103	2.05	.15	110	.90	.70			
				109	.70	.70	106	1.05	.50
June	85	1.25	None	107	.40	.50			
	104	.35	.25	107	1.30	.50			
	96	1.35	None	100	1.10	.10			
	97	1.45	None	104	.40	.35	107	None	.55
	101	1.40	.10	101	.90	.10	105	.25	.50
	98	1.35	None	102	.50	.20			
	94	1.00	None	101	.30	.10			
July	92	1.15	None	109	.35	.65			
				108	.35	.60			
				109	None	.75			
				108	.05	.60	106	None	None
				111	.05	.75	108	None	.25
				110	None	.55			
				112	None	.50			
				115	.20	.95	111	None	None
August	109	.60	.60	110	None	.40	111	None	.30
				117	None	.60	107	None	None
	98	.55	None	111	None	None	111	None	None
				113	None	None	106	None	.30
				108	None	.35			
September	104	1.25	.30	112	None	None			
				108	None	.40			

Supersaturation arising from these two processes can be distinguished if the concentration of nitrogen is known. Nitrogen and oxygen which enter solution from the atmosphere bear a nearly constant ratio to one another, expressed by the equation $O_2 = .577\ N_2 - .22$ (Rakestraw and Emmel, 1938). This equation indicates the amount of oxygen which ought to be in solution for any given concentration of nitrogen. Oxygen in excess of this amount represents that added by photosynthesis; the difference between the calculated oxygen concentration and the oxygen concentration at saturation represents the excess or deficit of atmospheric oxygen.

Nitrogen observations were made only intermittently in the present study; the observations, however, together with source composition of excess oxygen are given in table 1. As can be seen, the greatest nonphotosynthetic oxygen supersaturation and supersaturation of nitrogen occurred usually in April or May or occasionally in midsummer.

The physical causes of supersaturation could be intensified by the coastal topography. Numerous protected and shallow embayments permit rapid warming of the water; tidal movement is strong and conducive to the mixing of warm and cold saturated water, producing supersaturation of the mixture; warming of subsurface waters is a possible result of the flooding of sunheated tidal flats. I have no evidence that these particular processes are, in fact, the cause of nonphotosynthetic oxygen supersaturation, but they are theoretically possible.

ECOLOGICAL SIGNIFICANCE

The immediate question posed when the first indications of supersaturation were noticed was whether this situation was unusual or a regular annual occurrence. On the basis of 4 years of observations, the answer seems to be that it is a regular occurrence, although annual variations in the seasonal cycle are marked. Longer term trends may also be indicated in the basic annual cycles.

The duration and degree of supersaturation declined with each passing year of the period studied.

Strong annual variations in the degree of supersaturation could very probably produce fluctuations in the abundance and distribution of marine organisms if these organisms can be affected by supersaturation. The most marked effect of supersaturation on fish and other organisms is gas bubble disease. This disease, however, does not appear unless certain conditions obtain. By convention, the percentage saturation of dissolved gases in the sea is the ratio between the observed concentration at some depth and the concentration which would exist at the sea surface in equilibrium with the atmosphere at the same temperature and salinity as the depth in question. Thus, water at moderate depths may be supersaturated according to this definition and yet because of the hydrostatic pressure actually be capable of holding much more gas in solution. Ricker (1934) has called the degree of saturation which is related not to a theoretical surface value, but to the absolute capacity of water at a given hydrostatic pressure, the "absolute saturation." "Gas disease" due to supersaturation alone can occur only in absolute supersaturation. Furthermore, this supersaturation must be extremely high if gas disease is to be caused by oxygen. Observations have been made of gas disease occurring in the natural environment at oxygen saturations of 250 percent (Renfro, 1963) and over 300 percent (Woodbury, 1942). I have experimentally induced gas disease in herring (*Clupea harengus harengus*) at saturations of pure oxygen of 300 percent, but could not produce the symptoms at less than 200 percent saturation. Nitrogen, however, seems to be dangerous to fish at saturations of 125 percent or more (Marsh and Gorham, 1905; Egusa, 1959). In air-supersaturated water, I have experimentally induced gas disease at saturations of 120 percent nitrogen and 130 percent oxygen. In my experiments, the herring showed a definite tendency to avoid the supersaturated water, but only when the saturation levels were high enough to produce gas disease.

Gas disease can occur, furthermore, only when the total gas pressure in the water exceeds the combined hydrostatic and atmospheric pressures. When the concentration of any gas is increased by the displacement of another gas, gas disease is unlikely as long as the total gas pressure is not increased. Fish have been exposed with little harm to oxygen saturations of up to 400 percent by bubbling this gas into the water at atmospheric pressure (Haempel, 1928; Bishai, 1960). Pathological symptoms occurred in some of Haempel's fish, but they seemed to be unrelated to gas disease.

The above evidence suggests very strongly that the levels of gas supersaturation along the Maine coast are not high enough to have a direct detrimental effect on fish in their natural environment. The situation under artificial conditions is much different, however. In aquaria, lobster pounds, and other similar installations where water is pumped from below the surface of the sea into relatively shallow tanks at sea level atmospheric pressure, any nominal supersaturation becomes absolute. This supersaturation, perhaps aggravated by elevations in temperature or by the pumping system itself could produce lethal conditions as it did in our laboratory in the summer of 1964. The most likely effect of supersaturation on fish populations, if there is any effect at all, would probably be indirect, but lack of evidence to demonstrate such effects precludes useful discussion of them at this time. The facts do show, however, that a condition does exist, and recurs annually in more or less cyclic fashion, which could conceivably play a definite role in the ecology of marine organisms.

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