VII. SEASONAL VARIATIONS IN THE DISSOLVED OXYGEN CONTENT OF THE WATER OF THE THAMES ESTUARY.

WITH SPECIAL REFERENCE TO THE PHENOMENON OF SUPERSATURATION

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THE observations recorded below were made as part of a general investigation of the River Thames undertaken primarily from a public health point of view and the phenomena have only been investigated so far as was compatible with the main objects of the scheme. Casual examination of the water of the estuary of the Thames in the summer of 1914, in the course of which determinations of dissolved oxygen and chlorions were made, yielded several results in which the proportion of dissolved oxygen was much greater than was required for saturation with atmospheric oxygen of water of the observed salinity. Systematic observations made in subsequent years showed that supersaturation with dissolved oxygen occurred to a greater or less extent in each spring and in a less systematic manner later in the year.

Until recently we have found no direct references in scientific literature to this phenomenon of supersaturation in sea water, although it has been observed and its cause properly assigned in fresh water. One of us has pointed out [Coste, 1917] that "supersaturation—at any rate with oxygen—is by no means rare." It is sometimes to be attributed to "rapid variations of temperature," but "more often to its excretion from vegetation as a residual product of photosynthesis." In this paper it is noted that Morren (1843), who investigated the gaseous content of the surface water near St Malo, found that the oxygen content of sea water was greatest and the carbon dioxide least in bright weather. It should also be noted that the New York Harbour Board investigators recorded several cases where the volume of dissolved oxygen found was greater than that required for saturation, although they refrained from recording a greater percentage saturation than 100.

Recently Dr J. H. Orton, with whom we have been in correspondence, called our attention to a paper by Schulz [1922] in which he records and discusses cases of supersaturation with dissolved oxygen in the North Sea. Schulz refers to an earlier paper by Gehrke [1916] in which supersaturations up to 16 % are recorded.

NOTE. There were no observations in June 1915.

Fig. 1. Polar diagram showing the percentage saturation with dissolved oxygen of Estuary Water off the Knock John Buoy for fortnightly periods in the years 1915-1921 inclusive.

The maxima for May and June are very much greater than in any other months, and the sequence of maxima shows that there is a growing tendency towards this maximum, with a progressive falling off from it towards the end of the year. The years 1916 and 1918 are outstanding as years of extremely high supersaturation. As to places, supersaturation was on the whole more pronounced in the neighbourhood of the West Oaze Buoy than in any other place and least frequent and less in amount at the upper stations, the Mucking and Chapman Lights and off Southend, although in 1916, very high figures were observed in May—above 50 % excess of dissolved oxygen—at all places from the Mucking Light to the Knob Buoy.

DISCUSSION OF RESULTS.

In the first place we would emphasise the fact that the supersaturation with dissolved oxygen is real. In the early stages of this work we realised that 2 % above or below saturation might be allowed for experimental error + the uncertainty of the standard figure adopted, and that high barometric pressure might at times cause the standard figure based on a pressure of 760 mm. to be about 2 % below the actual figure appropriate to such high pressure. If all these errors by an unfortunate combination were of the same sign, they might cause a figure of 104 % to be obtained when the true figure was only 100, but they would not account for the much higher figures frequently obtained. If water, say from polar regions, could somehow be raised from 0° to 15° without losing dissolved oxygen, this would raise 100 % saturation to about 140, but such supersaturation of oxygen would be accompanied by a similar supersaturation of “nitrogen” (N + A).

It should be mentioned, however, that while this range of possible error must be recognised, the lower degrees of supersaturation conformed to the rule which characterised the higher ranges. They were uniform—with minor variations—for each point of observation and they represented a definite rise through a period often of several days, as contrasted with prolonged returns of figures at or slightly below the saturation point. While admitting them with caution and subject to possible errors which have not been eliminated, it would we think be a mistake to dismiss them as due entirely to the possible sources of error mentioned. It is desired to note in passing, merely, that our observations suggest that variations in the amount of dissolved oxygen in estuarial waters above or below the saturation point are of not infrequent occurrence and are observed under conditions which are not likely to be explained by the periodic photosynthesis associated with the higher figures of supersaturation. Similar small divergencies from saturation have been noticed in the North Sea by Schultz.

Any explanation of the phenomenon of natural supersaturation based on the assumption of retention of oxygen in water recently subject to a rise of temperature such as might occur in the case of polar currents reaching the

North Sea fails, as will be seen from the following observations, to account for all the facts. Using Winkler's gasometric method, E. T. Butler and F. J. East in 1917 found that the proportion of nitrogen in water supersaturated with oxygen was normal, *i.e.* was approximately equivalent to that required for nitrogen saturation at the observed temperature. One result where the proportion of oxygen was rather less than 100 % is included in the table.

Table II. *Showing the percentage saturation of estuary water with oxygen and nitrogen in June, 1917.*

Place	Date	Temp.	Cl.	Dissolved gases cc. per litre		Percentage saturation	
				Oxygen	Nitrogen	Oxygen	Nitrogen
West Oaze	June 12	17.7°	1860	8.1	11.1	134	104
Nore	" 14	18.0°	1845	7.9	11.0	150	104
"	" 15	18.6°	1860	8.5	10.7	162	102
"	" 18	19.7°	1870	7.44	10.7	145	104
Chapman	" 19	20.3°	1505	4.89	11.0	90	104
West Oaze	" 22	19.10°	1875	6.13	10.5	119	101

The one obvious explanation of supersaturation with oxygen only in spring is to be found in the normal vernal phenomena. An increased duration of daylight and greater penetrating power of the sun's rays lead to the rapid growth of the varied algal flora of the sea [cf. Moore, 1921] and thus to photosynthesis. The rising temperature of the water increases the velocity of photosynthesis as it does of other chemical reactions. This point has been investigated by Osterhout and Haas [1919] who found the temperature coefficient to be about 1.81 per 10° between 17° and 27°.

That water should become and remain appreciably supersaturated with a gas whilst it is in free contact with air is at first startling, and as we have indicated, we were at pains to satisfy ourselves of the reality of the phenomenon.

It is obvious that, given a source of pure oxygen (such as a growing plant) in water, the water around this source will take up the oxygen very rapidly if it is generated all over (or within) the surface of contact between water and plant without the formation of a limited interface which would occur if bubbles were generated. It would in fact appear that there will be no tendency to form bubbles until the concentration of dissolved oxygen is nearly five times as much as in water in equilibrium with air, since it is pure oxygen and not air which is evolved by the plant. Hence very little loss by reason of non-absorption by the water of oxygen generated is likely to occur. Loss may, however, occur in two ways: (1) by combination of the oxygen with oxidisable matter either with or without the aid of living organisms; (2) by escape into the air at the interface of air and water, following an upward diffusion of oxygen in solution. The amount of oxygen which can be liberated by photosynthesis is limited on the one hand by the relative abundance of chlorophyllous organisms and, on the other, by the available carbonic acid. Prideaux, Moore

and Herdman [1915] have shown that in sea water the removal of CO_2 from bicarbonate by a green algal growth can go on until the transformation

is complete, but not beyond this point. This represents a p_{H} of about 9.1.

Sea water contains about 2.4 milliequivalents per litre of "uncompensated" base mostly as bicarbonate. If it be considered as all present as bicarbonate, then 2.4 milliequivalents of CO_2 are available for liberation and transformation into organic compounds and oxygen. The evolution of oxygen has been shown by Schulz [1922] to be equivalent within small limits to the CO_2 transformed. It is therefore possible in one litre of sea water to liberate 1.2 millimols. of oxygen or about 27 cc. of oxygen at N.T.P. This is from four to five times the amount required to saturate sea water in equilibrium with air. It is, in fact, almost enough to saturate it if under an atmosphere of pure oxygen. Further, the sea water is usually approximately saturated (with respect to the 21 % of oxygen in air) already, and also an increase of the alkalinity of sea water will cause it to take up more CO_2 (from which more oxygen can be liberated) from the air. There is, therefore, no difficulty in accounting for the liberation of oxygen in the required amount, given the presence of quick-growing organisms. It is reasonable, however, to expect that this liberation of oxygen should be accompanied by a decreased hydrion concentration.

Casual determinations of hydrion concentration during 1920 showed that there was a seasonal alteration of the kind expected (Table III). The results expressed as p_{H} , *i.e.* Briggsian log. of reciprocal of hydrion concentration—were as follows for sets of samples in March, April, May and June, 1920.

Table III. *Hydrion concentration of river water. Spring and early summer, 1920. (Expressed as p_{H} .)*

	Mar. 26	Apr. 22	May 5	June 7	June 9
Erith	7.78	7.78	about	7.76	7.69
Greenhithe	7.78	7.76	7.76	7.78	7.69
Gravesend	7.75	7.78	or less	7.78	7.69
Mucking Light	7.88	7.78	7.78	8.08	8.08
Chapman Light	—	7.78	7.88	8.21	8.20
Southend	7.88	7.88	8.20	8.41	8.31
Nore Light	7.94	7.88	8.20	8.41	8.31
West Oaze Buoy	7.94	7.94	8.20	8.41	8.30
Knock John Buoy	7.94	7.94	8.20	8.41	8.31
Edinburgh Light	7.94	7.94	8.20	8.31	8.20

It will be noted how the real alkalinity, as shown by hydrion concentration, on the whole increased at stations from the Chapman Light downward from March to June.

From June 1921, a regular series of observations was made, using Prideaux's method of double titration [1919]. The results of these are set out for one typical place in the estuary—the Knock John Buoy in Fig. 2, which shows the variation in p_{H} (hydrion concentration) for the period in question. It will be seen that during a great part of the period—from July 1921 to April 1922—

Fig. 2.

the water was acid, becoming from April 1922 to June 1922 more and more alkaline, with some indications of a falling off from June. Further the water was alkaline at the beginning of the period—June 1921.

These figures agree with the argument just developed that marked alkalinity and supersaturation should go on together, or rather that if supersaturation is observed, it should be at periods of high alkalinity (low hydron), the latter being a more lasting record of photosynthesis than supersaturation.

There is some positive evidence of an increase of microscopical green organisms in the estuary water towards summer. It was obviously impossible to include in an investigation undertaken from a public health point of view, a full examination of microplankton but a regular microscopical examination of the sediment from the water was begun in July 1921 and the results returned, in respect of light green growths, dark (blue) green growths and diatoms, as trace (1), few (2), many (3), chiefly (4). The numbers attached were used to represent approximate orders of magnitude, and as nearly all the observations were made by one worker (Mr E. T. Butler) they should be sufficient to indicate a general increase or decrease of green organisms. Fig. 3 shows in graphic form the seasonal variation which, on the whole, follows the course suggested in this discussion.

Fig. 3.

Sir W. A. Herdman [1922] has discussed "The distribution of the plankton as a whole and of its various constituents throughout the year" in the Irish sea. He says "The spring maximum of phyto-plankton starting in March, when the sea has still a low temperature and increasing to a climax in April, May or June; the diatom minimum at the height of summer in July or August; the secondary lesser maximum in autumn (generally September or October), very variable both in extent and in constituent organisms; and finally, the winter minimum have been recorded for every year and need no further demonstration."

The interaction between a gas (such as air) and a liquid in which it is soluble (such as water) is only a special case of heterogeneous reaction. It has been discussed generally by one of us [Coste, 1917] and the side of the equilibrium where the liquid is supersaturated with the gas was investigated by C. Bohr for solutions of carbonic acid [1899]. The case of unsaturation has recently been carefully investigated by Adeney and Becker [1919, 1, 2]. The general equation for the course of this action when the liquid is of uniform composition below the surface

$$\frac{C - x_t}{C - x_0} = e^{-kt} \text{ whence } \frac{dx}{dt} = k(C - x)$$

where C = the concentration corresponding to saturation, x_0 the initial concentration, x_t the concentration at any period of time t from the beginning of the action and k a constant which is really the evasion constant (a multiple of the *coefficient of evasion* of Bohr) is applicable to cases of supersaturation as well as to unsaturation, the only difference being that $C - x$ has a negative value both above and below the line on the left of the equation, as also has dx . Since this general equation implies that the rate of approach to saturation is, all other conditions being similar, proportional to the difference from saturation, it follows that around saturation, towards which the value converges, the rate of exchange becomes very slow, whether the liquid is supersaturated or unsaturated with the gas. The value of k will be small if the motion of water or air is slight, but it will increase rapidly if the molecules at the interface are rapidly changed, or if the area is enlarged. Hence still weather, when the motion of air and water is small, will tend to preserve supersaturation, whilst rough weather, when both air and water are in rapid motion, and waves, spray and air bubbles increase the interfacial area, will tend to bring about mere saturation, that is, stable equilibrium more rapidly. The effect of windy weather in increasing the dissolved oxygen in unsaturated water has been observed by R. H. Gould [1922] in the water of the Arthur Kill, New York Harbour. Our own observations on supersaturated water conform to those of these observers. Supersaturations in the estuary disappear rapidly under agitated conditions of the water, due to wind, and the comparatively low supersaturations observed in the years 1919–1922 are not improbably due to the coincidence of disturbed weather with the period of highest photosynthetic activity.

In still weather, the vertical movement of water due to convection by reason of the cooling and concentration of salts in the surface layer by evaporation is at a minimum and exchanges of dissolved gas (oxygen produced under the surface) between layers of water in different vertical planes will proceed more nearly by pure diffusion according to Fick's law [1855] causing a gradient of concentration, and less by the more efficient process of mixing. The considerable depth of the sea renders the formation of a gradient more easily possible.

Two experiments made by us illustrate the slowness of escape of oxygen from still water and the accelerating effect of agitation.

1. A large Winchester bottle was filled with tap water and inverted over water so that about $\frac{1}{2}$ litre of oxygen could replace some of the water. The bottle was stoppered and shaken repeatedly, and then left inverted with a water seal all night. Next day the water was siphoned off into another bottle which was filled to the neck. At intervals, samples were removed with suitable precautions for the determination of dissolved oxygen. The first three samples were taken within one hour and as the surface exposed was small, the loss of dissolved oxygen, although distinct, was small. The water level then reached the shoulder of the bottle and the surface exposed after this was practically constant. The results are shown in Table IV.

Table IV.

Time (hours)	0	$\frac{1}{2}$	1	3	47		51	52	144
Temperature	16.8	16.85	17.0	17.3	17.8	17.8 ¹	18.9	19.4	16.0
Dissolved oxygen cc. per litre	24.4	24.4	24.3	24.2	11.44	10.8	11.12	10.8	6.36
% saturation	351	351	355	356	173	151	171	168	92.0

¹ Taken at top of water. All others siphoned from bottom. Value of k calculated from 47 hours = 0.026.

These results show how slowly still water parts with an excess of oxygen and those for 47 hours illustrate the working of Fick's law. The last result is to be explained by temperature changes. Barometric variations were considered in calculating the saturation values.

2. Similarly prepared water was placed in a cylindrical glass jar, exposing a surface of 95 cm.² and stirred with a spiral glass stirrer at such a rate as not to break the surface. The results are stated in Table V.

Table V.

Time (hours)	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$	1	2	3	4
Temperature	16.6	16.7	16.6	16.6	16.6	16.8	17.1	17.4
Dissolved oxygen cc. per litre	23.34	21.56	19.38	18.2	16.95	13.38	10.05	8.85
% saturation	338	312	281	264	253	195	148	127.5

Value of k about 0.5.

The effect of stirring in accelerating the exchanges between air and water is very marked, the value of the evasion constant being increased about 20 times [cf. Becker, 1921]. The experiment illustrates the effect of rough weather in rapidly dissipating supersaturation of sea water with oxygen or indeed with any dissolved gas.

It may be remarked that whereas the water of such rivers as the Thames or Seine is always much supersaturated with carbonic acid, that is, with calcium bicarbonate—in sea water which is much more agitated and mixed with the air the equilibrium is more closely approached [cf. Prideaux, 1919].

If what we have observed in the Thames estuary is true generally, not only of the seas around our coasts but also of the oceans beyond, the phenomenon is of more than academic interest. The vernal supersaturation of sea water, which from the nature of our observations was necessarily striking, is

only an index of a process which cannot fail to have results in much wider and unexplored fields. The seas at these times are a great natural factory where free oxygen is produced on a scale which, having regard to the relative areas of sea and land, may conceivably exceed that of land vegetation. The oxygen of supersaturation is but a proportion and probably a small one, of the volume set free by marine photosynthesis. It is tempting to speculate on the part played by these gases in the contribution to the salubrity of sea air. The tidal convection of oxygen during periods of supersaturation is no negligible datum among the purifying factors of polluted estuarial waters. The seas breaking on the shores at these times are liberating their surcharge of oxygen in its most active state and it is seen that not the chemist or the marine biologist alone is interested in a phenomenon which has for its theatre of operations the vast tracts of oceans and the littorals of continents.

It has always been realised that the sea acts as a great stabiliser of the CO_2 content of the air by reason of the bicarbonate-carbonate equilibrium. It appears that it is equally efficacious in the positive work of keeping up by continual contributions a steady proportion of oxygen in the air.

We have mentioned various co-workers in the body of the paper. We wish particularly to acknowledge the work of our colleagues Messrs E. R. Andrews, J. W. H. Biggs and E. T. Butler, the latter of whom carried out most of the work afloat. They have all, often under circumstances of difficulty, discomfort, and even danger, in a variety of ways, contributed to the elucidation of the points now set forth. In the conduct of the observations their work has been indispensable, and the accumulated data essential to an adequate survey of the phenomenon are a tribute to the assiduity of their co-operation.

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