

LETTERS TO THE EDITORS

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Conditions for the Vernal Increase in the Phytoplankton and a Supposed Lag in the Process

IN his recent discussion of the fertility of ocean waters, Harvey¹ mentions that "A phenomenon which seems to lack explanation is the time at which phytoplankton start to increase rapidly at the beginning of the year", for by mid-winter all the known nutrient salts have been regenerated and, in spite of the bright light of spring, the steep increase in the phytoplankton, as shown by the decrease in phosphate, becomes apparent in the English Channel normally only between March and April, and even much later elsewhere. He mentions the well-known effect of turbulence in carrying the cells down into regions of low illumination, and suggests that there are unrecognized factors controlling the inception of growth in some areas. Sverdrup² also states: "This conditioning of the water may well be a factor in the initial outburst of phytoplankton growth when other conditions are optimum"; thus he also alludes to an unknown factor.

In 1923 I obtained decisive evidence that light alone is necessary for the full development of the phytoplankton up to complete exhaustion of the phosphate supply³. This was done by taking water from the surface of the English Channel about 15 km. out to sea on December 18, 1922, January 16, February 12 and March 8, 1923. These samples were exposed side by side in a south window from March 24 after storing in the dark. It took thirty days to exhaust the phosphate in the December sample, slightly less in the January one and only about five days for the February and March samples. The explanation offered was that the spring samples contained a larger number of cells. "In winter, however, the much smaller numbers present can apparently be doubled or quadrupled with but little effect upon the amount of phosphate as ascertained by analysis."

A culture of the diatom *Nitzschia closterium* W.Sm. showed that half a milligram of phosphorus produced 0⁹ diatoms, so this number must be present per cubic metre before any diminution in phosphate can possibly be detected, as 0.5 mgm./m.³ is the limit of sensitivity. The lag in production follows as a mathematical necessity, since in winter the number of plankton cells is relatively much reduced. Using a north window culture of the diatom, it was ascertained that a fourfold increase required sixteen days, March 27–April 13. Thus one cell would, after eight successive doublings, become 256 and the process would require 64 days, and similarly for any other rate of increase.

Where vertical mixing is reduced one may find the spring outburst well under way even by February 21, as in the middle of the Channel in 1928; the surface water contained only 5 mgm./m.³ of phosphorus⁴, though near the Eddystone and off Lshant there was more than double as much, as also an mid-Channel from 5 metres down. The stability of the water column is thus of fundamental importance, and as already shown⁵ the thermal stability of sea water is much greater than that of fresh water,

which has maximum density at 4° C. as against – 2° C. for sea water. For the same temperature difference, resistance to mixing increases as the temperature rises. Oceanographers appear to have overlooked these two factors.

Dr. Harvey kindly showed me his proofs in 1943 during my temporary return to Plymouth, and I regret that I did not then direct his attention to the early work. Dr. Harvey still considers that "there is a reasonable *suspicion* that something else besides light, turbulence and grazing plays a part".

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¹ Harvey, H. W., "Recent Advances in the Chemistry and Biology of Sea Water" (Cambridge, 1945).

² Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., "The Oceans" (New York, 1942).

³ Atkins, W. R. G., *J. Mar. Biol. Assoc.*, **13**, 119 (1923).

⁴ Poole, H. H., and Atkins, W. R. G., *J. Mar. Biol. Assoc.*, **16**, 297 (1929).

⁵ Atkins, W. R. G., *J. Mar. Biol. Assoc.*, **13**, 693 (1925); and *J. Conseil Internat. Expl. de la Mer*, **1**, 99 (1926).

Energy of the Hg—C Bond and the Heat of Atomization of Carbon

It has not yet been possible to make a final choice, from spectroscopic and vapour pressure data, between the two alternative values of 124.3 and 170.6 kilocalories/gram atom for the heat of atomization of carbon ($\Delta H_{291^\circ K}$ for the change $C_{diamond} \rightarrow C_{gas}$), though the most recent treatment favours the higher value², and this also makes easier the correlation of some kinetic and thermochemical data³.

An argument in support of the higher value may be got from the energy of the Hg—C link. The heats of combustion of mercury dimethyl, diethyl and diphenyl in their standard states at constant pressure are 432, 735 and 1,565 k.cal./gm. mol. respectively⁴. These values may be analysed with the help of the following data: heats of atomization (k.cal./gm. atom) C 124.3; H 51.7⁵; Hg 14.6⁶; associated bond energy terms (k.cal./gm. mol. C—C 58.6⁷; C=C 106⁸; C—H 87.3⁷; benzene nucleus resonance energy 39 k.cal./gm. mol.⁹; latent heats for the phase changes (standard state to gas) HgMe₂ 8, HgEt₂ 9, Hg(C₆H₅)₂ 23 k.cal./gm. mol.¹⁰. The energies so obtained for the Hg—C bond are: from the dimethyl 1.5, from the diethyl 6.5, and from the diphenyl 3.5; mean 4 k.cal./gm. mol. Even though the energy needed to break the first C—Hg bond is probably greater by about 30 per cent than the mean value for the two bonds¹¹, 4 k.cal./gm. mol. is an unprecedentedly low value for a chemical bond, and is of the order of the van der Waals attractions.

If we use the higher value 170.6 for the heat of atomization of carbon (with the corresponding changes in the C—H, C—C, and C=C values) the Hg—C energy is increased by $(170.6 - 124.3)/4 = 11.5$, and becomes 15.5 (energy necessary to break the first C—Hg bond probably about 20 k.cal./gm. mol.). This seems much more probable; it is still very low, but of the same order as the P—P and As—As bonds (18.9 and 15.1¹²).

That the energy of the Hg—C link is very small is supported by many other facts. For example, the spontaneous decomposition of the dialkyls and (on heating) the cyanide to mercury and hydrocarbon