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VOLUME XV

OCEANOGRAPHY OF
LONG ISLAND SOUND, 1952-1954

By

GORDON A. RILEY
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GEORGIANA B. DEEVEY
ROBERT J. CONOVER
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HOWARD L. SANDERS

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OCEANOGRAPHY OF LONG ISLAND SOUND, 1952-1954

III. CHEMICAL OCEANOGRAPHY

By

GORDON A. RILEY

AND

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ABSTRACT

Nitrate is virtually absent from the water column from the end of the spring flowering until the following September; a gradual increase follows, culminating in a midwinter maximum of some 20 $\mu\text{g-at N/l}$. The phosphate concentration is about 0.5 $\mu\text{g-at P/l}$ at the end of the spring flowering, declines a little more during the spring months, then increases slowly through the summer and more sharply in autumn. Even in midwinter, the N:P ratio is only about 8:1. Oxygen is reduced in the bottom waters in summer, with minimum concentrations of about 50% saturation. Data on the chlorophyll content of phytoplankton and on the displacement volume of zooplankton are included for comparison with chemical cycles. The available information on the horizontal distribution of phosphate, nitrate, and chlorophyll is examined. It is postulated that the two-layered transport system in the Sound provides a mechanism whereby plant growth and accompanying positive gradients in nutrients automatically lead to retention of nutrients within the Sound and regulate the supply at a slightly higher level than that in adjacent oceanic waters.

METHODS

Oxygen was determined by the Winkler method. Prepared samples of 100 ml were titrated with thiosulfate of a strength such that the titer approximated milliliters of oxygen per liter in the sample. The thiosulfate was standardized with potassium dichromate.

The Atkins-Denigès method was used for inorganic phosphate. The sulphuric acid and ammonium molybdate, stored separately, were mixed just prior to use. Stannous chloride was freshly prepared for each set of analyses. The color was measured in a Klett-Summerson photoelectric colorimeter, using a No. 66 filter and a 40 mm cell. Suitable corrections were made for reagent blank, turbidity in the seawater sample, and salt error. Measurements were generally made on the day following collection of the samples. This delay conceivably introduced some error into the determinations. Riley (1941) reported a series of 65 experiments on changes occurring in phosphate and other nonconservative elements in Long Island Sound water stored in light and dark bottles for periods of three or four days. There was an average decrease of $0.10 \mu\text{g-at P/l}$ in a day's time in the light bottles and an increase of $0.05 \mu\text{g-at}$ in the dark. Possible errors of this magnitude in the results reported below would not seriously alter the conclusions.

Nitrate analyses during the first year were carried out according to the strichnidine method described by Zwicker and Robinson (1944). Subsequently the amount of strichnidine in the sulfuric acid was reduced to one-half, following a recommendation by Francis A. Richards (personal communication). Measurements were made on the Klett, with 12 mm diameter tubes and a No. 54 filter. Differences in replicates and in successive standardization curves indicate an analytical error of at least $\pm 10\%$. In addition, there is probably a small systematic error, since it has been common in spring and summer to find seawater readings that are slightly lower than the blanks.

Material for plant pigment determinations was obtained by filtering a citrate bottle (375 ml) of sea water through a No. 42 Whatman filter paper immediately after collection of the sample. The filter paper was put in 90% acetone for 16 to 24 hours, and the extract was then refiltered to remove any particles in suspension. The volume was adjusted to 5 ml, and the Klett readings were made with 12 mm tubes and a No. 66 filter.

Filtration was carried out with light suction to minimize loss of phytoplankton through the filter. Ordinarily half an hour to an hour was required to filter each sample; a shipboard battery of six filter holders was sufficient to carry out the operation. To obtain an analysis with only 375 ml is feasible in the rich waters of Long

Island Sound provided considerable care is taken in colorimetric readings. Larger samples tended to clog the filters.

On two occasions, comparative measurements have been made with millipore filters having a pore size of about 0.5μ . During the spring flowering of 1954, aliquot samples were poured through the two types of filters. No significant difference was detected. On a later occasion, when the total crop was smaller and when the proportion of small cells had increased, the test was repeated more carefully. The filtrate from four paper-filtered samples was caught and passed through a millipore filter. The phytoplankton that passed through the paper and was retained by the millipore filter gave a reading of $0.14 \mu\text{g chlorophyll } a/l$, as compared with an average of $2.1 \mu\text{g}$ in the paper-filtered samples. Further examinations are needed, but at the present time it appears that the loss of phytoplankton through the paper filters is a relatively insignificant fraction of the total population.

The plant pigment readings were recorded as the colorimetric equivalent of chlorophyll *a* in μg per liter, although it is presumed that other pigments have some slight effect on total extinction. The method was standardized with the aid of a crude chlorophyll concentrate which was obtained from the American Chlorophyll Division of Strong, Cobb, and Co. and which contained by analysis 13.2% chlorophyll *a* and 3.9% chlorophyll *b*. Weighed samples of the concentrate were dissolved in 100% acetone, and successive dilutions in 90% acetone were measured on the Klett. Data by Edmondson and Edmondson (1947) on the absorption characteristics of chlorophyll *a* and *b* and of the Klett 66 filter indicate that the chlorophyll *a* in the samples was responsible for 89.1% of the total extinction. The calibration curves were corrected accordingly.

On several occasions duplicate measurements have been made on phytoplankton pigment extracts using the method described above as well as visual colorimetric comparison with the Harvey (1934) plant pigment standard. Results are shown in Fig. 1. On the average, $1 \mu\text{g}$ of chlorophyll is equivalent to 4.4 Harvey units, and the general relationship throughout the range of concentrations examined is sufficiently accurate to permit comparison of present results with previous analyses by the Harvey method.

Some of the previous work on Long Island Sound and Georges Bank (Riley, 1941, 1941a) has included chlorophyll measurements

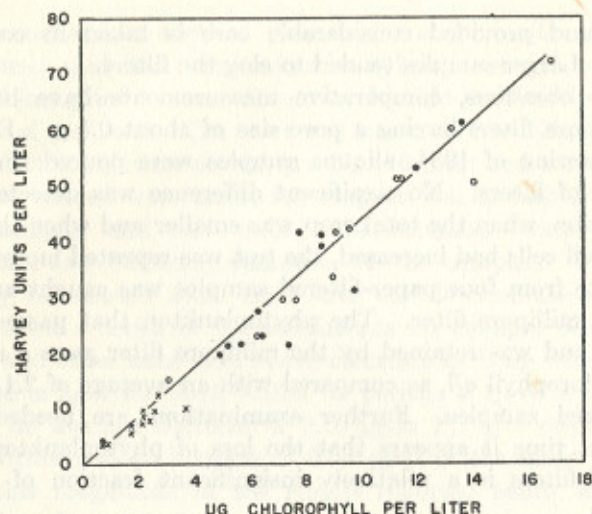


Figure 1. The Harvey (1934) method of plant pigment measurement compared with the chlorophyll method described in the text. Each point represents a measurement by each method of the pigments in an acetone extract of a natural phytoplankton sample from central Long Island Sound. Dots represent samples taken on May 21, 1952; circles, June 11, 1952; x's, October 9, 1952.

in which the carotenoids and chlorophyll were separated by chemical methods, the latter having been measured by visual colorimetry against an arbitrary standard calibrated with a pure chlorophyll preparation. Riley (1941a) listed analyses of 22 samples of net phytoplankton in which 1 μg chlorophyll, so determined, was equivalent to 3.9 Harvey units. Somewhat different results were obtained in routine analyses of the total plankton filtered from a liter of sea water. Average ratios in both Long Island Sound (21 unpublished observations) and Georges Bank (Riley, 1941a) were about 1 μg chlorophyll to 3 Harvey units. It is possible that there was a significant error in the earlier standardization or, more likely, a tendency to over-read dilute chlorophyll concentrations because of a slight turbidity in the prepared solutions.

SEASONAL CYCLES IN THE CENTRAL PART OF THE SOUND

Figs. 2 and 3 show seasonal cycles of phosphate, nitrate-nitrite, chlorophyll, and total zooplankton displacement volume as averages of inshore and offshore stations, respectively. Discussion of the

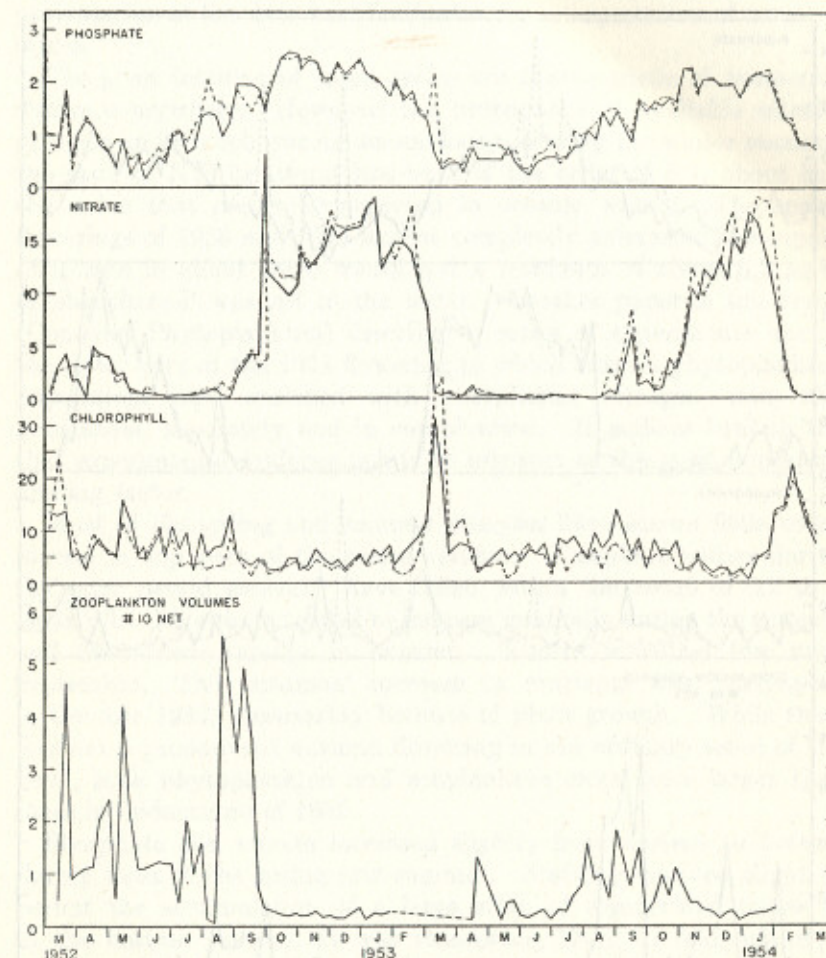


Figure 2. Weekly averages of observations at inshore Sts. 1, 6, 7, and 8. Phosphate and nitrate are plotted as $\mu\text{g-at}$ per liter, chlorophyll as μg per liter. Solid line shows surface averages; broken line, bottom. Zooplankton displacement volumes are plotted as milliliters per cubic meter in an oblique tow from near bottom to surface. During the spring flowering, the zooplankton volume could not be determined because the catch included large quantities of phytoplankton. This period is indicated by a broken line.

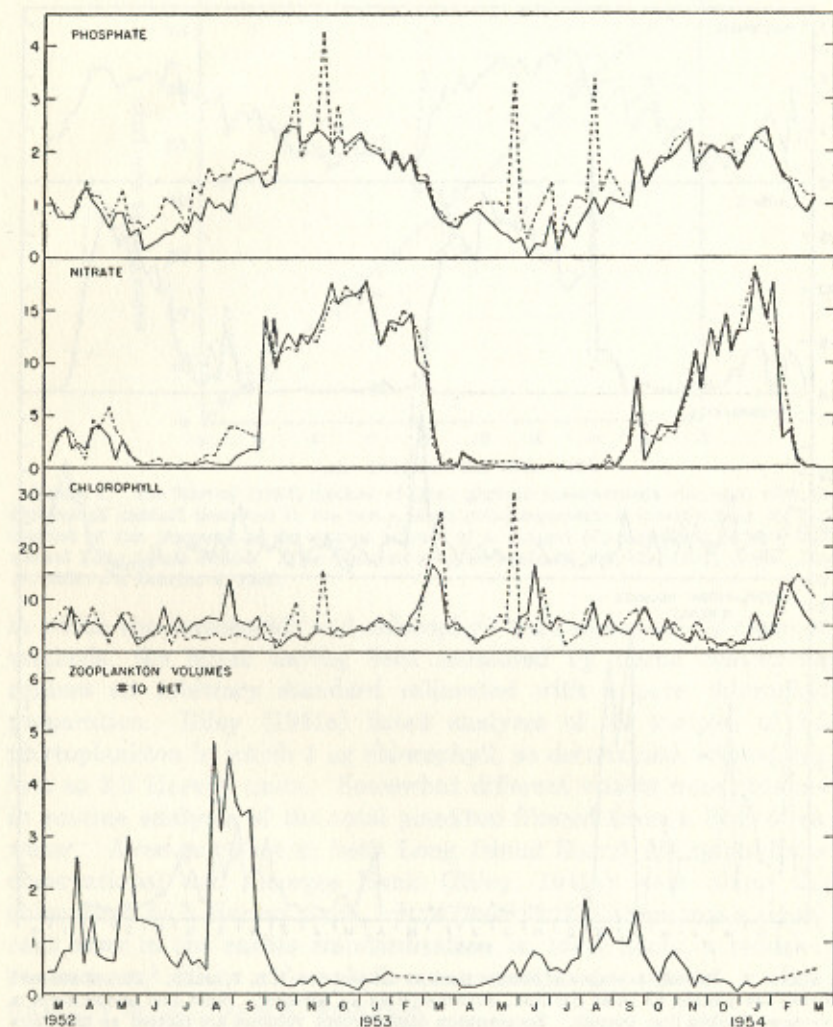


Figure 3. Weekly averages of phosphate, nitrate, chlorophyll, and zooplankton volume at offshore Sts. 2 to 5. Method of plotting as in Fig. 2.

plankton is largely relegated to other papers in this volume, but presentation of the data here facilitates the interpretation of nutrient cycles.

The gross features of these cycles are characteristic of temperate waters everywhere. However, the proportions of available nitrate-nitrogen and phosphorus are anomalous. During the winter maxima, the ratio of N:P by atoms has been of the order of 8:1, about half the value that might be expected in oceanic waters. The spring flowerings of 1953 and 1954 almost completely exhausted the supply of nitrate in about three weeks but a residuum of about $0.5 \mu\text{g-at}$ of phosphate-P was left in the water. Another paper in this series (Conover: Phytoplankton) describes a series of experiments during the latter part of the 1954 flowering in which natural phytoplankton populations were enriched with phosphorus, nitrogen, iron, and manganese, separately and in combination. It suffices here to say that experimental evidence points to nitrogen as the most important limiting factor.

Most of the spring and summer analyses have shown little or no nitrate in any part of the water column. Phosphate values during the same period generally have fallen within the range of 0.2 to $1 \mu\text{g-at P/l}$. Phosphate tended to increase gradually during the summer and then more rapidly in autumn. Nitrate remained low until September. The autumnal increase in nutrients was interrupted in October 1953, presumably because of plant growth. While there was not a pronounced autumn flowering in the ordinary sense of the term, both phytoplankton and zooplankton crops were larger than those in midautumn of 1952.

Phosphate and nitrate increased slightly from surface to bottom during most of the spring and summer. Stability was too slight to permit the accumulation of a large store of regenerated nutrients in the bottom waters. It was reasonable, then, to find neither a pronounced summer period of phytoplankton impoverishment nor a marked flowering following the destruction of the summer thermocline. Slight and variable vertical gradients were observed in autumn and winter. It was fairly common in autumn to find significant decreases in phosphate and nitrate in the bottom waters. Reasons for this peculiar phenomenon will be apparent in the later discussion of horizontal distribution and transport.

Oxygen data are shown in Fig. 4, again as averages of inshore and

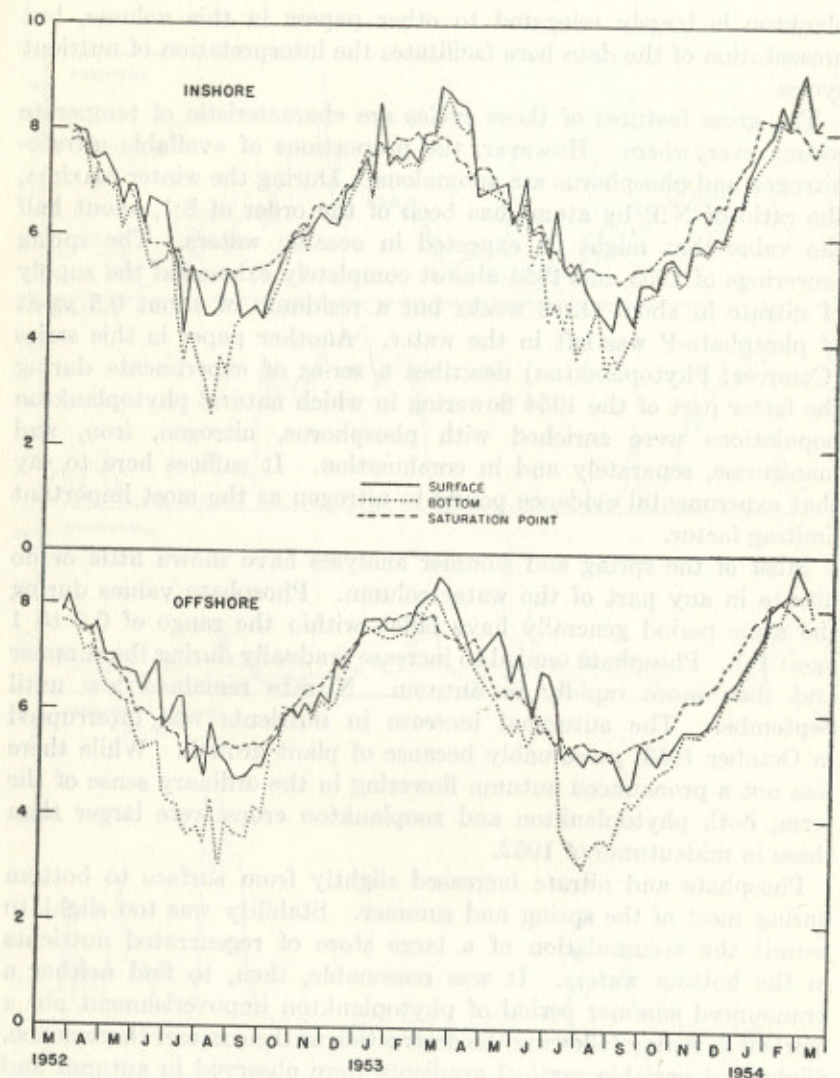


Figure 4. Weekly averages of oxygen concentration in milliliters per liter at inshore and offshore stations. Solid line, surface; dotted line, bottom; broken line, calculated values for 100% saturation at the surface at the observed temperature and salinity.

offshore stations, together with the computed values for 100% saturation at the surface. Supersaturation of the surface layer occurred during the spring flowering and to a lesser extent on various other occasions. The oxygen content of the bottom water declined during the spring and early summer. Minimum values recorded at individual stations were about 50% saturated. Vertical gradients in oxygen were more pronounced than those of phosphate and nitrate. The form of the vertical distribution indicates that maximum oxygen production by phytoplankton occurred between the surface and 5 m and that photosynthesis exceeded utilization of oxygen by the plankton community in the upper 10 or 15 m. However, the nitrate and phosphate gradients suggest considerable utilization of these substances by phytoplankton at depths of 15 m or more.

During autumn and early winter, the oxygen was generally slightly undersaturated from surface to bottom. Three factors are probably involved: (a) a slight lag between surface cooling and oxygen uptake; (b) an acceleration of vertical mixing and convection, which increased the oxygen content of the bottom water and correspondingly lowered the concentration in the remainder of the water column; and (c) an excess of oxidation over production in most of the water mass, as indicated by the autumn increase in nutrients.

HORIZONTAL DISTRIBUTION

While there is a considerable body of previous data on temperature and salinity for the Sound, biological and chemical work has been scanty and has been concerned almost entirely with seasonal cycles in localized areas. The present survey has included an examination of the distribution of oxygen, phosphate, nitrate, and plankton during three cruises that covered most of the Sound. This obviously does not provide an adequate treatment of horizontal distribution, but certain problems are revealed that deserve preliminary mention at this time and which will be studied more intensively during the remainder of the survey.

Fig. 5 shows the distribution of phytoplankton chlorophyll at the surface in June 1952 and in the latter part of September and early October of the same year. During the first cruise there was a general east-west gradient, the maximum concentration in the north-central part of the Sound being some four times the average crop in the

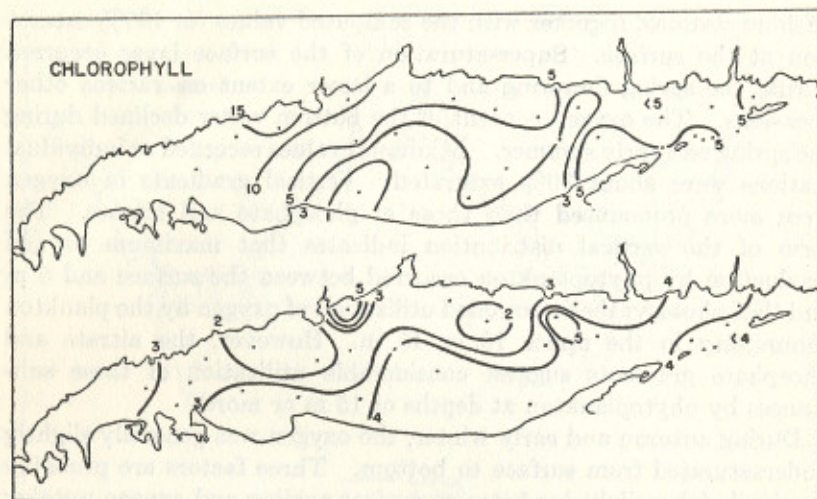


Figure 5. Horizontal distribution of chlorophyll in μg per liter at the surface. Upper figure, June 4 to 11, 1952; lower, Sept. 29 to Oct. 9, 1952.

vicinity of the eastern passes. A similar gradient was found in April 1953 (not figured here). Previous comparison of seasonal cycles in Block Island Sound and in the central part of Long Island Sound (Riley, 1952b) has also indicated a much larger average concentration in the latter. An east-west gradient of the type pictured thus appears to be fairly common, at least during the spring and summer. It was not present during the autumn cruise shown in the lower part of Fig. 5.

With respect to nutrients, the opposite situation obtained. In June 1952 there was a slight east-west gradient in phosphate (Fig. 6) and essentially no nitrate gradient (Fig. 7). In early autumn the gradients were very large. Autumn regeneration of nutrients was well underway in the western end of the Sound. It is not altogether clear whether the east-west gradient represented a difference in the amount of materials available for regeneration or a difference in the time when this phase of the cycle began, or both.

The relation between surface and subsurface nutrients and chlorophyll concentrations is shown in Fig. 8 as a series of longitudinal profiles. During the June cruise, the phosphate concentration generally increased from surface to bottom, as might be expected when the phytoplankton exists in a state of active growth. Maximum nitrate values were found in patches of surface water of reduced

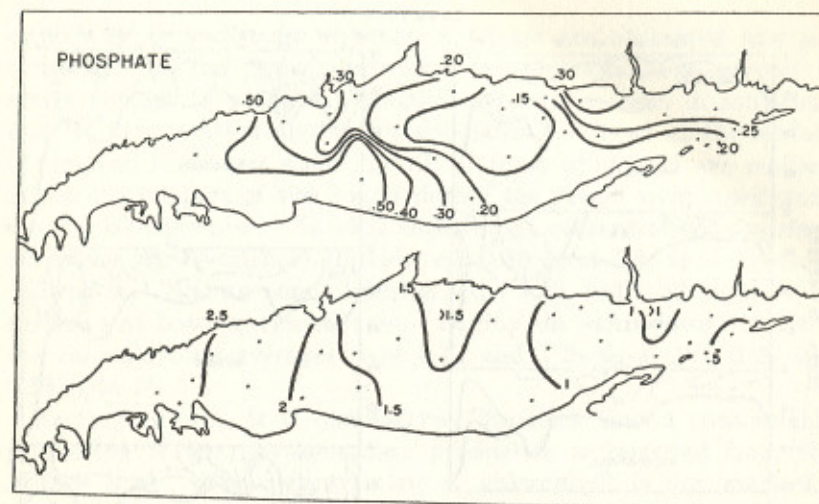


Figure 6. Horizontal distribution of surface phosphate in $\mu\text{g-at}$ per liter. Upper figure, June 4 to 11, 1952; lower, Sept. 29 to Oct. 9, 1952.

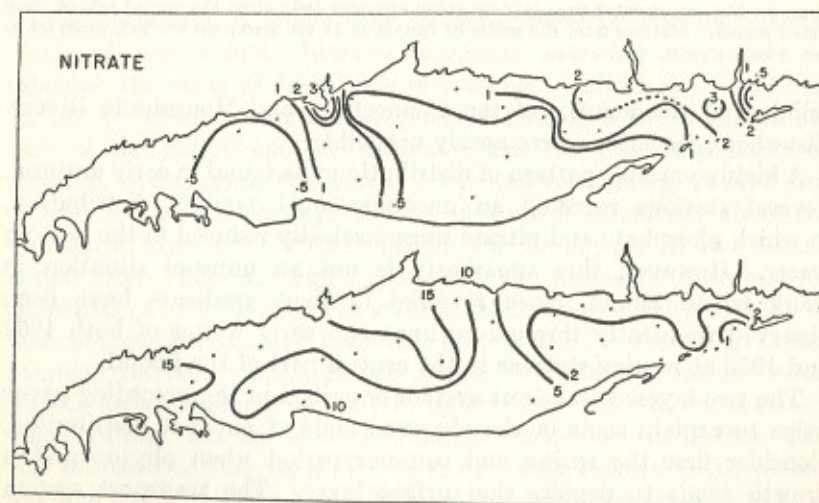


Figure 7. Horizontal distribution of surface nitrate in $\mu\text{g-at}$ per liter. Upper figure, June 4 to 11, 1952; lower, Sept. 29 to Oct. 9, 1952.

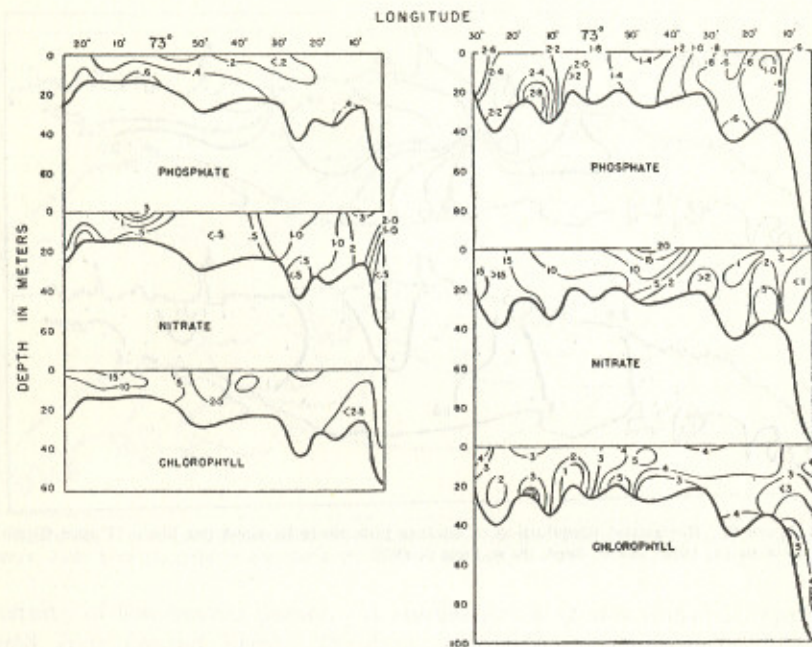


Figure 8. Longitudinal profiles of phosphate and nitrate in $\mu\text{g-at}$ per liter and chlorophyll in μg per liter, constructed from stations taken approximately along the central axis of Long Island Sound. Stations from the cruise of June 4 to 11 are shown on the left, Sept. 29 to Oct. 9 on the right.

salinity off the mouths of the Connecticut and Housatonic Rivers. Elsewhere, variations were nearly negligible.

A highly variable pattern of distribution was found in early autumn. Several stations revealed an unconventional type of distribution, in which phosphate and nitrate were markedly reduced in the bottom water. However, this apparently is not an unusual situation in Long Island Sound, since reversed nutrient gradients have been observed frequently through autumn and early winter of both 1952 and 1953 at routine stations in the central part of the Sound.

The two-layered transport system described in the preceding paper helps to explain some of the observed facts of nutrient distribution. Consider first the spring and summer period when phytoplankton growth tends to deplete the surface layer. The transport system gradually removes the nutrient-poor surface layer. The bottom water that moves in is richer in nutrients. Thus the transport system

establishes a mechanism whereby nutrients are conserved and accumulated in the Sound, provided (a) phytoplankton growth is active enough to produce a positive vertical gradient in nutrients, and (b) a proportion of the phytoplankton produced at the surface is removed to deeper water. Both of these conditions are realized in the central part of the Sound during the period from April until the end of September. In 1952 the average concentration of surface phosphate at the offshore stations was $0.86 \mu\text{g-at P/l}$, at the bottom $1.19 \mu\text{g-at}$. Nitrate concentrations were 1.78 and $2.52 \mu\text{g-at N}$ at surface and bottom, respectively. During the same period in 1953, the corresponding averages were 0.70 and $1.28 \mu\text{g-at P/l}$, 0.29 and $0.63 \mu\text{g-at N}$.

As to point (b), it is qualitatively apparent that a considerable proportion of the phytoplankton production is removed from the surface layer. The concentration of chlorophyll is not markedly greater at the surface than it is at the bottom during the period in question. The presence of a large bottom fauna is sufficient evidence in itself that surface production has been removed to the bottom by one means or another.

An accurate quantitative treatment of this problem awaits further work on both mass transport and nutrient cycles in the Sound as a whole. However, a preliminary estimate based on average summer transport values and observed inorganic nutrients may serve to establish the order of magnitude of transport enrichment. At Long. $72^\circ 30' \text{ W}$, which is a convenient point of division between the eastern part of the Sound and the central basin, the preceding paper on Physical Oceanography indicated a net eastward transport of $10,200 \text{ m}^3/\text{sec.}$ in the surface layer and a westward movement along the bottom of 9100 m^3 . If these figures can be applied to the general period from April through September, the westward movement is estimated to be 3.10 times the volume of the Sound west of $72^\circ 30' \text{ W}$, and the surface transport to the east is 3.46. According to the average nutrient values quoted above, transport exchange would lead to an average increase of $0.71 \mu\text{g-at P/l}$ of water in the area as a whole during the six months' summer period of 1952. For 1953 the estimate is $1.55 \mu\text{g-at P}$. Corresponding estimates for nitrate are 1.65 and $0.96 \mu\text{g-at N/l}$ in 1952 and 1953, respectively.

The final analysis of productivity problems will require not only a revision of the estimates of transport enrichment, with additional

data on ammonia and nutrients in organic combination, but also a consideration of enrichment by freshwater drainage. A few analyses of river water during the spring and summer of 1954 have shown a wide variation in nitrate content, from 0 to 37 $\mu\text{g-at N/l}$. While there is no doubt that drainage has a significant effect with regard to nitrate enrichment, it probably does not exceed the effect of transport exchange. Phosphate concentrations in the rivers are about the same as those in the Sound, and it seems unlikely that drainage materially alters the distribution of this element.

Returning to the problem of transport effects, it is apparent that a two-layered exchange system will result in nutrient accumulation only if phytoplankton growth is sufficiently active to create a vertical gradient in nutrients. If growth is so slight that regeneration exceeds consumption, the accumulation of nutrients is expected to cease, and the direction of nutrient transport may be reversed. In the particular case noted in October 1952, when there were strong east-west gradients in nitrate and phosphate, both lateral diffusion and an eastward transport of the surface layer would tend to move these nutrients out of the Sound. Under such circumstances transport exchange would also be expected to create negative vertical gradients in nutrients. The frequent occurrence of these gradients suggests that loss of nutrients from the Sound during the autumn and early winter is as distinctive a part of the nutrient problem as the accumulation in summer.

In conclusion, the quantitative details of this phenomenon remain to be established, but a general hypothesis is obvious. The two-layered transport system provides a mechanism whereby the biological association automatically regulates the nutrient supply at a slightly higher level than that in the adjacent oceanic waters. Moderate nutrient deficiency accelerates the accumulation, although the system tends to break down when, as in the case of nitrate, severe deficiency depletes the entire water column. An unusable excess of nutrients is automatically dissipated. Both aspects of the phenomenon are conceivably important in maintaining a normal, productive population. Preliminary estimates suggest that the summer accumulation of phosphate by transport exchange constitutes a considerable fraction of the total available store of this element. The accumulation of nitrate by the combined effects of transport and freshwater drainage is relatively less significant. However, no general conclusions about

nitrogen accumulation are warranted until data have been obtained on other nitrogenous compounds.

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