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# HYDROGRAPHIC STUDIES, ESPECIALLY ON THE CARBON DIOXIDE SYSTEM, IN GRaNE LANGSø 

BY

GUNNAR NYGAARD



København 1965
Kommissionær: Ejnar Munksgaard
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## 1. Introduction

For anyone who likes nature, the Danish lake Grane Langsø is a remarkable lake. At the shores one may observe how the sundew plants (Drosera rotundifolia and $D$. intermedia) catch dragon-flies. In spite of the lime-deficiency of the water the crayfish (Astacus fluviatilis) thrives excellently, several of the individuals being remarkable through their blue colour. If these crustaceans in very shallow water are lit up with a hand lamp on a summer night, a bright red light is reflected from their darkadapted eyes. On visiting the lake in May or June one may hear the chinking croaking of the natterjack (Bufo calamita) in the afternoon from the sunny shores.

When rowing to the centre of the $11^{1} / 2$ metres deep lake, one is surprised to observe the blue-green colour of the water and its great transparency, a white disc being still visible at a depth of $11^{1} / 2$ metres in June, July, or August and December. A botanist will be specially interested in e.g. a club-moss as Lycopodium inundatum, rare submerged mosses and liverworts (a deep-water modification of Fontinalis antipyretica, Cephaloziella subdentata, Chiloscyphus polyanthus, Scapania undulata var. purpurascens, and Riccardia sinuata var. submersa), and in the rare water-wort (Elatine hexandra), which forms small submerged meadows in shallow water. In the summer plankton he will find i.a. the indicative and sporadic Dinobryon bavaricum var. Vanhoeffenii; further Elakatothrix gelatinosa, Stichogloea olivacea, and many desmids. Besides the indifferent var. asterionelloides of the diatom Tabellaria flocculosa, the ecologically significant var. Teilingii, indicating oligotrophy, also occurs. For an angler, however, there is not much to be got here, perch (Perca fluviatilis) being the only fish present.

I think it is worth while to subject this acid Lobelia-Isoetes-Littorella lake, unique by Danish standards, to a closer investigation.

Johs. Iversen (1929, p. 311) comments on the lake after a single visit in the summer 1927.

Ulrik Røen (1954) has given an account of the entomostracan fauna in Grane Langsø, based on collections from 1951-52. Noteworthy are Eucyclops lilljeborgi, new to Denmark, and three other species of rare occurrence.

Gunnar Nygaard (1955) has published date on the primary production of i.a. Grane Langs $\varnothing$ in relation to the Compound Index, on the basis of monthly investigations in 1950-51. In connection with these facts an estimate of the trophic status of the lake is formed, vz. oligotrophy.

Kaj Hansen (1957) has published the results of his many years' work on the bottom deposits of Danish lakes. These sediments are made up of three components: (1) the organic compounds, (2) the minerogenic component, chiefly consisting of quartz, and (3) the inorganic, biogenic substances, predominantly made up of diatom frustules and lime, precipitated by organisms. Out of 14 lakes of various types Grane Langs $\varnothing$ has the smallest content, expressed in percentages, of carbon and nitrogen in its gyttja and the smallest loss on ignition. Total $\mathrm{SiO}_{2}$, however, constitutes no less than about 75 per cent of the deposit, diatom $\mathrm{SiO}_{2}$ about 2 per cent. The minerogenic component thus amounts to more than 70 per cent of the gyttja, a unique quantity within the range of lakes examined. In agreement with the fact the dark greyish sediment from the central part of Grane Langsø feels like fine, sandy mud.

Sigurd Olsen (1958 and 1958 a) has tried, with the aid of radioactive phosphate, to approach the difficult problem of phosphate ion exchange between lake water and bottom sediment. An experimental method was developed, by with is it possible to measure the two opposite processes. Differences between the experimental conditions and the natural ones are, however, so great that estimating the rate and final result is at present difficult (1958 a, p. 96). During identical experimental conditions, however, the graphs of the net quantities of phosphate adsorbed from the water by the gyttja take a different course in Grane Langsø and the eutrophic Furesø (1958, fig. 7, graph a, and fig. 8, graph $\mathrm{a}_{\mathrm{ox}}$ ).

Gunnar Nygaard (1958) has published a bathymetric map of the lake, surveyed by Tyge Møller. An account is given for the quantitative benthic distribution of the individual plant species, based upon bottom samples taken by a frogman in 1954 and 1955. The total weights of vegetable dry matter per $\frac{1}{20}$ square meter were determined for each meter along two section lines from the shore to the deepest part of the lake. Further the productivity of Nostoc and Nitella flexilis has been determined to about 2.8 and 2 per cent daily increase in July, respectively, indicating the plants of Grane Langsø to be slowly growing.

In his paper of 1961 Ulrik RøEn has correlated the productivity results of NyGaARD (1955) with the quantities of planktonic crustacea of Grane Langs $\varnothing$ in 1950-51. Simultaneously with the monthly determination of the gross production below one square metre per day for a vertical column of 10 m length, I took 3 vertical hauls from the 10 m depth to the lake surface by means of a tow-net exclusively used for this purpose. Fig. 1 in RøEn's paper indicates a reasonably good agreement between the two factors in question. Minor discrepancies are explained by the presumption that not all plankton algae are of the same nutritious value for the crustacea.

This agreement between the producers and the consumers of the plankton in Grane Langsø is notable, though the Infusoria and Rotatoria were not considered, and one of the Crustacea is occasionally carnivorous, another exclusively carnivorous (RøEN 1961, p. 19) ; further some disadvantages by the sampling method may influence the reliability of the number of Crustacea counted. I think that the scarcity of Leptodora
hyalina in Grane Langsø should be explained by the fact that it is a representative of the third link in the food chain: phototrophic algae - herbivorous consumerscarnivorous consumers of the first degree. As fig. 1 in Røen's paper of 1961 shows the dependance of the crustacean zooplankton on the primary production of the algae, the conclusion can be drawn that Grane Langsø constitutes a good example of a lake where the grazing of the zooplankton is an important factor in determining the size of the standing stock of phytoplankton. In a contamined and highly productive lake as e.g. the Danish lake Frederiksborg Slotssø, the size of the standing crop of planktonic algae is insignificantly influenced by grazing.

From October 1956 to July 1961 continuous instrument readings of the light climate in $11^{1 / 4} \mathrm{~m}$ subsurface depth were plotted automatically by a three colour recorder. The radiant energy can be computed in $\mu$ watt per square centimetre from each of three graphs, blue, green, and red, covering the three spectral regions of $400-$ $500 \mathrm{~m} \mu, 500-600 \mathrm{~m} \mu$, and $600-700 \mathrm{~m} \mu$, respectively. From May 1958 to July 1961 these measurements were extended to include also corresponding registrations of the light climate in $1 / 4 \mathrm{~m}$ subsurface depth.

In connection with these investigations monthly or fortnightly determinations of the spectral transmission of the individual water layers were carryed out from March 1957 to July 1961, partly by in vitro experiments, partly by the in situ method. Beckmann's spectrophotometer, photoelements furnished with interference filters or the Chance glass filters OB $10, \mathrm{OGr} 1$, and OR 2 were employed.

The total carbon dioxide has been determined monthly or forthnightly from March 1958 to July 1961 for the subsurface depths of $0,2,4,6,8,10$, and 11 meters. The oxygen content of the water from the same depths has been measured regularly in the period from March 1958 to March 1959.

Series of temperature measurements have been taken regularly from October 1956 to July 1961. At the same time tow-net samples and quantitative plankton samples have been collected. "Column water" from $0-11$ metres was taken by means of a 12 m long and 1 inch thick plastic tube. Moreover, 10 ml samples for counting have been collected from the above mentioned depths since December 1957.

The ${ }^{14} \mathrm{C}$-technique was used for determining primary production at the subsurface depths previously mentioned from July 1958 to July 1961. These determinations have been undertaken twice a month since July 1959. Investigations of the respiration of the planktonic algae were started on February 1960, using the method described by Steemann Nielsen and Vagn Hansen (1959). Coincidently with these investigations the phytoplankton from the corresponding depths has been counted in a living state by means of the counting chamber of Kolkwitz.

Finally the photosynthesis and respiration of Nitella flexilis have been determined fortnightly with the light and dark bottles method during one year (July 1959 to July 1960). Carbon dioxide and oxygen as well were analysed.

The subjects of this paper are primarily the yearly fluctuations of carbon dioxide, hydrogen carbonate ion, specific conductivity, and hydrogen ion concentration.


Fig. 1. Bathymetric map of lake Grane Langso, measured by Tyge Moller in May 1951, when the maximum depth was 11.1 m .

## 2. Geology and Morphometry of Grane Langsø

The district including Grane Langs $\varnothing$ has not been treated in the Danish geological series of D.G.U. (Danish Geological Investigations). Kaj Hansen (1958, p. 543) has, however, written of the tunnel-valleys in this district and the adjacent ones (cf. also J. Humlum and Knud Nygaard 1961, map 6 ).

I am indebted to Dr. Helge Gry, who is working on the quaternary geology of the district in question, for information on the origin of the lake and its environment.


Fig. 2. The areas of the isobaths plotted against their corresponding depths.

Grane Langs $\quad$ ( $56^{\circ} 1^{\prime} \mathrm{N}$. and $9^{\circ} 27^{\prime} 30^{\prime \prime}$ E.) is situated in a tunnel-valley, formed in stratified drift by a subglacial stream during the Baltic Glaciation. Later on the stagnant ice melted away, but large ice masses remained in the tunnel-valley. Lateglacial sand and gravel were then deposited by more recent glacial streams in the tunnel-valley. Finally the lake appeared as a basin, where a great ice mass had been buried.

Glacial hilly country of diluvial sand lies east of the lake, while late-glacial deposits of sand form still higher hills west of the lake. The lake basin is thus situated in stratified drift. The sand is not pure quartz sand, but contain small amounts of other minerals from the Scandinavian bed-rock, especially felspars and ferruginous minerals.

The altitude of Grane Langsø is 74 m , and the lake lies near to the water-shed between Denmark's two largest catchment areas, those of Gudenå and Skernå.

The area of this glacial tunnel-lake is 11.38 ha . The maximum depth is 11.5 m at normal water level (cf. Fig. 3). The lake volume amounts to about 805900 cubic
meters. The areas of the contours on the bathymetric map of Grane Langsø (Fig. 1) are shown relative to their depths on Fig. 2. By means of this figure it is easy to find the volume between two given levels in the lake.

The volume between the 8 m level and the 11 m level is about 119300 cubic meters. The 8 m level has been chosen, because the thermocline normally lies in this depth in June-July (cf. Table 37, p. 88). The hypolimnic volume thus amounts to 15 per cent of the total lake volume in the two summer months mentioned.

The mean depth is 7.1 m , consequently no less than 62 per cent of the maximum depth. This percentage indicates that the lake basin of Grane Langsø markedly deviates from a conical depression, which is characterized by the ratio of mean depth to maximum depth $=33$ per cent. Fig. 1 and 2 also demonstrates that the lake basin has steep sides, in places very steep indeed, by Danish standards.

Another Danish lake, Gribsø, covers nearly the same area, 10.08 ha, as Grane Langsø and exhibits a similar maximum depth, 11 meters. Its mean depth, is however, only 4.8 meters (Berg and Clemens Petersen 1956, p. 12). According to Lundbeck (1926, p. 11) some North German small lakes are recorded to be much deeper than Grane Langsø: Pluss-See has an area of 13.5 ha , and its maximum depth is no less than 26 meters! The area of Kleiner Ukleisee, to which I shall return, is only 2.5 ha, but the depth of this lake is 16 meters.

## 3. On the Water Balance of Grane Langsø

Grane Langs $\varnothing$ has neither a superficial inlet nor a visible outlet. As the precipitation on the lake surpasses the evaporation, however, the lake must have a sublacustrine run-off. By means of the following equation I shall try to contribute to methods by which it will be possible to compute the water balance of the lake, provided that better information is available than at present.

$$
\begin{equation*}
P+I_{s}+I_{z}=O_{s}+O_{z}+E+\Delta R \tag{1}
\end{equation*}
$$

$P=$ precipitation
$I_{s}=$ superficial inlet, here $=0$
$I_{z}=$ sub-lacustrine inlet
$O_{s}=$ superficial outlet, here $=0$
$O_{z}=$ sub-lacustrine outlet
$E=$ evaporation from the lake surface
$\Delta R=$ increment of the water volume within a definite period.
For the lake in question the equation (1) can be simplified to

$$
\begin{equation*}
P+I_{z}=O_{z}+E+\Delta R \tag{2}
\end{equation*}
$$

On Fig. 3 the monthly precipitation of $1958-61$ can be compared with the variations in water level of the lake during the same period. The distance from the meteorological station at Bryrup to Grane Langsø is just under 4 km .

Fig. 3 indicates that the water level generally reached its maximum height in April, more rarely in March. In July or August a renewed increase took place; if the precipitation of both months were high, as in 1958, the lake surface even rose to the April-level. A rather low water level could occur in August or July, but the lowest



Fig. 3. The monthly precipitation of Bryrup and the water level of Grane Langsø in the period 1958-61. The small dotted lines in the upper diagram indicate the monthly means of precipitation in 1926-55, while the horizontal dotted line of the lower diagram represents the mean water level, estimated by Mr. Niels Agerskov, who has lived at the lake the last 45 years.
level was observed in October, more rarely in late November. In February to April 1959 the lake surface was unusually high.

The difference between the highest and lowest water level was 28,36 , and 38 cm for the years 1958,1959 , and 1960 , respectively. This fluctuation is rather small. The corresponding amplitude of lake Gribs $\varnothing$ amounted to 45 cm in 1942 (Berg and Clemens Petersen 1956, p.97). This lake, 11 m deep and covering a similar area as that of Grane Langsø, has affluents, but normally no visible outlets.

The evaporation from the surface of Grane Langsø is an unknown quantity. The annual evaporation of the Zealandic lake Søndersø has been measured as about

650 mm in the years $1943-47$ and as about 568 mm in 1957 (AslyNG 1959, Table I, p. 57). According to the paper Danmarks Klima (1933, p. 134), the relative humidity of the winds over Jutland was virtually identical to that measured at Zealandic meteorological stations in the years previous to 1925 . Grane Langs $\varnothing$ is, however, highly wind-sheltered by coniferous forests on the hills around the lake; therefore the yearly evaporation is roughly estimated as about 450 mm . The monthly values of evaporation in Table 1 consequently have been reduced to about 69 per cent of the Søndersøvalues from 1943-47.

The mean precipitation of Bryrup for the period 1886-1925 was 695 mm (Danmarks Klima 1933, p. 140). Mr. Ingolf Sestoft, State Meteorologist, has kindly informed me that the corresponding value for the period $1926-55$ is 772 mm . The precipitation of the four years of investigation amounted to

| 1958 | 1959 | 1960 | 1961 |
| :---: | :---: | :---: | :---: |
| 887 mm | 781 mm | 858 mm | 836 mm |

In the following calculations the value 770 mm has been used.
An examination of how the surface level of Grane Langsø reacts in relation to the monthly surplus precipitation gave the result that these surpluses, considering the sign, were in fairly good agreement with the corresponding rises and falls of the lake level. By way of example may be cited the figures of 1958 in Table 1.

Table 1. The monthly surplus precipitation (P-E) compared with the corresponding rise of the lake level $(\Delta R)$ in 1958 , both factors being stated in mm .

|  | Temp. measured | $\begin{gathered} \mathrm{P} \\ \text { measured } \end{gathered}$ | $\begin{gathered} \text { E } \\ \text { estimated } \end{gathered}$ | $\begin{gathered} \mathrm{P}-\mathrm{E} \\ \text { estimated } \end{gathered}$ | $\Delta \mathrm{R}$ <br> measured |
| :---: | :---: | :---: | :---: | :---: | :---: |
| January . | -1.8 | 78 | 7 | 71 | 40 |
| February . | $-1.7$ | 115 | 7 | 108 | 90 |
| March . | $-1.8$ | 24 | 14 | 10 | 130 |
| April. | 4.1 | 28 | 35 | $-7$ | $0 \quad(-20)$ |
| May | 10.2 | 74 | 69 | 5 | - 10 |
| June . . . | 14.3 | 45 | 76 | -31 | -30 |
| July | 16.3 | 136 | 86 | 50 | 10 (50) |
| August. | 15.1 | 140 | 69 | 71 | 50 |
| September | 13.5 | 59 | 48 | 11 | -40 |
| October | 9.5 | 60 | 21 | 39 | 10 (30) |
| November | 5.1 | 37 | 10 | 27 | $-30$ |
| December | 1.5 | 91 | 7 | 84 | 40 |

This fairly good agreement indicates that the sub-lacustrine outlet of Grane Langso $\left(O_{z}\right)$ probably is small and presumably constant during the year.

At the planter-house, situated in Kongso plantation about 2 km SE of Grane Langs $\sigma$ and lying in level 86 m , a boring has been performed. The core indicates that
the soil consists of various thin layers of e.g. moraine clay, coarse sand, loam, sharp gravel, and dark fine sand; it contained several horizons of groundwater. If this section reflects the soil conditions of the tunnel-valley containing Grane Langs $\varnothing$, it is very difficult to make out the groundwater conditions of the environment. The watertable of the Kongsø-boring mentioned possibly lies at level 79 m .

At the farm Højvang, situated 650 m NE of Grane Langsø, a 56 m deep boring has been made. The groundwater table of this well lay at level 67 m on July 29th, 1962 ; at this time the water level of Grane Langsø was -10 cm .

Kaj Hansen has performed several borings in the bottom of Grane Langso. The deepest one went down to well over 18.5 m below the lake surface, i. e. about 7 m below the lake bottom. Dr. Hansen, whom I thank for information on the cores, estimates the maximum depth of the ancient lake basin to be about 18.5 m . By far the greatest part of most of the cores is gyttja containing fine sand. The cores, all of them, indicate that the ancient lake basin is covered by a layer of loam, 20-110 cm thick, which in all cores rests on the substratum of diluvial sand. This loam is rather easily crushed in dry state by the fingers, but the sand is hardly perceptible between the finger tips. Hutchinson (1957, p. 248) writes: "Most small lakes not in rock basins are separated from the ground water by a clay seal, formed as an early lake sediment."

Lake Hampen $\mathrm{S}_{\varnothing}$ (level about 79 m ), lake Torup $\mathrm{S} \varnothing$ (level about 78 m ), and lake Grane Langsø (level about 74 m ) seem to be situated in a rather broad valley of a west-easterly course. The hilly country north and south of this valley exhibits ground levels of a little more than 100 m . The tunnel-valley containing Grane Langs $\varnothing$ intersects the broad valley in a northerly direction, and the surface of its 4 lakes, Rævsø, Grane Langsø, Kalgård Sø, and Kongsø, lies at the 74 m level. The two northernmost lakes, Rævsø and Grane Langsø, have no visible inlet or outlet. Kålgård Sø has no superficial affluent, but an insignificant affluent to Kongsø, which has a negligible outlet slightly inclining to the south.

It is conceivable that a stream of groundwater is moving to the eastward from Hampen $\mathrm{S} \varnothing$ and Grane Langs $\varnothing$; from there it continues in north-eastern direction to lake Kuls $\varnothing$ (level about 54 m ), which drain off to the brook Salten $\AA$. If so, the groundwater level is falling downgrade 1 in 93 from Grane Langsø to the Højvang well, and 1 in 100 from this well to Kulsø. These considerations imply a good contact, however, between the lake and the groundwater.

Before passing on to examine whether the water balance of Grane Langso is determinable by means of the $\mathrm{Cl}^{-}$concentrations of the air, the precipitation, and the lake, I should comment on two possibilities concerning the interaction of the lake water and the groundwater. These possibilities should not be considered as alternatives, as they quite well may be concurrent.
(i) The sides of the lake basin procure a good contact between the lake and its surrounding layers of sand, through which a groundwater stream may be flowing. The accordance between the moments of the highest and lowest level of the ground-
water and the lake surface, normally April and October, speaks in favour of this possibility.
(ii) The lake is lying in a basin covered with loam, through which the water slowly, but rather continually, seeps down to a subjacent stream of groundwater. The reaction of the lake soon after the precipitation speaks in favour of this possibility. A further support for this assumption is to be found in the fact that the difference between highest and lowest water level amounted to only $28-38 \mathrm{~cm}$ in the three years of investigation. If the lake had received a fairly vigorous sub-lacustrine inlet, the fluctuations of the lake level would undoubtedly have been greater. Finally, the great annual thermal fluctuation of the lake, together with the rather long duration of the ice-cover, is not indicative of a good contact with a groundwater stream flowing into the lake.

Which of the two possibilities mentioned fits the facts cannot be decided on the basis of the available information.

As $\Delta R$ in the equation (2) on p. 8 can be neglected, provided that the period considered is long (Lyshede 1959, p. 15), we get when $P=770 \mathrm{~mm}$ and $E$ is estimated as 450 mm

$$
\begin{equation*}
O_{z}=I_{z}+320 . \tag{3}
\end{equation*}
$$

As the lake surface is 113800 square meters, 320 mm correspond to 36416 cubic meters. Therefore the average annual sub-lacustrine run-off is 36416 cubic meters greater than the sub-lacustrine affluent, on condition that the yearly evaporation from the lake surface really is 450 mm .

If the $\mathrm{Cl}^{-}$-content of the rain water over Grane Langso is estimated to be equal to the average value of the $\mathrm{Cl}^{-}$-quantities of the Borris rain and the Ødum rain, the result is $4.6 \mathrm{mg} \mathrm{Cl}{ }^{-} \cdot \mathrm{l}^{-1}$. According to Drischel's survey (see Hutchinson 1957, p. 545 ) a quantity of about $5 \mathrm{mg} \mathrm{Cl}{ }^{-} \cdot \mathrm{l}^{-1}$ should be expected, as the lake is removed about 80 km from the North Sea.

Borris is situated in the westernmost part of Jutland, just E of the large lagoon at Ringkøbing. Ødum lies in eastern Jutland, between Aarhus and Randers (see Jensen 1962, Fig. 1). Grane Langsø is located halfway between these two stations.

In order to get an idea of the variation in the chloride quantities of rain water from year to year, their values are given in Table 2.

It is evident from Table 2 that the yearly variations from the average value $3.1 \mathrm{mg} \mathrm{Cl}{ }^{-} \cdot \mathrm{l}^{-1}$ at most amount to $2.6 \mathrm{mg} \mathrm{Cl} \cdot{ }^{-} \cdot \mathrm{l}^{-1}$ within a period of 6 years.

If we imagine the lake lying in a basin covered with loam, through which a slow seepage takes place to an underlying groundwater stream, and being fed nearly exclusively by rainwater, the evaporation E can apparently be calculated from the chloride concentration of the precipitation and the lake water:

$$
\begin{gathered}
4.6 \mathrm{mg} \mathrm{Cl} \cdot \mathrm{I}^{-1} \cdot \frac{770}{770-E}=11.3 \mathrm{mg} \mathrm{Cl} \cdot \mathrm{I}^{-1} \\
E=457 \mathrm{~mm} .
\end{gathered}
$$

Table 2. The quantities of chloride in mg per litre of the Borris rain and the Ødum rain each year.

|  | 1955 | 1956 | 1957 | 1958 | 1959 |
| :--- | :---: | :---: | :---: | :---: | :---: |$| 1960$

Chloride in the accumulated rainfall within the period

|  | 1955-1960 |
| :---: | :---: |
| Borris | unknown |
| Ødum | $3.5 \mathrm{mg} \cdot \mathrm{l}^{-1}$ |

The precipitation is not the only source, however, that carries $\mathrm{Cl}^{-}$to the lake; also some dry fallout of airborne chlorides must take place on the lake surface. The rate of the latter process is probably much smaller than the capture by vegetation of condensation nuclei, but it is unknown. The dry fallout has the effect that the true value of E becomes somewhat smaller than 457 mm in the hypothetic case before us.

It is, however, quite conceivable that a good contact between Grane Langsø and the groundwater exists; the lake then receives rainwater ( $P=770 \mathrm{~mm}$ yearly) and groundwater $\left(I_{z}\right)$, as well. The yearly actual evaporation of great parts of Jutland is about 350 mm (Aslyng 1959, p. 48).

If the chloride content of the precipitation on the lake itself is separately considered, the evaporation 450 mm must alter the concentration in the following way:

$$
4.6 \mathrm{mg} \mathrm{Cl}^{-} \cdot \mathrm{l}^{-1} \cdot \frac{770}{770-450}=11.1 \mathrm{mg} \mathrm{Cl}^{-} \cdot \mathrm{l}^{-1}
$$

This value is believed to be at a lower limit of the true value owing to some dry fallout of airborne chlorides on the lake surface.

The precipitation over the surrounding country with coniferous woods, heaths, and moorland fields must be concentrated by the actual evaporation:

$$
4.6 \mathrm{mg} \mathrm{Cl} \cdot \mathrm{l}^{-1} \cdot \frac{770}{770-350}=8.4 \mathrm{mg} \mathrm{Cl}^{-} \cdot \mathrm{l}^{-1}
$$

In this case, however, the vegetation capture of sea salt particles must be drawn into the picture. By how much should the value 8.4 be increased owing to this process? Eriksson (1960, p. 82) has pointed out that the ratio

$$
\frac{\text { precipitation-chloride } \cdot \mathrm{l}^{-1}}{\text { riverwater-chloride } \cdot \mathrm{l}^{-1}}=\text { about } 0.32
$$

for the densely wooded countries Sweden and Finland. "Multiplying rainwater chloride amounts by three can therefore be expected to give a fair estimate of the total amount of $\mathrm{Cl}^{-}$brought to the ground" (Eriksson loc. cit.).

This rule, applied to the precipitation of the environment of Grane Langsø, yields the result $13.8 \mathrm{mg} \mathrm{Cl} \cdot \mathrm{l}^{-1}$ for the groundwater. If this value is used for calculating $I_{z}$, we get

$$
\begin{gathered}
\frac{770 \cdot 4.6+I_{z} \cdot 13.8}{(770-450)+I_{z}}=11.3 \\
I_{z}=30 \mathrm{~mm}
\end{gathered}
$$

According to equation (3) on p. 12 the sub-lacustrine outlet then becomes

$$
O_{z}=30+320=350 \mathrm{~mm}
$$

As the mean depth of Grane Langs $\varnothing$ is 7100 mm , the water renewal rate should be about 20 years .

This is a slow rate of replacement. BERG (1938, p. 19) has estimated the water renewal rate of Esrom Sø to 7.5 years on condition that the annual evaporation from the lake surface is 780 mm . If Aslyng's evaporation value of Søndersø, 600 mm , is employed, the renewal rate becomes 8.5 years. A similar renewal rate, about 8 years, was calculated for Cayuga Lake by Henson, Bradshaw, and Chandler (1961, p. 1617). It should be emphazised, however, that Grane Langsø is a typical seepage lake, while Esrom Lake and Cayuga Lake are drainage lakes.

The groundwater from the Højvang well, previously mentioned, has been analysed as to $\mathrm{Cl}^{-}$. According to Mr. Hans Mathiesen, Master of Science, to whom I am indebted for the analysis, the chloride quantity amounted to $11.6 \mathrm{mg} \mathrm{Cl}{ }^{-} \cdot 1^{-1}$.

It may be a matter of chance that this groundwater, removed 650 m from the lake, exhibits the same $\mathrm{Cl}^{-}$concentration as Grane Langs $\varnothing$. The conformity may, however, also be due to a groundwater stream, moving from the environment of Hampen Sø through Grane Langsø and the Højvang well to Kulsø, as mentioned on p. 11 .

The reasons why the chloride quantity of the Højvang ground water does not rise to about $3 \times 4.6 \mathrm{mg} \cdot 1^{-1}=13.8 \mathrm{mg} \cdot 1^{-1}$ probably are to be sought for in one fact, that Eriksson advanced his rule on the basis of an analytical material originating from a densely forested region. Such areas as stratified drift and sandy moraine covered with heaths, moorland fields, and coniferous plantations must be poorer devices in the capture of airborne salts than densely wooded countries such as Sweden and Finland, as the coniferous forests are able to filter a much greater air-volume per time-unit than the other vegetations mentioned.

It is a fact that the leaves of the plants assimilate $\mathrm{Na}^{+}, \mathrm{Cl}^{-}$, and other ions from the captured sea salt particles, $\mathrm{Na}^{+}$at least being a micronutrient. By harvest of the crops on the fields thus i.a. $\mathrm{Cl}^{-}$quantities are removed (cf. Table 14 bis), which in a natural vegetation would be brought down to the ground water partly by rain, partly by decay. This removal is hardly compensated by the insignificant quantities of $\mathrm{Cl}^{-}$ present as impurity in the fertilizers. As is evident from table 14 bis below, the substances removed by wood-felling are quantitatively much smaller than those removed by harvest of the agricultural products. This difference probably also holds good for $\mathrm{Cl}^{-}$.

Jensen has given a summary on the average quantities of airborne salts and the salts of the precipitation from 10 Danish stations (1962, p. 905). His Table 14 is translated and reproduced below.

Table 14 bis (after Jensen 1962).

|  | kg pr. ha |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Supply | S | Cl | $\mathrm{NO}_{3}-\mathrm{N}$ | $\mathrm{NH}_{3}-\mathrm{N}$ | Na | K | Mg | Ca | B |
| Precipitation | 13 | 26 | 2 | 5 | 16 | 3 | 3 | 7 | 0.03 |
| Air . . . . . . . . . . . . . . . . . . . | 25 | 30 | ? | 8 | 20 | 3 | 3 | 7 | ? |
| total... | 38 | 56 | ? | 13 | 36 | 6 | 6 | 14 | ? |
| Removal by an average crop |  |  |  |  |  |  |  |  |  |
| Corn . . . . . . . . . . . . . . . . . . . | 10 | 15 |  |  | 5 | 40 | 7 | 15 | 0.012 |
| Root crops . . . . . . . . . . . . . | 20 | 15 |  |  | 10 | 150 | 15 | 90 | 0.06 |
| Grass . . . . . . . . . . . . . . . . . | 11 | 40 |  |  | 6 | 100 | 12 | 45 | 0.012 |
| Spruce forest . . . . . . . . . . . . | 2 | ? |  |  | 2 | 3 | 2 | 10 | ? |

"From Swedish investigations on the relation between the content of plant food in the air and the precipitation, the quantities of the atmospheric supply to the crop have been computed . . It should be strongly emphazised, however, that the values stated represent a rough estimate on the average quantities, from which great deviations can be found in special cases" (Jensen 1962, p. 905).

According to Jensen's calculations the ratio between the total supply of $\mathrm{Cl}^{-}$ and the $\mathrm{Cl}^{-}$content of the precipitation is $\frac{56}{26}$. Employing this value on the precipitation over the country around Grane Langsø, where the yearly evaporation is 350 mm , we get

$$
4.6 \mathrm{mg} \mathrm{Cl}^{-} \cdot \mathrm{l}^{-1} \cdot \frac{56}{26} \cdot \frac{770}{770-350}=18.2 \mathrm{mg} \mathrm{Cl} \cdot \mathrm{l}^{-1}
$$

On condition that this value represent the chloride value of the inflowing groundwater, and the evaporation 450 mm from the lake surface is correct, $I_{z}$ can be computed:

$$
\begin{gathered}
\frac{770 \cdot 4.6+I_{z} \cdot 18.2}{(770-450)+I_{z}}=11.3 \\
I_{z}=11 \mathrm{~mm} ; \quad O_{z}=11+320=331 \mathrm{~mm}
\end{gathered}
$$

Under these conditions the water renewal rate should be about 21 years.
The information given above demonstrates that too many unknown or approximately known factors make the results obtained questionable. The reader is invited to consider this section as a preliminary study on the water balance of a lake, devoid of visible affluents and effluents. The problems may be solved when the composition and succession of the various soil strata are eluciated by borings west and east of the lake, measurements of the water level in these borings are made simultaneously with determinations of the levels of Grane Langsø and its neighbouring lakes, and finally seasonal analyses of chloride are carried out concurrently in the borings and lakes.

## 4. The Carbon Dioxide System

Some recent investigators, e.g. E. Naumann, considered the " N and P standards of the water" as primarily responsible for the rate of organic production in lakes. $\mathrm{CO}_{2}$, just as vital as N and P , was hardly realized to be a factor of production. It seemed to be tacitly assumed that the lakes had $\mathrm{CO}_{2}$ enough for their photosynthetic processes. Grane Langsø represents, however, an example of a lake where the $\mathrm{CO}_{2}$ factor at any rate occasionally acts as a limiting factor in the primary production.

It is a well-known fact that the carbon dioxide system in water consists of the following components: $\mathrm{CO}_{2}, \mathrm{CO}_{2} \mathrm{aq}, \mathrm{HCO}_{3}^{-}$, and $\mathrm{CO}_{3}^{--}$. Buch (1917) and Faurholt (1924) a.o. have shown that a definite interrelation of these components exists, the equilibrium condition being dependent on $\mathrm{p}_{\mathrm{H}}$, ionic concentration, and temperature. The components occur at any pH value, being present, however, in widely different concentrations. Thus in the case of a pH value smaller than 4 the only component of importance is $\mathrm{CO}_{2}$. At the pH value 8.4 the $\mathrm{HCO}_{3}^{-}$component constitutes nearly 98 per cent of the total quantity of $\mathrm{CO}_{2}$. When pH surpasses 12.5 , practically only $\mathrm{CO}_{3}^{--}$is present. The ratio of the concentrations of $\mathrm{CO}_{2}$ aq to $\mathrm{CO}_{2}$ is constant at all pH values, amounting to about 3 thousandths (Hutchinson 1957, p. 655). Faurholt (1924, p. 56) has published graphs which demonstrate this interrelation.

Normally it is possible to determine the amount of total $\mathrm{CO}_{2}$ is freshwater, if titration alkalinity, pH , and temperature are known. Alkalinity is often determined by titration of a 100 ml sample with $\mathrm{N} / 10 \mathrm{HCl}$ until the pH has fallen to 4.3 . According to Ruttner (1931, p. 208) a deduction of 0.06 ml must be made. The alkalinity 1 is defined by the hydrogen-carbonate content of 1 litre $\mathrm{N} / 1000 \mathrm{Ca}\left(\mathrm{HCO}_{3}\right)_{2}$, this being 61 mg HCO 3 .

Steemann Nielsen (1944, p. 20) finds this titration method unsatisfying and refers to Gripenberg's more exact method (1936), which, however, like other titration methods, is applicable only in the absence of humic compounds.

In Kaj Berg and Ib Clemens Pedersen's work of the Danish humic Lake Gribso (1956, p. 130-131) the results of a usual alkalinity titration have been compared with the results obtained with the aid of Krogh and Rehberg's method. This comparison clearly demonstrates that the alkalinity titration affords far higher $\mathrm{HCO}_{3}^{-}$-values than the latter method, which in all probability is safe.

As far as Grane Langs $\varnothing$ is concerned, where the quantity of humic substances must be negligible, an analysis from August 9th, 1950 shoved the following results: pH was 5.5 , the temperature was measured as $20^{\circ} \mathrm{C}$, and the alkalinity titration value amounted to only 0.05 ml of $\mathrm{N} / 10 \mathrm{HCl}$ per 100 ml lake water. If 0.06 ml of $\mathrm{N} / 10 \mathrm{HCl}$ is deducted, the alkalinity must be $-0.01 \cdot 61 \mathrm{mg} \mathrm{HCO}_{3}^{-}$per litre. According to Krogh and Rehberg's method, however, a content of 1.22 mg total $\mathrm{CO}_{2}$ per litre was found on august 9th, 1950. Employing the equation (4) (p.44) on this quantity, a $\mathrm{HCO}_{3}^{-}$ content of 0.2 mg per litre was obtained by the pH value and temperature mentioned.

It only remains to say that water from the 11 m subsurface depth always is pale brown just before the vernal and autumnal turn-overs set in. The analytic results referred to, and the occasional occurrence of brown substances, led to a rejection of the titration method in favour of Krogh and Rehberg's technique, even if a single analysis can hardly be performed in less than half an hour.

## 5. Analytic Methods

By Krogh and Rehberg's method (1930) the total $\mathrm{CO}_{2}$, liberated by adding $\mathrm{H}_{3} \mathrm{PO}_{4}$ to a given volume of sample water, is distilled off in vacuo into a definite volume of baryta water containing 5 per cent of $\mathrm{BaCl}_{2}, 2 \mathrm{H}_{2} \mathrm{O}$. By this procedure a part of the $\mathrm{Ba}(\mathrm{OH})_{2}$ is transformed into $\mathrm{BaCO}_{3}$; the remaining part is then titrated with N HCl . A Rehberg micro-burette was used for this purpose, and the titration was finished at a pH value of $8.6-8.8$, thymol blue being added as an indicator.

The result required can be computed from the difference between a standardization value ( s cmm N HCl ) and an analysis value (a cmm N HCl ). The standardization is carried out exactly as an analysis, except that $1 \mathrm{ml} \mathrm{CO}_{2}$-free water is distilled off instead of 5 ml from a definite volume of the water sample ( v ml ). As 1 cmm N HCl is equivalent to $0.022 \mathrm{mg} \mathrm{CO} \mathrm{C}_{2}$, the final result must be

$$
\frac{(\mathrm{s}-\mathrm{a}) \cdot 0.022 \cdot 1000}{\mathrm{v}} \mathrm{mg} \mathrm{CO} 2 \text { per litre. }
$$

As the quantity of total $\mathrm{CO}_{2}$ in Grane Langsø normally lies as low as $1-2 \mathrm{mg}$ per litre, the volume (v) of water to be analysed was always fixed at 100 ml . By all analyses and standardizations $0.5 \mathrm{ml} \mathrm{M} \mathrm{H} \mathrm{H}_{3} \mathrm{PO}_{4}$ and $1 \mathrm{ml} \mathrm{CO}_{2}$-free water were injected into the flask (Fig. 4, A). The distillation, performed at a temperature of $95-100^{\circ} \mathrm{C}$, was continued until a total of about 5 ml was distilled off into the recipient (Fig. 4, D).

One of the many operations which were to be done during the analysis proved very difficult to carry out in a safe manner, unless one is professor August Krogh or professor Brandt Rehberg. When the glass apparatus has been filled with $\mathrm{CO}_{2}{ }^{-}$ free air to a pressure slightly above the atmosphere, the recipient should be released so much that the capillary tube of a syringe pipette just can be introduced, in order to empty 0.5 ml of baryta water into the recipient. I therefore let a glass-blower mount


Fig. 4. The glass apparatus used for the determination of total carbon dioxide in water after Krogh and Rehberg' method. The glass container with a 100 ml mark on its lowest tube, which can be connected with the tube of $B$, is not shown. Half natural size.
a small side tube with glass stopper on to the recipient (Fig. 4, E). In agreement with this improvement the capillary tube of the syringe pipette was drawn out to a thickness of only 1 mm (Fig. 4, F). In order to make the ground joints B, C, and E of Fig. 4 airproof, Dow Corning High Vacuum Grease was employed with a satisfying result.

During each visit at the lake, a 600 ml -sample for determination of total $\mathrm{CO}_{2}$, a 300 ml - and a 60 ml -sample for pH measurement and counting of the phytoplankton organisms, were taken from each of the following subsurface depths: $0,2,4,6$, 8, 10, and 11 metres. For collecting, the water-sampler described in Nygard 1958, p. 151 was employed. This apparatus was improved by replacing the wooden operat-
ing rod ( 7 on fig. 4 loc. cit.) and its two wooden sides serving as a shaft bearing, with Perspex acryl material. The water-sampler fills within 40 seconds.

All these samples were collected between 10 and 12 hrs . in Pyrex glass bottles with glass stoppers, all bottles being completely filled without air-bubbles. They were stored at temperatures approximately the same as those encountered during collecting.

The pH measurements and the counts were undertaken a few hours later, but the $\mathrm{CO}_{2}$-determinations were carried out two days later in the laboratory in Hillerød. In order to avoid interference through respiration of the plankton organisms, all the 600 ml -samples were acidified by means of 10 drops of concentrated sulphuric acid. The 100.0 ml glass container, placed with the aid of a small piece of rubber tube on the glass-tube of B on Fig. 4, was flushed out with at least 200 ml of sample water. The slow siphoning was carried out with both glass tubes placed at the bottom of the two vessels.

The pH was measured electrometrically by means of the glass electrode. Attempts were made on October 9th, 1960 to determine pH colorimetrically, but the results deviated highly from those obtained with the aid of electrometrical determinations, the colorimetric values being 0.71 pH -unit lower than the electrometric ones. In agreement with this fact the pH of the indicator itself (brom cresol purple) was determined electrometrically as 3.48. The pH of the water from Grane Langsø, poor in buffer substances, consequently cannot be determined colorimetrically. When determining pH of the lake water, I always allowed 30 seconds for stirring (turning) the small cup with the sample water, and the final reading was undertaken after a further lapse of 60 seconds. Experience has taught me that the water from Grane Langsø can alter in pH appreciably after some extremely small contamination. Suspecting this has happened, one must replace the sample in the small cup with intact water from e.g. one of the other bottles, without adding KCl and without rinsing the electrodes with distilled water. This procedure may have to be repeated. After each series of 7 pH -determinations, the buffer adjustment was controlled by means of the initial buffer solution.

The buffer solutions used have been subjected to careful measurements by Radiometer's civil engineers, who employed the method for standardizing the pH scale, used by the National Bureau of Standards, USA. The pH -values of these precision buffers are thus in accordance with pH 4.00 of a 0.05 M potassium hydrogenphthalate, a standard buffer solution used also in e.g. Great Britain and France.

## 6. The Uncertainty of the Analyses

The material of $\mathrm{CO}_{2}$ determinations available for a statistical analysis consists of many short measuring series, the parameter values $\xi$ of which are dissimilar. The analyses have been made under approximately similar experimental conditions, the accuracy therefore being virtually identical for all of the series.

By the method here employed for estimating the standard deviation $\sigma$, the value measured directly has not been conceived as the primary variable. As such, however, is regarded the sample sum of squares, computed from any measuring series: $\mathrm{q}=\left(\mathrm{v}^{2}\right)$. The distribution of q does not depend on the true mean value $\xi$. The method thus allows us to determine the standard deviation of different measuring series, $\xi$ being dissimilar for any series (Arley and Buch 1958, p. 109).

The results of the theoretical considerations are as follows. One is given m measuring series, each consisting of $n_{1}, n_{2}, n_{3} \ldots n_{m}$ determinations of $\mathrm{CO}_{2}$. The $m$ sample sums of squares are designed $q_{1}^{2}, q_{2}^{2}, q_{3}^{2} \ldots \ldots q_{m}^{2}$, respectively. The $m$ measuring series then furnish the respective estimates

$$
s_{1}=\sqrt{\frac{q_{1}^{2}}{n_{1}-1}}, \quad s_{2}=\sqrt{\frac{q_{2}^{2}}{n_{2}-1}}, \quad s_{3}=\sqrt{\frac{q_{3}^{2}}{n_{3}-1} \ldots \ldots s_{m}=\sqrt{\frac{q_{m}^{2}}{n_{m}-1}} \text {. }}
$$

for the parameter $\sigma$. As the $m$ measuring series must be considered mutually independent, we get the best estimate of $\sigma$ as follows

$$
\begin{aligned}
\sigma \approx s & =\sqrt{\frac{\left(n_{1}-1\right) s_{1}^{2}+\left(n_{2}-1\right) s_{2}^{2}+\left(n_{3}-1\right) s_{3}^{2} \ldots \ldots\left(n_{m}-1\right) s_{m}^{2}}{\left(n_{1}-1\right)+\left(n_{2}-1\right)+\left(n_{3}-1\right)+\ldots \ldots\left(n_{m}-1\right)}} \\
& =\sqrt{\frac{{q_{1}{ }^{2}+q_{2}{ }^{2}+q_{3}{ }^{2}+q_{4}{ }^{2}+\ldots q_{m}{ }^{2}}_{n-m}^{n-m}}{}}
\end{aligned}
$$

where $\mathrm{n}=n_{1}+n_{2}+n_{3}+\ldots \ldots n_{m}$ or the total number of analyses. The standard error of the standard deviation is computed by

$$
\sigma(s)=\frac{s}{\sqrt{2(n-m)}} .
$$

For the determination of the standard deviation $\sigma$ on the analyses of water from Grane Langsø, two series of figures are available:
(1) a fairly large number of analyses in duplicate, originating from the experiments on the productivity of Nitella flexilis;
(2) a rather large number of analyses from the circulation periods, when the lake consequently was uniform throughout all levels as to physical and chemical properties. Samples were taken from subsurface depths of $0,2,4,6,8,10$, and 11 meters.
(3) For the determination of $\sigma$ of the standardization values originating from titrations of the baryta water with N HCl , several measuring series, normally including $2-4$ titrations, are available.

The results of these calculations are:
(1) from the analyses in duplicate ( 29 series with a total of 58 analyses) there is obtained

$$
\sigma_{\text {water sample }} \approx s=0.23 \mathrm{cmm} \mathrm{~N} \mathrm{HCl}
$$

which corresponds to 0.0051 mg CO 2 per 100 ml or 0.051 mg CO 2 per litre. $\sigma(s)=$ 0.03 cmm N HCl .
(2) the determinations from the circulations periods (11 series with a total of 70 analyses) afford the following estimate

$$
\begin{aligned}
\sigma_{\text {water sample }} \approx s & =0.22 \mathrm{cmm} \mathrm{~N} \mathrm{HCl} \\
\sigma(s) & =0.02 \mathrm{cmm} \mathrm{~N} \mathrm{HCl}
\end{aligned}
$$

(3) a total of 56 standardizations distributed in 17 series gives

$$
\begin{aligned}
\sigma_{\text {standardization }} \approx s & =0.21 \mathrm{cmm} \times \mathrm{HCl} \\
\sigma(s) & =0.03 \mathrm{cmm} \mathrm{~N} \mathrm{HCl}
\end{aligned}
$$

In order to determine the quantity of $\mathrm{CO}_{2}$ in a water sample, the difference between the standardization value and the analysis value must be found. The standard deviation on a single determination of total carbon dioxide is then

$$
\begin{aligned}
\sigma \approx s & =\sqrt{\left(\sigma_{\text {water sample }}\right)^{2}+\left(\sigma_{\text {standardization }}\right)^{2}}=\sqrt{0.23^{2}+0.21^{2}} \\
& =0.31 \mathrm{cmm} \mathrm{~N} \mathrm{HCl}, \text { corresponding to } 0.07 \mathrm{mg} \mathrm{CO}
\end{aligned} \text { per litre. } .
$$

This is the standard deviation on analyses of water samples of which 86 per cent contained only $0.27-1.74 \mathrm{mg}$ total $\mathrm{CO}_{2} 1^{-1}$. The standard error of the standard deviation is 0.03 cmm N HCl , equivalent to $0.007 \mathrm{mg} \mathrm{CO}_{2}$ per litre. Therefore the final result is stated with 2 decimals.

As the calibration of the Rehberg's microburette may be considered approximate, the capillary glass burette was weighed out with mercury of a definite temperature on a balance with an accuracy of $\pm 0.1 \mathrm{mg}$. On the basis of the many figures thus obtained, a correction table was prepared for the individual graduations of this microburette, the deviations at most being 0.05 cmm .

The syringe pipette employed to empty 0.5 ml baryta water into the recipient, gave a fairly good accuracy, the standard deviation on a single discharge being 0.16 cmm $(n=28)$, and the standard error of the standard deviation is 0.03 cmm ; the coefficient of variation consequently amounts to 0.03 per cent. The volume 0.16 cmm baryta water is equivalent to 0.05 cmm N HCl , this being about 16 per cent of the standard deviation on a single determination of total $\mathrm{CO}_{2}$. The accuracy of Krogh and Rehberg's method may be increased, if one can get a more exact syringe pipette of small size. The 5 ml syringe pipette used for oxygen analyses is of great accuracy, exhibiting a coefficient of variation of only 0.006 per cent. This exactitude in connection with photoelectrically controlled titration gives rise to a standard deviation of only $0.024 \mathrm{mg} \mathrm{O}_{2}$ per litre on a single oxygen analysis by means of the Winkler method; the standard error of this standard deviation is $0.0015 \mathrm{mg} \mathrm{O}_{2}$ per litre. The 50 ml syringe pipette used for the ${ }^{14} \mathrm{C}$-determinations likewise is very exact, having a coefficient of variation as small as 0.004 per cent.

## 7. Iron and Phosphate in Grane Langsø

The concentration of the ferrous ions was determined colorimetrically by means of dipyridyl dissolved in N/10 HCl (cf. Standard Methods 1946, p. 51-52). One crystal of $\mathrm{Na}_{2} \mathrm{SO}_{3}$ and one drop concentrated HCl were then added to the test tubes in order to reduce the ferric ions possibly present to ferrous ions. The colorimetric determination by means of an EEL colorimeter was repeated, and the concentration of the $\mathrm{Fe}^{3+}$ was found as the difference between the value last obtained and that of the $\mathrm{Fe}^{2+}$.

Phosphate as orthophosphate was determined colorimetrically by Deniges's method (Standard Methods 1946, p. 80); the comparison of the samples and standards was made 20 minutes after their preparation, however.

The vertical distribution of the ferrous and ferric ions was determined merely on June 26th, 1951. As shown in Fig. 5 it was not possible to detect any $\mathrm{Fe}^{2+}$ in the lake, and the quantity of $\mathrm{Fe}^{3+}$ was very small, amounting to $0.005-0.01 \mathrm{mg} \cdot \mathrm{l}^{-1}$. For the sake of comparison the oxygen graph has been inserted on Fig. 5.

The oxygen saturation was computed on the basis of Table 74 in Hutchinson's great work of 1957 (p. 580). The altitude $h$ of Grane Langs $\varnothing$ being 75 m , the pressure $P_{h}$ at the lake surface has been calculated according to the equation

$$
\log P_{h}=\log P_{0}-\frac{273 h}{18421\left(273+\theta_{z}\right)} .
$$

According to Danmarks Klima (1933, t. I, II, III, and IV) the mean atmospheric pressure, reduced to the sea-level, varied for Grane Langsø between the following values

$$
\begin{array}{ll}
\text { January: } & 761.1 \mathrm{~mm} \\
\text { April: } & 759.75 \mathrm{~mm} \\
\text { July: } & 759.35 \mathrm{~mm} \\
\text { October: } & 759.9 \mathrm{~mm}
\end{array}
$$

Mean annual pressure $=759.9 \mathrm{~mm}$.
$P_{0}$ of the equation mentioned is put equal to $759.9 \mathrm{~mm} . \theta_{z}$ stands for the temperatures of the individual water-layers analysed for oxygen. The result required then becomes

$$
\frac{\left[O_{2}\right]}{\left[O_{2}\right]_{s}} \cdot \frac{P_{h}-p_{w}}{760-p_{w}}
$$

where $\left[\mathrm{O}_{2}\right]$ is the oxygen quantity, stated as $\mathrm{mg} \mathrm{l}^{-1}$, of a given water-layer; $\left[\mathrm{O}_{2}\right]_{s}$ is the oxygen saturation value at the temperature of this water-layer, taken from Table 74 in Hutchinson's work, and $p_{w}$ is the partial pressure of the water vapor at the temperature concerned.

Fig. 5 indicates that Grane Langsø was nearly saturated with oxygen from the surface to a depth of 5 m . A metalimnic oxygen maximum, amounting to about 111
per cent, occurred at a depth of 7 m ; the water volume from 7 to 11 m was also supersaturated with oxygen.

As will be shown in a paper to come, the oxygen saturation graphs of Grane Langs $\varnothing$ within the period from late May to the beginning of August exhibit a metalimnic oxygen maximum in subsurface depths of 8 or 10 m , amounting to $101-126$ per cent saturation. The surface water from $0-2 \mathrm{~m}$ simultaneously contained quantities of oxygen corresponding to $99-103$ per cent saturation, while the hypolimnion usually


Fig. 5. The vertical distribution of the ferrous and ferric ions in Grane Langsø on June 26th, 1951. The other graphs illustrate the variation of temperature, specific conductivity, and oxygen down through the lake.
was supersaturated attaining percentages of saturation from 101 to 117 . This oxygen distribution is not identical with what $\AA$ berg and Rodhe call the positive heterograde distribution (1942, p. 192-193), as the hypolimnic saturation values exceed those of the epilimnion.

The large quantities of oxygen in Grane Langso on June 26th, 1951, probably explain why ferrous ions were undetectable on this occasion.

While it was not possible to trace ferrous ions on June 26 th 1951 , values between 0.01 and $0.03 \mathrm{mg} \mathrm{Fe}{ }^{++} \cdot \mathrm{l}^{-1}$ were found in the layers from 1 m to 10 m subsurface depths on February 23rd, 1951. At this moment the corresponding oxygen values lay between 73.5 and 93 per cent of saturation (see p. 91 ).

For the sake of comparison the fluctuations in the vertical distribution of iron in the acid, humic lake Gribso are given in Table 3 . The extremes observed were 0.02 and 2.4 mg total iron $\cdot 1^{-1}$. I made the colorimetric determinations of "total iron"
by means of ammonium sulphocyanate. The ferrous ions possibly present were beforehand transformed to ferric ions by 30 per cent hydrogen peroxide. The concentration of ferrous ions were afterward determined colorimetrically by means of ortho-phenantroline-monohydrate and hydroxylamine chloride (Standard Methods 1946, p. 52). The concentrations of $\mathrm{Fe}^{3+}$ was found as the difference between the concentrations of "total iron" and $\mathrm{Fe}^{2+}$.

Table 3. The quantities of iron in lake Gribsø in 1949-50, stated as $\mathrm{mg} \cdot \mathrm{l}^{-1}$. The values in brackets represent $\mathrm{Fe}^{2+}$.


During the stagnation periods an accumulation of iron took place, and analyses in September and October proved this iron to be present principally as ferrous ions, at the end attaining a concentration of $2,4 \mathrm{mg} \mathrm{Fe}{ }^{2+} \cdot \mathrm{l}^{-1}$. The autumnal circulation, here called ciau (cf. p. 50), set in on November 10th, 1949 ( $\pm 2$ days), but the analysis of November 5 th indicates a nearly complete circulation before this time. The vernal circulation, here called cive (cf. p. 50), occurred on March 12th, 1950, and in the following month the quantities of "total iron" amounted to $0.1-0.2 \mathrm{mg} \cdot \mathrm{l}^{-1}$, just as during the autumnal circulation. The maxima of $\mathrm{Fe}^{2+}+\mathrm{Fe}^{3+}$ thus occurred in -1. to -2. ciau and -1 . cive, while the minima were observed in the circulation periods.

According to Einsele's theory (1936) $\mathrm{H}_{2} \mathrm{~S}$ in the presence of $\mathrm{CO}_{2}$ is able to reduce some form of precipitated ferric phosphate to ferrous sulphide + ferrous hydrogencarbonate + free, soluble phosphate. This process implies an oxygen-concentration smaller than $0.7 \mathrm{mg} \mathrm{O}_{2} \cdot \mathrm{l}^{-1}$. The quantitative interrelation of the substances mentioned depends i.a. on pH and the $\mathrm{H}_{2} \mathrm{~S}$-concentration.

The oxygen-concentration of the bottom layers in eutrophic lakes declines strongly during summer stagnation. Coincidently the quantities of $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{~S}$ are rising, although hydrogen sulphide is not necessarily liberated. Conditions are soon established for starting the transformation mentioned, resulting in i. a. an accumulation of phosphate in the bottom layers. Also phosphate ions liberated by decay of the seston under the prevailing anaerobic conditions contribute to the final phosphatequantity just before ciau. When circulation sets in, $\mathrm{Fe}^{2+}$ is oxidized to $\mathrm{Fe}^{3+}$, which in statu nascendi recombines with phosphate ions to form the nearly insoluble ferric phosphate.

A comparison of Table 3 with Table 4 demonstrates that Gribso provides a good illustration to Einsele's theory. This lake is, however, not eutrophic, but mesotrophic in the humic, acid phase.

Lake Gribsø proceeds to phase IV of stagnation (Hutchinson 1957, p. 724) as early as -4 . ciau, as the 11 m water smelled of hydrogen sulphide already on July 15th, 1949. On August 3rd, 1949 the 10 m and 11 m layers contained 0.32 and 0.65 $\mathrm{mg} \mathrm{H}_{2} \mathrm{~S} \cdot \mathrm{l}^{-1}$. In September-October the 8 m and 9 m samples also smelled of $\mathrm{H}_{2} \mathrm{~S}$, and even on November 5th, 1949, the 11 m water had a faint smell of hydrogen sulphide.

This gas was determined quantitatively by means of $\mathrm{CdSO}_{4}$, which precipitated the $\mathrm{H}_{2} \mathrm{~S}$ in the unfiltered water as CdS. After centrifugalization and washing out the cadmium sulphide was treated with a definite volume of " $\mathrm{N} / 100$ " iodine solution and hydrochloric acid. After reduction of some of the iodine by $\mathrm{H}_{2} \mathrm{~S}$ to HJ, the remaining iodine was titrated with $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ (cf. Ohle 1936, p. 206).

On August 3rd, 1949 the quantity of total $\mathrm{CO}_{2}$ in the 1 m layer amounted to $2.3 \mathrm{mg} \cdot \mathrm{l}^{-1}$. The 11 m layer contained no less than 21.7 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$, sufficient for the formation of ferrous hydrogen-carbonate. Simultaneously the pH of the 11 m water was 6.25 ; one month earlier it amounted to only 5.2 . The pH of the 11 m layer
increased from 5.15 on June 29th, 1949, to 6.45 on October 29 th, 1949 (cf. Table 28 on p. 76). The considerable rise of pH during the summer stagnation period may be a result of the accumulation of ferrous hydrogen-carbonate in the bottom water of lake Gribso.

The oxygen-content of the 11 m layer had declined to $0.9 \mathrm{mg} \cdot \mathrm{l}^{-1}$ already on June 29th, 1949. On August 3rd, 1949 the 10 m and 11 m layer contained 0.36 and $0.07 \mathrm{mg} \mathrm{O}_{2} \cdot \mathrm{l}^{-1}$, thus less than the critical value $0.7 \mathrm{mg}_{2} \cdot \mathrm{l}^{-1}$ (cf. Berg and Clemens Petersen 1956, p. 127). In the following summer the oxygen was depleted in the bottom layers even as early as July 28th, 1950 :

| Depth in m | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Temperature | 20.0 | 20.0 | 19.4 | 19.3 | 18.5 | 11.9 | 8.6 | 7.3 | 6.9 | 6.7 | 6.7 | 6.7 |
| $\mathrm{mg} \mathrm{O} \mathrm{O}_{2} \cdot 1^{-1}$ | 7.97 | 8.11 | 8.28 | 8.18 | 8.14 | 2.34 | 2.48 | 2.24 | 0.65 | 0 | 0 | 0 |
| saturation | $90 \%$ | $92 \%$ | $93 \%$ | 91\% | $89 \%$ | $22^{\circ} / 0$ | $22^{\circ} /$ | $19 \%$ | $6 \%$ | $0{ }^{0}$ | $0 \%_{0}$ | $0^{0} \%$ |

The quantity of phosphate in the bottom water of lake Gribso increased concomitantly with the rise of the $\mathrm{Fe}^{2+}$-concentration (cf. Table 3 with Table 4). At the onset of the autumnal circulation the phosphate concentration decreased concurrently with the iron-concentration, no doubt essentially caused by oxidation of $\mathrm{Fe}^{2+}$ to $\mathrm{Fe}^{3+}$.

From September 3rd, 1949 to December 3rd, $19496.60 \mathrm{~g} \mathrm{Fe}^{2+}$ per square metre disappeared, being oxidized to ferric compounds. In the same period only 0.458 g $\mathrm{PO}_{4}-\mathrm{P}$ per square metre disappeared. Assuming that this phosphorus quantity is transformed into $\mathrm{FePO}_{4}$, whereby 31 g P is equivalent to $56 \mathrm{~g} \mathrm{Fe}, 0.458 \mathrm{~g} \mathrm{PO}-\mathrm{P}$ is able to bind only 0.83 g Fe . By far the greatest part of the $6.60 \mathrm{~g} \mathrm{Fe}{ }^{2+}$ per square metre consequently was oxidized to $\mathrm{Fe}_{2} \mathrm{O}_{3} \cdot \mathrm{nH}_{2} \mathrm{O}$, which settled on the lake bottom together with a much smaller quantity of $\mathrm{FePO}_{4}$.

Even in very shallow waters the $\mathrm{Fe}^{2+}$ concentration can increase and the $\mathrm{Fe}^{3+}$ concentration decrease towards the bottom. This is seen from the analyses of July 6 th, 1951 , from Kattehale Mose, only 1.3 m deep and wind-sheltered:

$$
\begin{aligned}
& 0.1 \mathrm{mpH} 4.94,0.265 \mathrm{mg} \mathrm{Fe}^{2+} \cdot \mathrm{l}^{-1}, 0.280 \mathrm{mg} \mathrm{Fe}^{3+} \cdot \mathrm{l}^{-1}, 43 \text { per cent } \mathrm{O}_{2} \text { saturation } \\
& 0.5--4.94,0.335-\mathrm{Fe}^{2+} \cdot \mathrm{l}^{-1}, 0.195-\mathrm{Fe}^{3+} \cdot \mathrm{l}^{-1}, 7 \text { per cent } \mathrm{O}_{2} \text { saturation } \\
& 1.0--5.73,1.43-\mathrm{Fe}^{2+} \cdot \mathrm{l}^{-1}, 0.05-\mathrm{Fe}^{3+} \cdot \mathrm{l}^{-1}, 0 \text { per cent } \mathrm{O}_{2} \text { saturation }
\end{aligned}
$$

Analyses of phosphate as orthophosphate were performed monthly in Grane Langsø during one year. Fig. 6 gives an idea of the vertical distribution of phosphate phosphorus during the period from August 1950 to July 1951. The absolute maximum, 7-9 $\mu g \cdot l^{-1}$, was found in December, at the beginning of the winter stagnation period. As shown in the chapter on the hydrogen ion concentration certain biological processes may take place in Grane Langsø in late November or in the first half of December. The rich bottom vegetation of Nitella is for the most part dying at the end of November or in early December. The release of ions by the decay of this dead material may explain the large phosphate maximum on December 20th, 1951.

One month later the quantities at all levels examined had fallen to the absolute minimum, $1 \mu \mathrm{~g} \mathrm{PO}_{4}-\mathrm{P} \cdot \mathrm{l}^{-1}$. A re-determination of phosphate in the water samples from January 24th, 1951 yielded the same surprising result. I believe that an uptake of phosphate had occurred by the phytoplankton, the evergreen littoral vegetation of Littorella, Lobelia, and Isoetes, and by the bottom vegetation of Nitella, Drepanocladus etc.

Surprisingly, relatively large quantities of phosphate, $3-4 \mu \mathrm{~g} \cdot \mathrm{l}^{-1}$, were observed at the end of February. Their origin is obscure; it must be admitted, however, that pH behaves similarly. Low pH values were determined only in December and Febru-


Fig. 6. The vertical distribution of phosphate-phosphorus in Grane Langsø during the period August 8th, 1950 to July 20th, 1951.
ary, the two winter months when Grane Langso contained comparatively large quantities of phosphate.

In late March, when photosynthesis of pelagic algae such as Ankistrodesmus falcatus, and of the benthic charophyte Nitella, had begun in spite of the ice-cover, the phosphate quantity in $1-10 \mathrm{~m}$ depth decreased to its autumnal value, $2 \mu \mathrm{~g} \mathrm{l}^{-1}$. The content of phosphate in the 11 m layer is, however, unknown.

The secondary maximum, $6 \mu \mathrm{~g} l^{-1}$, occurred in April, after the vernal overturn. These surprisingly large quantities, present in spite of a strongly increasing photosynthesis implying an uptake of phosphate, may have been supplied by groundwaterstreams.

During May and June the phosphate quantities decreased slightly in the intermediate part of the lake and the bottom water, but not in the upper water layers. Productivity determinations by means of the oxygen technique demonstrated the greatest production values of May 23 rd and June 26th, 1951 to lie in 7 m and 10 m depth, respectively. The ${ }^{14} \mathrm{C}$-determination of the primary production in the same months of 1960 and 1961 likewise indicated the greatest production to take place in either $2-4 \mathrm{~m}$, or 8 m , or $10-11 \mathrm{~m}$, but never in the top layer, depending on the light conditions and the vertical distribution of phytoplankton.

In July the phosphate values have further decreased to $2 \mu \mathrm{~g} \mathrm{l}^{-1}$ in the layers between depths of 1 to 10 m .

In August phosphate increased from $1 \mu \mathrm{~g} \cdot \mathrm{l}^{-1}$ in the upper 5 meters to $7 \mu \mathrm{~g} \cdot \mathrm{l}^{-1}$ in the 10.8 m layer, in spite of a content of 97 Uroglena-colonies $\cdot \mathrm{ml}^{-1}$ at this level.

In the circulation period from early September to the beginning of December, about $2 \mu \mathrm{~g} \cdot \mathrm{l}^{-1}$ of phosphate was observed throughout the lake.

This review of the phosphate conditions of Grane Langsø suffers from the disadvantage that only a few of the analyses include the 11 m -layer, this layer undoubtedly exhibiting the largest yearly fluctuations of phosphate. On the other hand,

Table 4. Phosphate-phosphorus of lake Gribs $\varnothing$ in $1949-50$, stated as $\mu \mathrm{g} \cdot \mathrm{l}^{-1}$.


Table 5. Phosphate-phosphorus of Kattehale Mose in $1950-51$, stated as $\mu \mathrm{g} \cdot \mathrm{l}^{-1}$.

|  |  | ci |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Aug. 22 | Sept. 15 | Oct. $13$ | Nov. 7 | Dec. 6 | Jan. 9 | Febr. 9 | Mar. 6 | ${ }_{\text {Apr }}{ }_{7}$ | May 7 | June 7 | July 6 |
| 0 m | 3 | 10 | 2 | 2 | 7 | 10 | 1 | 20 | 7 | 1 | 0 | 6 |
| $1 / 2 \mathrm{~m}$ | 7 | 9 | 2 | 2 | 6 | 10 | 2 | 22 | 7 | 3 | 1 | 6 |
| 1 m | 12 | 11 | 2 | 2 | 7 | 12 | 1 | 20 | 8 | 12 | 2 | 8 |
| mg below one square metre | 7.3 | 9.8 | 2.0 | 2.0 | 6.5 | 10.5 | 1.5 | 21.0 | 7.3 | 4.8 | 1.0 | 6.5 |

the account demonstrates that monthly analyses of Grane Langsø during one year gave values never attaining to $0.01 \mathrm{mg} \cdot l^{-1}$ of phosphate-phosphorus. This indicates Grane Langsø to be a lake poor in phosphate.

In order to compare the phosphate quantities of Grane Langsø with those of other Danish lakes and ponds, my own analythical results from lake Gribsø, Kattehale Mose, and Frederiksborg Slotsso have been stated in Tables 4, 5, and 6. The monthly analyses of phosphate in the photosynthetic zone of lake Fures $\varnothing$ are published in "Furesøundersøgelser" (Kaj Berg et al. 1958, p. 102).

In Gribsø the greatest quantity of phosphate below one square metre, 608 mg , was measured in October ( -2 . ciau; probably as a rule in -1 . ciau). The second largest, 270 mg , was observed in -1 . cive (February). The smallest values, 11 and 18 mg below one square metre, occurred in cive +1 . (April) and cive +3 . (June). The fluctuations from year to year can be considerable: in February 1950270 mg was measured, while in February 1951390 mg was found; in July 1949167 mg was observed, in July 1951 no less than 363 mg .

GESSNER (1934, p. 153-154) has demonstrated that humic colloids are able to absorb phosphate ions, a fact which possibly influences the phosphate determinations of Gribsø water by means of Deniges's method.

The largest phosphate content of Kattehale Mose, 21 mg below one square metre, occurred in -1 . cive (March). The largest but one, 10.5 mg , was measured in ciau +3 . (January). The smallest quantities, $1-1.5 \mathrm{mg}$, were observed in cive +3 . (June) and -2 . cive (February).

Frederiksborg Slotssø exhibited its largest quantities, $2610-2710 \mathrm{mg} \mathrm{PO}_{4}-\mathrm{P}$ below one square metre, in -1 . to -2 . cive (March to April). Great quantities, 2230 mg , were liberated in ciau +3 . (November), and, as was the case with Kattehale Mose, also in September: 2460 mg . The minimum, 970 mg , occurred in cive +1 . (April); the secondary minimum presumably lay in cive +3 . (June). Nygaard (1938, t. 7 , Abb. 28) pointed out an enormous maximum, $1500 \mu \mathrm{~g} \cdot \mathrm{l}^{-1}$, in the surface water of Frederiksborg Slotssø on November 16th, 1929. Assuming uniformity of the layers of water on this date, the lake must have contained $7500 \mathrm{mg} \mathrm{PO}_{4}-\mathrm{P}$ below one square metre.

Table 6. Phosphate-phosphorus of Frederiksborg Slotsso in 1950-51, stated as $\mu \mathrm{g} \cdot \mathrm{l}^{-1}$.


Nygatrd (1938, p. 553 , 624, and 639) compared his regular investigations on phosphate in 14 North Zealandic ponds both between the ponds and with British, American, German, and Japanese investigations. The result was a jumble of maxima and minima occurring in any month of the year, but in the greatest part of the localities the maximum or maxima lay in the periods November-March or June-September.

In Lyngby Sø, 2.8 m deep and permanently alkaline, Sigurd Olsen (1955, Fig. 43 on p. 98) demonstrated the greatest quantities of phosphate in the period November-March, amounting to as much as $300 \mu \mathrm{~g} \cdot \mathrm{l}^{-1}$ in March.

Summarising the results from Grane Langs $\varnothing$ and the Tables 4-6, it is necessary to realize that phosphate in lakes and ponds can be bound and liberated in two quite different ways: (1) by assimilation and decay of hydrophytes and phytoplankton, (2) by transformation to ferric phosphate by means of $\mathrm{Fe}^{3+}$, and liberation when this solid is retransformed to ferrous hydrogencarbonate.

The survey given in Table 7 demonstrates that the phosphate-maxima lay in - 1. cive (February and March) and ciau +3 . to + 4. (November, December, and January).

Table 7. The occurence of maxima and minima of phosphate in four Danish waters.

|  | Maxima | Minima |
| :---: | :---: | :---: |
| Gribsø | $\frac{-1 . \text { cive (February) }}{-1 . \text { to }-2 . \text { ciau (October to }} \text { November) }$ | $\mid \underline{\mid c i v e}+1$. (April) <br> \|cive $+3 .($ June ) |
| Kattehale Mose . | $\mid-1$. cive (March) <br> -1. ciau (September) <br> ciau +3 . (January) | $\begin{aligned} & \text { - 2. cive (February) } \\ & \underline{\mid c i v e}+3 .(\text { June) } \end{aligned}$ |
| Frederiksborg Slotssø | -1 . to -2 . cive (March to April) <br> ciau +1. (September) <br> ciau +3. (November) | $\frac{\underline{\mid c i v e}+1 .(\text { April }) \mid}{\underline{\mid \text { cive }+3 .(\text { June }) \mid}}$ |
| Grane Langsø | $\begin{gathered} \text { cive }+1 . \text { (April) ! } \\ \text { ciau }+4 .(\text { December }) \end{gathered}$ | - 3. cive (January) |

Gribsø and Kattehale Mose, both rich in iron, normally exhibited one of their maxima in -1 . ciau (September and October).

The phosphate minima normally occurred in cive +1 . (April) and +3 . (June). One more minimum was observed in several of the localities in question: about one month after the maximum within the period November to January the phosphatequantity declined strongly. This decrease was observed in Grane Langso (1951), Kattehale Mose (1951), Frederiksborg Slotssø (1929), and Lyngby Sø (1945-46, Sigurd Olsen loc. cit.). The reason is obscure, but may be that the submerged vegetation secures a supply as soon as phosphate is available.

## 8. The Specific Conductivity of Grane Langsø

The survey below shows that the values of specific conductivity fluctuate between 48 and 57, in most cases only between 48 and 51 reciprocal megohms. When water is freezing it liberates its ions to the water below the ice. This fact explains the values of 55 and 54 on January 18th and February 8th, 1959, respectively. In 1958 the lake was ice-covered, however, to the middle of April. The fairly low value of 48 below the ice on April 5th must in this case be due to melting of the underside of the ice.

During winter stagnation a small increase of the ion concentration in the bottom water takes place, especially during a long ice-cover. A similar increase is not observed during the summer stagnation period. On August 24th, the end of the summer stagnation of 1958 , the bottom water contained large quantities of $\mathrm{CO}_{2}$ and $\mathrm{HCO}_{3}^{-}$, larger than those at the end of winter stagnation. This increase of $\mathrm{HCO}_{3}^{-}$is evidently too small to influence the specific conductivity. The consumption of ions by Nitella in the summer months, where its growth is largest, may, however, counteract an accumula-

Table 8. Specific Conductivity of the water from Grane Langs $\varnothing$, given as $\varkappa_{20} \cdot 10^{6}$. April 5th, 1958 to March 26th, 1959.

|  | 5. IV <br> ice | 2. <br> V | 26. <br> V | 18. <br> VI | 15. <br> VII | 24. <br> VIII | 28. <br> IX | 23. <br> X | 23. <br> XI | 29. <br> XII | 18. I <br> ice | 8. II <br> ice | 26. <br> III |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $0 \mathrm{~m} \ldots$. | 48 | 48 | 48 | 49 | 51 | 51 | 49 | 49 | 50 | 50 | 55 | 54 | 49 |
| $2-\ldots$ | 51 | 48 | 48 | 49 | 51 | 51 | 49 | 49 | 50 | 50 | 50 | 50 | 49 |
| $4-\ldots$. | 51 | 48 | 48 | 49 | 51 | 51 | 49 | 49 | 50 | 50 | 50 | 50 | 49 |
| $6-\ldots$ | 51 | 48 | 48 | 48 | 51 | 51 | 49 | 49 | 50 | 50 | 50 | 50 | 49 |
| $8-\ldots$ | 51 | 48 | 48 | 48 | 50 | 51 | 49 | 49 | 50 | 50 | 50 | 50 | 49 |
| $10-\ldots$ | 53 | 48 | 48 | 48 | 49 | 51 | 49 | 49 | 50 | 50 | 52 | 51 | 49 |
| $11-\ldots$ | 57 | 48 | 48 | 48 | 49 | 51 | 49 | 49 | 50 | 50 | 53 | 52 | 49 |

tion of ions in the bottom water, originating from the exchange between water and mud. During winter stagnation the Nitella association decays greatly, and no photosynthesis has been observed of the remaining individuals. Consequently an accumulation of ions from mud and decaying Nitella material must take place in this period, causing a slight rise in the specific conductivity.

Which ions constitute this specific conductivity of about 50 reciprocal megohms? A quantitative analysis of the most important ions in the lake water was carried out in August 1950 and December 1961. I am indebted to Mr. Werner Christensen, Department Geologist to the Geological Survey of Denmark for the latter analysis.

The quanties of $\mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Ca}^{++}, \mathrm{Mg}^{++}, \mathrm{SO}_{4}^{--}, \mathrm{Cl}^{-}$, and $\mathrm{PO}_{4}^{---}$were determined according to Standard Methods (1946, p. 62, 64, 60, 61, 83, 73, and 80, respectively). $\left[\mathrm{NH}_{4}^{+}\right]$was measured colorimetrically by the Nessler reagent, $\left[\mathrm{NO}_{3}^{-}\right]$colorimetrically by diphenylamine dissolved in sulphuric acid, while $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{HCO}_{3}^{-}\right]$were calculated from the analyses of total $\mathrm{CO}_{2} \cdot 1^{-1}$. Several litres of unfiltered surface water were concentrated to one tenth by evaporation in a quartz evaporating dish in order to obtain a reasonable concentration of the seven ions first mentioned. The slight discrepancy between the equivalent content of anions and cations is due to uncertainties

Table 9. The most important ions of Grane Langso.

| Cations |  |  | Anions |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \text { August } \\ 1950 \end{gathered}$ | $\begin{gathered} \text { December } \\ 1961 \end{gathered}$ |  | $\begin{aligned} & \text { August } \\ & 1950 \end{aligned}$ | $\begin{gathered} \text { December } \\ 1961 \end{gathered}$ |
| $\mathrm{Na}^{+}$ | $6.0 \mathrm{mg} \cdot \mathrm{l}^{-1}$ | $6.3 \mathrm{mg} \cdot \mathrm{l}^{-1}$ | $\mathrm{SO}_{4}^{2-}$ | $8.3 \mathrm{mg} \cdot \mathrm{l}^{-1}$ | $5.6 \mathrm{mg} \cdot \mathrm{l}^{-1}$ |
| $\mathrm{K}^{+}$ | 0.46 - | 0.75 - | $\mathrm{Cl}^{-}$ | 10.9 - | 11.6 - |
| $\mathrm{Mg}^{2+}$ | 1.1 | 0.68 - | $\mathrm{HCO}_{3}^{-}$ | $0.2-$ | 0.2 - |
| $\mathrm{Ca}^{2+}$ | 1.84 - | 3.6 - | $\mathrm{NO}_{3}^{-}$ | 0 - | 0 - |
| $\mathrm{NH}_{4}^{+}$ | 0 - | 0 - | $\mathrm{PO}_{4}^{3-}$ | $1 \mu g \cdot l^{-1}$ | 0 - |
| $\mathrm{H}^{+}$. | $10^{-5 \cdot 5} \mathrm{~g} \cdot \mathrm{l}^{-1}$ | $10^{-5 \cdot 5} \mathrm{~g} \cdot \mathrm{l}^{-1}$ |  |  |  |

on the analytic values; further, all the ions present are not included in the investigation. Hutchinson ( 1957 , p. 554 ) thinks that the discrepancy may be due i. a. to cations being held by organic matter.

Table 10. The most important ions of Grane Langs $\varnothing$ given as milliequivalents per litre.

| Cations |  |  | Anions |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \text { August } \\ 1950 \end{gathered}$ | $\begin{gathered} \text { December } \\ 1961 \end{gathered}$ |  | $\begin{gathered} \text { August } \\ 1950 \end{gathered}$ | $\begin{gathered} \text { December } \\ 1961 \end{gathered}$ |
| $\mathrm{Na}^{+}$ | 0.261 | 0.274 | $\mathrm{SO}_{4}^{2-}$ | 0.174 | 0.117 |
| K+ | 0.012 | 0.019 | $\mathrm{Cl}^{-}$ | 0.307 | 0.327 |
| $\mathrm{Mg}^{2+}$ | 0.090 | 0.056 | $\mathrm{HCO}_{3}^{-}$ | 0.003 | 0.003 |
| $\mathrm{Ca}^{2+}$ | 0.092 | 0.180 | $\mathrm{NO}_{3}^{-}$ | 0 | 0 |
| $\mathrm{NH}_{4}^{+}$ | 0 | 0 | $\mathrm{PO}_{4}^{3-}$ | 0 | 0 |
| $\mathrm{H}^{+}$. | 0.003 | 0.003 |  |  |  |
| Total | 0.458 | 0.532 | Total | 0.484 | 0.447 |

August $1950\left\{\begin{array}{l}0.458 \text { millieq. cations } \cdot \mathrm{l}^{-1} \\ 0.484 \text { millieq. anions } \cdot \mathrm{l}^{-1}\end{array}\right\} 0.94$ millieq. ions $\mathrm{l}^{-1}$
December $1961\left\{\begin{array}{c}0.532 \text { millieq. cations } \cdot \mathrm{l}^{-1} \\ 0.447 \text { millieq. anions } \cdot \mathrm{l}^{-1}\end{array}\right\} 0.98$ millieq. ions $\mathrm{l}^{-1}$.
It is possible by a calculation to check the specific conductivity of the lake on the basis of the August analysis from 1950.

The contribution yielded by the individual ion to the specific conductivity can be computed from the equation

$$
\varkappa_{i}=\Lambda_{\mathrm{mol}}^{i} \cdot \frac{c_{i}}{1000}
$$

where $\chi_{i}$ is the contribution of the ion to the specific conductivity, $\Lambda_{\text {mol }}^{i}$ is the molar conductance of the ion, and $c_{i}$ the molar concentration of this ion. If the equivalent conductance is employed, defined by

$$
\Lambda_{\mathrm{eq}}^{i}=\frac{1}{z_{i}} \cdot \Lambda_{\mathrm{mol}}^{i}
$$

where $z_{i}$ is the number of positive or negative charges of the ion, the question above gets the form

$$
\varkappa_{i}=\Lambda_{\mathrm{eq}}^{i} \cdot z_{i} \cdot \frac{c_{i}}{1000}=\Lambda_{\mathrm{eq}}^{i} \cdot \frac{n_{i}}{1000}
$$

where $n_{i}$ is the "normality" of the ion in question.

Table 11. Calculation of the specific conductivity of Grane Langs $\varnothing$ on August 1950.


The equivalent conductance values of the ions referred to are cited from K. A. Jensen (1959, p. 682). The specific conductivity of Grane Langs $\varnothing$ has thus been calculated to 62.6 reciprocal megohms by a temperature of $25^{\circ} \mathrm{C}$.

As the conductivity decreases by about 2 per cent for each degree by which the temperature falls, it amounts to about $56.7 \cdot 10^{-6}$ at $20^{\circ} \mathrm{C}$, a value in reasonably good agreement with those commonly measured by means of the Dionic Water Tester. A corresponding calculation, based on the December analysis from 1961, yielded the result $\kappa_{20}=$ about 58 reciprocal megohms.

As to the diagrams of Fig. 7, I can inform the reader that the ionic diagram representing seawater has been constructed on the basis of Tabelle 14 in Maucha's work of 1932 (p.86). According to this table the $\mathrm{HCO}_{3}^{-}$amounts to 0.41 per cent of the total anion quantity in the Adriatic, no $\mathrm{CO}_{3}^{--}$, however, being stated. Seawater normally contains about $45 \mathrm{ml} \cdot \mathrm{l}^{-1}$ of total $\mathrm{CO}_{2}$. Provided that the salinity is 3.5 per cent, the temperature $15^{\circ} \mathrm{C}$, and pH 8.2 , the ratio of $\mathrm{HCO}_{3}^{-}$to $\mathrm{CO}_{3}^{--}$is 85 to 15 . Of the 45 ml total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}, 0,3 \mathrm{ml}$ is present as 0.6 mg free $\mathrm{CO}_{2}+\mathrm{CO}_{2} \mathrm{aq}$, while 38 ml are confined to 103.5 mg HCO mann Nielsen (1944, p. 11). Maucha's figure may represent the total $\mathrm{CO}_{2}$ converted to $\mathrm{HCO}_{3}^{-}$.

The analyses of the most important ions demonstrate Grane Langso to be a sodium chloride lake, contrary to most of the Danish lakes, which can be characterized as
calcium hydrogen-carbonate lakes (Rodhe 1949, p. 378). The ionic diagrams of Grane Langsø (see Fig. 7) exhibit a striking resemblance to that of seawater, the equivalent percentages of $\mathrm{K}^{+}, \mathrm{Na}^{+}, \mathrm{Mg}^{2+}, \mathrm{Cl}^{-}, \mathrm{HCO}_{3}^{-}$and $\mathrm{CO}_{3}^{2-}$ being of the same order of size. In two respects there are marked differences, however, the equivalent percentages of $\mathrm{SO}_{4}^{--}$and especially $\mathrm{Ca}^{++}$in Grane Langsø are far greater than the corresponding ones of seawater.

All the surface water and ground water of the continents have once been rainwater. The aqueous vapours, which become condensed to precipitation, are contained in winds from the oceans and the continents. The evaporation of the oceans is greater than the precipitation over them. In exorheic regions, however, the evaporation is smaller than the precipitation, the surplus of the latter being converted to rivers. As about 70 per cent of the earth surface is covered by the seas, the greatest part of the global precipitation is of oceanic origin.

Besides the aqueous vapours the maritime winds also carry minute, hygroscopic particles of sea salt, called condensation nuclei, over the continents. Breaking waves produce great quantities of air-bubbles in the sea-surface; when these bubbles burst, minute droplets are emitted into the air. Raindrops and snowflakes striking the ocean surface produce very small air-bubbles, which burst and give off extremely small particles. After arriving in the atmosphere the diameter of these particles are reduced by evaporation; the speed of falling is accordingly decreasing.

The Swedish investigator Erik Eriksson, who has made a close study of the subject in question, estimates the airborne salts to be produced over the oceans with a rate of about 1080 mill. tons per years (1959, p. 397). As about 180 mill. tons per year of airborne salts return to the oceans by rivers (Eriksson 1960, p. 72, table 4.5) and an unknown quantity by the ground water, at most 80 per cent of the 1080 mill. tons of airborne salts fall out over the oceans themselves.

The sea salt particles are removed from the atmosphere by three processes: deposition by dry fallout, wash-out by rain, and their capture by the vegetation.

Eriksson (1959, p. 397) estimates the sinking velocity of the airborne salts to be about 1 cm per second over the seas, and about 2 cm per second over land.

Small obstacles, as e.g. grass-leaves and spruce needles, have proved effective in the capture of condensation nuclei from moving air (Eriksson 1955, p. 245). The effectiveness of this capture increases with increasing wind velocity and decreasing radius of the obstacle. The accretion of the hygroscopic airborne salts, which are said to be washed down by rain (see p. 15 , however), may be a selective process. Eriksson is of the opinion that only giant condensation nuclei, of radii greater than $1 \mu$, are large enough to be captured by pine and spruce needles. These nuclei are mostly NaCl -particles. He admits, however, that ions other than $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$are captured by coniferous forests, citing in support Tamм's investigations (1953, p. 88-90). This author found much more $\mathrm{Ca}^{++}$and $\mathrm{K}^{+}$, and up to 3 times more $\mathrm{Na}^{+}$, in rain water percolating through the outer part of a spruce tree crown than in rain water simultaneously collected in the open. This obvious difference was observed merely at the onset of

the rainy spell; later on it disappeared. The remarkable result was obtained after a period of dry weather.

Comparing the ion diagrams of Grane Langsø with those of the Borris and Ødum rainwater on Fig. 7, it is evident that the $\mathrm{SO}_{4}^{--}$mval-percentages of rainwater surpass those of the lake. The chloride percentages are, however, smaller than those found in Grane Langsø. The diagram of the airborne salts from Ødum is markedly dominated by $\mathrm{SO}_{4}^{--}$.

If the Borris rain and Ødum rain is supplied with $\mathrm{Cl}^{-}$, their mval-percentages of $\mathrm{Cl}^{-}$of course will rise, and the $\mathrm{SO}_{4}^{--}$-percentages consequently decrease. According to Eriksson (1955, p. 246) the vegetation capture of condensation nuclei is a selective progress, by which essentially NaCl -particles are captured. On condition that especially the airborne chlorides are captured by the coniferous forests, and that a great part of this accretion is washed out into the lake by rain, we have an explanation of the fact, that the chloride percentage of Grane Langsø is greater than that of the rain, and its $\mathrm{SO}_{4}^{--}$-percentage in consequence is smaller than the corresponding one of rainwater.

How much are the individual ion concentrations increased owing to the concentrating effect of the evaporation and the addition of airborne salts and soil substances? In order to get some understanding of this problem, the ion concentrations of two of the British lakes examined by Gorham (1957, p. 174) are placed in Table 12, together with the ion concentrations of Grane Langs $\varnothing$ and the rainwater over these three lakes. Further, the ratios of the individual cations and anions of the lake water to the corresponding ions of the rainwater are given in Table 13.

In Newton Mere an abundant growth of the green alga Gloeococcus Schroeteri takes place as in Grane Langsø, whereas Crose Mere, which is mentioned merely as an example of the hydrogen-carbonate type, is characterized by dense water blooms of bluegreen algae.

Table 12. Important ions of three lakes and the rain over them, stated as mval $\cdot \mathrm{l}^{-1}$.

|  | $\mathrm{K}^{+}$ | $\mathrm{Na}^{+}$ | $\mathrm{Ca}^{2+}$ | $\mathrm{Mg}^{2+}$ | $\mathrm{SO}_{4}^{2-}$ | $\mathrm{Cl}^{-}$ | $\mathrm{HCO}_{3}^{-}$ | $\begin{gathered} \text { mval- } \\ \text { sum } \end{gathered}$ | pH | $\left\lvert\, \begin{gathered} \varkappa_{20} \cdot 10^{6} \\ \text { (com- } \\ \text { puted) } \end{gathered}\right.$ | $\frac{\mathrm{Ca}}{\mathrm{Mg}}$ | $\frac{\mathrm{K}+\mathrm{Na}}{\mathrm{Ca}+\mathrm{Mg}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Lake District rain. | 0.005 | 0.083 | 0.015 | 0.016 | 0.066 | 0.092 | 0 | 0.309 | 4.5 | 27 | 0.94 | 2.84 |
| Newton Mere | 0.205 | 0.360 | 0.365 | 0.130 | 0.325 | 0.440 | 0.275 | 2.100 | 6.8 | 121 | 2.81 | 1.14 |
| Crose Mere | 0.145 | 0.490 | 3.400 | 0.700 | 1.060 | 0.580 | 3.040 | 9.465 | 8.1 | 488 | 4.86 | 0.15 |
| Borris rain <br> (3 years)... . | 0.013 | 0.146 | 0.046 | 0.044 | 0.128 | 0.169 | 0.0001 | 0.646 | 4.6 | 46 | 1.04 | 1.78 |
| Ødum rain (6 years)... | 0.010 | 0.092 | 0.047 | 0.032 | 0.109 | 0.099 | 0.0019 | 0.480 | 4.82 | 33 | 1.44 | 1.29 |
| Grane Langsø (August and | 0.012 | 0.261 | 0.092 | 0.090 | 0.174 | 0.307 | 0.003 | 0.94 | 5.5 | 57 | 1.02 | 1.24 |
| December . . | 0.019 | 0.274 | 0.180 | 0.056 | 0.117 | 0.327 | 0.003 | 0.98 | 5.5 | 58 | 3.21 | 1.50 |

Table 13. The proportions between the ion concentrations, given as mval $\cdot \mathrm{l}^{-1}$, of the 3 lakes and their corresponding precipitation.

|  | K ${ }^{+}$ | $\mathrm{Na}^{+}$ | $\mathrm{Ca}^{2+}$ | $\mathrm{Mg}^{2+}$ | $\mathrm{SO}_{4}^{2-}$ | $\mathrm{Cl}^{-}$ | $\mathrm{HCO}_{3}^{-}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Newton Mere |  |  |  |  |  |  |  |
| Lake District rain | 41 | 4.3 | 24.4 | 8.1 | 4.9 | 4.8 | $\infty$ |
| Crose Mere |  |  |  |  |  |  |  |
| Lake District rain | 29 | 5.9 | 226.7 | 43.8 | 16.1 | 6.3 | $\infty$ |
| Grane Langso (average) |  |  |  |  |  |  |  |
| Borris rain | 1.2 | 1.8 | 3.0 | 1.7 | 1.1 | 1.9 | 30 |
| Grane Langso (average) |  |  |  |  |  |  |  |
| Ødum rain | 1.6 | 2.9 | 2.9 | 2.3 | 1.3 | 3.2 | 1.7 |

The specific conductivity values, computed for the British localities, do not include the $\mathrm{NH}_{4}^{+}$and $\mathrm{NO}_{3}^{-}$ions; therefore the value of 27 reciprocal megohms is nearly at a lower limit of the true value for the Lake District rain.

It is evident from Table 13 that Grane Langsø is far less changed than is Newton Mere, in comparison with the rain over them. The ion concentrations of the latter (apart from $\mathrm{HCO}_{3}^{-}$) are 4.3-41 times as much as those of the Lake District rain, while the ion concentrations of Grane Langsø are only 1.1-3.2 times increased in relation to the corresponding concentrations of the Borris rain and Ødum rain. The ratio of lake- $\mathrm{HCO}_{3}^{-}$to rain- $\mathrm{HCO}_{3}^{-}$is also much greater for Newton Mere than for Grane Langs $\sigma$.

The specific conductivity of Newton Mere is 4.5 times as great as that of the Lake District rain, whereas the specific conductivity of Grane Langsø is only increased by the factor $1.25-1.75$ in relation to the specific conductivity of the Borris and Ødum rain (see Table 12). The ratio of the alkali metals to the alkaline earths can be influenced by adsoption and ion exchange of the various colloids confined to the bottom sediments. This ratio alters greatly from the Lake District rain to Newton Mere; the values of Grane Langsø and the rain water over Borris and Ødum are, however, of the same order of size.

Table 14 should demonstrate the percentages by which the individual constituents of Grane Langsø have been increased in proportion to the corresponding elements of the Borris and Ødum rain, due to evaporation and addition of airborne salts, atmospheric dust, and soil substances.

It is obvious that the concentrations of $\mathrm{K}^{+}$and especially $\mathrm{SO}_{4}^{2-}$ are slightly changed, while those of $\mathrm{Na}^{+}, \mathrm{Cl}^{-}, \mathrm{Mg}^{2+}, \mathrm{Ca}^{2+}$ are increased with a factor of about $2-3$. These facts prove that the rise in the concentration is not merely a result of evaporation of the rain water in question. Several factors interfere in this evaporation process, e.g.
(1) selection of ions in the rain water by the individual plant communities around the lake,

Table 14. The increase of ion concentrations from the Borris and Odum rain considered as a transformation to Grane Langsø water.

(2) weathering processes of e.g. $\mathrm{FeS}_{2}$ and $\mathrm{KAlSi}_{3} \mathrm{O}_{8}$ in the soil,
(3) influence of the sulphur bacteria and the sulphate-reducing bacteria on the $\mathrm{SO}_{4}^{2-}$ concentration,
(4) fixation of cations to colloidal clay minerals in about 18 m subsurface depth, by which the affinity is decreasing in the order $\mathrm{H}^{+}, \mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}, \mathrm{K}^{+}, \mathrm{NH}_{4}^{+}$,
(5) ion exchange by means of e.g. humic acids in the soil,
(6) ion adsorption to the neutral humus of the lake sediments,
(7) selective vegetation capture by impingement of airborne sea salt particles,
(8) fallout of atmospheric calcareous dust.

The importance of each individual factor is unknown, but Grane Langsø represents the final result of the combined effect of the evaporation of rain water and the factor complex mentioned, in which (7) and (8) are believed to be more important than the other factors.

In order to compare the ionic composition of Grane Langsø with that of softwater lakes other than Newton Mere, the individual quantities have been stated as mval $\%$ in Table 15 . The figures from the Wisconsin lakes are cited from HutchinSon (1957, p. 555 ), and those from the North German lakes originate from Ohle (1955, p. 243).

Grane Langsø has much in common with the North German lakes, i.a. the high percentages of $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$. This seems quite natural, as both are lying close to the margin of the Würm (Wisconsin) glaciation. The Wisconsin soft-water lakes are hydro-gen-carbonate lakes with high figures for $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$. Grane Langsø is probably better characterized, however, by the unusually small quantities of $\mathrm{HCO}_{3}^{-}$and free $\mathrm{CO}_{2}$ than by the great percentage quantities of $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$, because free $\mathrm{CO}_{2}$ and $\mathrm{HCO}_{3}^{-}$highly determine the production of the lake, while $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$are merely micronutrients.

In this connection the question may be put: is the deficiency of $\mathrm{CO}_{2}$ and $\mathrm{HCO}_{3}^{-}$ in Grane Langsø a result of the $\mathrm{CO}_{2}$-consumption by the rich and evergreen submerged vegetation and the phytoplankton, or is it a primary character of the lake? As shown

Table 15. The mval-percentages of the major constituents in some soft water lakes.

|  | Na | $\mathrm{K}+$ | $\mathrm{Mg}^{2+}$ | $\mathrm{Ca}^{2+}$ | $\mathrm{SO}_{4}^{2-}$ | $\mathrm{Cl}^{-}$ | $\mathrm{HCO}_{3}^{-2}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Wisconsin soft water lakes... | 10.9 | 4.8 | 37.7 | 46.9 | 20.5 | 9.9 | 69.6 |
| North German soft water lakes | 43 | 6.7 | 14.3 | 36 | 14.1 | 43.5 | 42.4 |
| Grane Langsø (August 1950 | 57.2 | 2.6 | 19.8 | 20.2 | 36.0 | 63.4 | 0.6 |
| $\quad$ and December 1961) ..... | 51.8 | 3.6 | 10.6 | 34.0 | 26.2 | 73.1 | 0.7 |

in section 11 the concentration of free $\mathrm{CO}_{2}$ during the periods of high productivity is so low (smaller than $0.6 \mathrm{mg} \cdot \mathrm{l}^{-1}$ at $20^{\circ} \mathrm{C}$ ), that atmospheric $\mathrm{CO}_{2}$ diffuses into the lake ; at the same time the $\mathrm{HCO}_{3}^{-}$concentration is quite insignificant. In winter, however, when the $\mathrm{CO}_{2}$ consumption of the phytoplankton and the hydrophytes approaches nil, Grane Langsø must also be characterized as a lake poor in $\mathrm{CO}_{2}$ and $\mathrm{HCO}_{3}^{-}$(see Survey of the Analyses). The deficiency of $\mathrm{CO}_{2}$ and $\mathrm{HCO}_{3}^{-}$consequently cannot be explained as a result of photosynthetic processes.

The ground water inflow contains more $\mathrm{CO}_{2}$ than the rain water, the $\mathrm{CO}_{2}$ content of ground air being about $0.3-1$ per cent (Werner Christensen 1962, p. 113). Mr. Hans Mathiesen, who kindly determined the $\mathrm{Cl}^{-}$quantity of the Højvang ground water (see p. 14), also determined its alkalinity as 0.4 mval $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$, and its pH as 6.62. This alkalinity corresponds to $24.4 \mathrm{mg} \mathrm{HCO}-\mathrm{H}^{-1} \cdot \mathrm{l}^{-1}$. By means of equation (4) on p. 44 the $\mathrm{a}_{\mathrm{CO}_{2}}$ at $10^{\circ} \mathrm{C}$ has been computed as 0.28 . On condition that the ionic strenght is very small, the total $\mathrm{CO}_{2}$ quantity of the Højvang ground water therefore amounts to 12.3 mg free $\mathrm{CO}_{2} \cdot 1^{-1}+17.6 \mathrm{mg}$ hydrogen-carbonate $-\mathrm{CO}_{2} \cdot 1^{-1}=$ about $29.9 \mathrm{mg} \cdot \mathrm{l}^{-1}$, thus greatly surpassing the largest quantity, 14.89 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$, ever measured in the lake. The sub-lacustrine influx of ground water is an unknown quantity, as stated on p. 16, but considering i.a. the deficiency of $\mathrm{CO}_{2}$ and $\mathrm{HCO}_{3}^{-}$ in the lake, I think that the influx rate is of secondary importance (cf. p. 14).

There are many indications that the very small quantity of $\mathrm{CO}_{2}+\mathrm{CO}_{2} \mathrm{aq}+\mathrm{HCO}_{3}^{-}$ in Grane Langsø may occasionally be a limiting factor for the production of organic matter. The lake is certainly rich in submerged vegetation (see Nyganrd 1958, Table 1 and Fig. 3), but its hydrophytes are all slowly growing species, and I think that they are obliged to be so.

The ratio Ca to Mg of the rain waters included in Table 12 varies from 0.94 to 1.44 in such a way that the lowest values seem to be confined to coastal rain, and the highest to inland rain. Hutchinson writes about this (1957, p. 550): "Both Ca and Mg increase with distance from the sea, but the calcium concentration rises more than that of magnesium." The ratio $\frac{\mathrm{Ca}}{\mathrm{Mg}}$ is lowest for Grane Langsø (average 2.11), greater for Newton Mere (2.81), and greatest, of course, for the hydrogen-carbonate lake Crose Mere.

Low values of the ratio $\frac{\mathrm{Ca}}{\mathrm{Mg}}$ can also be due to $\mathrm{Ca}^{2+}$ adsorption by colloidal
humic acids (Ohle 1955, p. 229), a discovery to be reconsidered in detail. The Ca Mg values of some North German humic lakes, poor in calcium, amounted to only $0.3-1.2$, while the values of the clear water lakes, rich in calcium, lay between 3.6 and 9.8 (Ohle 1955, Tab. 8).

The North German lake Kleiner Ukleisee normally contains

| Cations | mval $\cdot \mathrm{l}^{-1}$ | mval $10^{0} / 0$ |
| :--- | :---: | :---: |
| $\mathrm{Na} \ldots \ldots \ldots$ | 0.199 | 63.4 |
| $\mathrm{~K} \ldots \ldots \ldots$ | 0.047 | 15.0 |
| $\mathrm{Ca} \ldots \ldots \ldots$ | 0.037 | 11.7 |
| $\mathrm{Mg} \ldots \ldots .$. | 0.031 | 9.9 |

The ratio $\frac{\mathrm{mval} \mathrm{Ca}}{\mathrm{mval} \mathrm{Mg}}=1.2$, and the ratio $\frac{\mathrm{mval} \mathrm{Na}+\mathrm{K}}{\mathrm{mval} \mathrm{Ca}+\mathrm{Mg}}=3.6$. The latter value is exceptionally high, when one considers that the ratio of alkali metals to alkaline earths amounts to 1.29-2.84 for rain water, according to Table 12.

Professor W. Ohle, to whom I am indebted for this piece of information, further writes in his letter to me that a strong vernal influx of groundwater can change the ionic composition of the lake water considerably. The ratio $\frac{\mathrm{Na}+\mathrm{K}}{\mathrm{Ca}+\mathrm{Mg}}$ of the groundwater amounted to 0.69 owing to its great calcium concentration. By admixture to the lake water the analytical values of the litoral water were

| Cations | mval $\cdot{ }^{-1}$ | mval ${ }^{0} / 0$ |
| :---: | :---: | :---: |
| Na | 0.221 | 46.1 |
| K | 0.051 | 10.7 |
| Ca | 0.185 | 38.6 |
| Mg | 0.022 | 4.6 |

These results, partly stated in Ohle's paper from 1955 (Tab. 9), involve the mval-ratios $\frac{\mathrm{Ca}}{\mathrm{Mg}}=8.4$ and $\frac{\mathrm{Na}+\mathrm{K}}{\mathrm{Ca}+\mathrm{Mg}}=1.32$. When the increased inflow of groundwater to the lake Kl. Ukleisee has stopped, the ratio $\frac{\mathrm{Ca}}{\mathrm{Mg}}$ decreases to its normal value of 1.2 , and the ratio $\frac{\mathrm{Na}+\mathrm{K}}{\mathrm{Ca}+\mathrm{Mg}}$ increases to about 3.6 , both changes being the result of the $\mathrm{Ca}^{++}$adsorption by humic acids.

None of the Swedish lakes, investigated by Lohammar, can be described as a sodium chloride lake (Lohammar 1938). Högfjärden and Gärdefjärden certainly contain more $\mathrm{Na}^{+}$than $\mathrm{Ca}^{2+}$, but the $\mathrm{SO}_{4}^{2-}$ quantity is three times the chloride-quantity (Lohammar 1938, p. 161-162). Rodhe (1949, p. 378) considers these two lakes as representatives of the sulphate type.

There is a possibility, however, that some Swedish lakes examined by Quennerstedt (1955) may be characterized as sodium chloride lakes. Unfortunately Quennerstedt has not quantitatively determined the anions of his lakes, which are extremely poor in ions. The specific conductivity of Resemejaure is 3.7 reciprocal megohms, thus nearly the same as that of distilled water. The Lobelia-Isoetes lake Bergsjön (Quennerstedt 1955, p. 128), with a specific conductivity of nearly 10 reciprocal megohms, contained per litre $1.02 \mathrm{mg} \mathrm{Na}^{+}, 0.16 \mathrm{mg} \mathrm{K}^{+}, 0.38 \mathrm{mg} \mathrm{Ca}^{2+}$, and 0.32 mg $\mathrm{Mg}^{2+}$. This lake should possibly be classified as a sodium chloride lake like the Danish Lobelia-Isoetes lake Grane Langs $\sigma$.

Ohle's paper, cited above, on the ion exchange of the bottom sediments of two lakes in North Germany, is instructive and of considerable importance. The acid "Laubdy" of Kleiner Ukleisee ( pH of the lake water 5.85) contains great quantities of humic acids. Besides being able to liberate $\mathrm{H}^{+}$, they possess a strong and selective capacity for exchanging $\mathrm{H}^{+}$with $\mathrm{Ca}^{++}$. Simultaneously with this $\mathrm{Ca}^{++}$adsorption an equivalent quantity of $\mathrm{HCO}_{3}^{-}$is transformed to $\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$ with the aid of $\mathrm{H}^{+}$ from the humic acids. The magnesium ions were not affected by this process, in Ohle's opinion because in Kl. Ukleisee they are confined to $\mathrm{Cl}^{-}$, perhaps to $\mathrm{SO}_{4}^{--}$. An allochthonous addition of humic acids to a lake consequently results in a decrease of $\mathrm{Ca}^{++}$. The gradual accumulation of "Laubdy" gives rise to an autochthonous deficiency in calcium (Ohle 1955, p. 240).

The specific conductivity of Kl. Ukleisee is 52 reciprocal megohms (Ohle 1959, p. 21, Tab. 5), thus nearly the same as that of Grane Langsø, but its alkalinity, 0.14 mval $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$, is much higher than the alkalinity values of Grane Langsø, 0.002 0.01 .

Decaying leaves play no part in the bottom sediments of Grane Langso, which show an ignition loss of only about 10 per cent. According to Kaj Hansen (1959, p. 40-41) the humus of these sediments is neutral; the calcium content is low, 0.6 0.8 per cent. It would appear that the fixation of $\mathrm{Ca}^{++}$is of minor importance in Grane Langsø itself, but may be significant in the soil of the coniferous plantations and moorland areas around the lake. It is, however, for many reasons impossible to elucidate this influence at present, i. a. because the sublacustrine influent to the lake is an unknown quantity.

The adsorption of $\mathrm{Ca}^{++}$to acid humic compounds is important, however, for the understanding of the changes which took place in the Danish lake Gribso during the postglacial period. The qualitative composition of the diatom flora in the Atlantic Period is indicative of an alkaline reaction of the lake water; the finding of leaf-apices of the rapidly growing hydrophyte Ceratophyllum demersum supports this assumption (Nygatrd in Berg and Clemens Petersen 1956, p. 51). Therefore lake Gribso must have been rich in $\mathrm{HCO}_{3}^{-}$in this period, and no doubt an equivalent quantity of $\mathrm{Ca}^{++}$ was bound up with the $\mathrm{HCO}_{3}^{-}$.

During the first 8 centuries of the Subatlantic Period, which began about 400 B. C., the lake grew more and more acid judging from the pronounced qualitative
alterations of the diatom flora. The presumed deficiency of $\mathrm{Ca}^{++}$in the Sub-atlantic Period was explained by me as a result of a gradual washing-out and an increasing supply of acid humic substances from the raw humus in the forest floor. The investigation by pollen analysis of the core from Gribsø demonstrated that the woods surrounding the lake grew richer in beech at the expense of oak efter $400 \mathrm{~B} . \mathrm{C}$.

It is common knowledge that illumination at the beech forest floor is very small, whereas the mixed forests of oak together with other light-demanding trees as e.g. elm and especially ash, give more illumination. The layer of living leaves must consequently be much more compact in the beech forest than in the mixed forest with oak as the characteristic tree. In my opinion, the number of leaves per unit area is increasing as the beech gradually replaces the oak in the mixed forests.

In his brilliant studies on the relation of forest trees to light, Boysen Jensen (1910, p. 21-25) has pointed out that on an average the transmission of light in a beech wood is only 1.8 per cent of the global radiation, whereas an oak wood lets 11 per cent pass through its photosynthetic device. Boysen Jensen writes, in translation (1910, p. 25): "The light quantity absorbed by the tree-top is mainly determined by the quantity of leaves....this quantity being conditioned by their capacity for sustaining shade". The faculty for creating shade-leaves is especially well-developed by the beech.

A woodland lake as Gribsø has, all things considered, probably received a rising quantity of beech leaves when the surrounding forests were increasingly influenced by the beech during the centuries after 400 B . C. The dead leaves on the beech forest floor are presumably more easily carried out in the lake by winds than leaves on the oak forest floor, where the well-developed undergrowth will strongly prevent it (cf. Berg and Clemens Petersen 1956, p. 13 ; Figs. 1 and 5).

The intensified formation of "Laubdy" in lake Gribsø contributed in depressing the concentrations of $\mathrm{Ca}^{++}$and $\mathrm{HCO}_{3}^{-}$, thus opening the lake for immigration of Sphagnum.

One cannot exclude the possibility, however, that the humification of dead beech leaves involves chemical processes which differ essentially from the corresponding processes confined to the humification of leaves from mixed woods.

The decomposition of cellulose in leaves of beech and oak no doubt takes place according to identical chemical patterns. However, the considerable quantities of tannic acid present in oak leaves, as in leaves of heath plants, probably influence the course of the decomposition.

After defoliation the tannic acid and protein combine to form compounds containing nitrogen which is hardly accessible for the soil-microbes. Consequently the bacterial action is highly retarded, and so the formation of raw humus becomes a very slow process. The disintegration of a thick and compact layer of dead beech leaves must, however, also be a very slow process. Whether the decomposition of the leaves of oak and beech takes place similarly in a lake is an open question.

Several Danish woodland lakes situated on sandy morainic deposits have probably
been rich in calcium hydrogen-carbonate at the beginning of the post-glacial period, as the moraine at that time still contained some $\mathrm{CaCO}_{3}$. No doubt the fall of temperature early in the Subatlantic Period intensified the formation of raw humus at the expense of mull formation. The high precipitation, together with atmospheric $\mathrm{CO}_{2}$ and ground air $\mathrm{CO}_{2}$, simultaneously increased the washing-out of lime from the upper layers of the soil, thus preparing the ground for the formation of raised bogs. The concentration of calcium hydrogen-carbonate in the woodland lakes was strongly diminished, partly by washing-out owing to the great precipitation, but especially by ion exchange due to inflow of humic acids from Sphagnum bogs near the lakes, and to the increasing quantity of beech leaves in the lakes as the beech spread in the surrounding forests.

## 9. The Calculation of pH and the $\mathrm{HCO}_{3}^{-}$-quantities

As will be seen from sections 12 and $13, \mathrm{pH}$ and $\left[\mathrm{HCO}_{3}^{-}\right]$have been calculated from the concentrations of total carbon dioxide in Grane Langs $\varnothing$. Referring to Hutchinson's treatment of the chemical equilibria confined to the carbon dioxide system (1957, pp. 655-657), I give the equation which forms the basis of the calculations:

$$
\begin{equation*}
\frac{\mathrm{a}_{\mathrm{H}^{+}} \cdot \mathrm{a}_{\mathrm{HCO}_{\mathrm{s}}^{-}}}{\mathrm{a}_{\mathrm{CO}_{2}}}=\mathrm{K}_{\mathrm{CO}_{2} \mathrm{aq}} \tag{4}
\end{equation*}
$$

(in the following abbreviated to $\mathrm{K}_{\mathrm{CO}_{2}}$ ), where $\mathrm{K}_{\mathrm{CO}_{2}}$ is the product of the hydration constant of carbon dioxide and the first ionization constant of "carbonic acid", and $\mathrm{a}_{\mathrm{CO}_{2}}$ is put equal to the activities of $\mathrm{CO}_{2}$ and $\mathrm{CO}_{2}$ aq. As only about 0.3 per cent of the dissolved $\mathrm{CO}_{2}$ is present as " $\mathrm{H}_{2} \mathrm{CO}_{3}{ }^{\prime}{ }^{1}$ or rather $\mathrm{CO}_{2}$ aq, the error in setting $\mathrm{a}_{\mathrm{CO}_{3}}=$ $\mathrm{a}_{\mathrm{CO}_{2}+\mathrm{CO}_{2} \mathrm{aq}}$ at most amounts to about three thousanths within the temperatire interval $0^{\circ}$ to $25^{\circ} \mathrm{C}$. The standard deviation on total $\mathrm{CO}_{2}$ values around $1 \mathrm{mg} \cdot \mathrm{l}^{-1}$ amounts to about 7 per cent (cf. p. 21); on values of $10 \mathrm{mg} \cdot \mathrm{l}^{-1}$, very rarely met with in Grane Langsø, it is 0.7 per cent, twice the error in setting $\mathrm{a}_{\mathrm{CO}_{2}}=\mathrm{a}_{\mathrm{CO}_{2}+\mathrm{CO}_{2} \text { aq }}$.

Concerning the $\mathrm{K}_{\mathrm{CO}_{2}}$-values the reader is referred to the papers of Faurholt (1924, p. 55), Kurt Buch et al. (1932, p. 35), Shedlowsky and Mc. Innes (1935, p. 1710), Harned and Davis (1943), Harned and Bonner (1945, p. 1028), and Näsünen (1947, p. 208). Table 16 contains the $\mathrm{pK}_{\mathrm{CO}_{2}}$-values within the temperature interval commonly met with in lakes. The calculations in the present paper are based on the averages of the figures in the last three columns of the table.

Shedlowsky and Mc. Innes have given a graph which shows the interrelation of $\mathrm{pK}_{\mathrm{CO}_{2}}$ and the temperature (1935, p. 1709). This graph is modified in Fig. 8 in

1 In this connection I think it is better to talk about the dissociation constants of carbon dioxide water and the hydrogen carbonate ion in preference to the terms first and second dissociation constant of carbonic acid, as $\mathrm{H}_{2} \mathrm{CO}_{3}$ is probably a paper compound.


Fig. 8. $\mathrm{pK}_{\mathrm{CO}_{2}}$ values at various temperatures. The small circles close to Harned and Davis' graph represent NÄsÄnen's values.
such a manner, that $\frac{1000}{T}$ in the abscissa is replaced by $t$, making it possible to read off $\mathrm{pK}_{\mathrm{CO}_{2}}$ at any temperature between $0^{\circ}$ and $25^{\circ} \mathrm{C}$.

The problem whether the activities may be replaced by the concentrations can only be solved through a computation of the activity coefficient of $\mathrm{HCO}_{3}^{-}$. The activity coefficient of $\mathrm{CO}_{2}$ is put equal to 1 , because $\mathrm{CO}_{2}$ is a non-electrolyte.

The calculation of the activity coefficient can be based on the August analysis from 1950 of the most important ions of Grane Langsø. The following equation applies to the individual ion

$$
a_{i}=f_{i} \cdot c_{i}
$$

Table 16. Values of $\mathrm{pK}_{\mathrm{CO}_{3}}=-\log \mathrm{K}_{\mathrm{CO}_{2}}$ at $\mu=\mathrm{O}$.

|  | Shedlovsky and Mc. Innes, 1935 | Harned and Davis, 1943 | Harned and Bonner, 1945 | $\begin{gathered} \text { NÄSÄnen } \\ 1947 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| $0^{\circ} \mathrm{C}$. | 6.583 | 6.579 | 6.577 | 6.572 |
| $5^{\circ} \mathrm{C}$ |  | 6.517 | 6.517 | 6.514 |
| $10^{\circ} \mathrm{C}$. |  | 6.464 | 6.465 |  |
| $15^{\circ} \mathrm{C}$. | 6.429 | 6.419 | 6.420 | 6.421 |
| $20^{\circ} \mathrm{C}$. |  | 6.381 | 6.382 |  |
| $25^{\circ} \mathrm{C}$. | 6.366 | 6.352 | 6.351 | 6.349 |

Table 17.

| $i$ | $c_{i}$ | $z_{i}^{2}$ | $c_{i} \cdot z_{i}^{2}$ |
| :---: | :---: | :---: | :---: |
| $0.003 \mathrm{mg} \mathrm{H}+/ 1$. | $3 \cdot 10^{-6}$ | 1 | $3 \cdot 10^{-6}$ |
| $1.84 \mathrm{mg} \mathrm{Ca}^{+2} / \mathrm{l}$ | $46 \cdot 10^{-6}$ | 4 | $184 \cdot 10^{-6}$ |
| $1.1 \mathrm{mg} \mathrm{Mg}^{+2} / 1$. | $45 \cdot 10^{-6}$ | 4 | $180 \cdot 10^{-6}$ |
| $6 \mathrm{mg} \mathrm{Na}{ }^{+} / 1$ | $261 \cdot 10^{-6}$ | 1 | $261 \cdot 10^{-6}$ |
| $0.46 \mathrm{mg} \mathrm{K}+/ 1$ | $12 \cdot 10^{-6}$ | 1 | $12 \cdot 10^{-6}$ |
| $10.9 \mathrm{mg} \mathrm{Cl}{ }^{-} / 1$ | $307 \cdot 10^{-6}$ | 1 | $307 \cdot 10^{-6}$ |
| $8.3 \mathrm{mg} \mathrm{SO}_{4}^{-2} / \mathrm{l}$ | $87 \cdot 10^{-6}$ | 4 | $348 \cdot 10^{-6}$ |
| $0.2 \mathrm{mg} \mathrm{HCO}-1$. | $3 \cdot 10^{-6}$ | 1 | $3 \cdot 10^{-6}$ |

where $a_{i}$ is the ionic activity, $f_{i}$ is the activity coefficient, and $c_{i}$ the molar concentration of the ion. By infinite dilution the limit of $f_{i}$ is $1 ; a_{i}$ is then equal to $c_{i}$. This means that if the activity coefficient according to calculations lies only slightly below 1, the activity of the ion in question can be replaced by the concentration.

The ionic strength $\mu$ can be computed from the equation

$$
\mu=\frac{1}{2} \sum c_{i} \cdot z_{i}^{2}
$$

where $z_{i}$ is the charge of the ion considered (c.f. Table 17).
The ionic strenght $\mu$ is then

$$
\mu=\frac{1}{2} \sum c_{i} \cdot z_{i}^{2}=650 \cdot 10^{-6}=0.00065
$$

According to Debye - Hückel's limiting law the activity coefficient is characterized by

$$
-\log f_{i}=\frac{1}{2} \cdot z_{i}^{2} \cdot \sqrt{\mu}
$$

As the $\mathrm{HCO}_{3}^{-}$has the charge 1, we obtain

$$
-\log f_{\mathrm{HCO}_{3}^{-}}=\frac{1}{2} \sqrt{0.00065}=0.01275 ; f_{\mathrm{HCO}_{3}^{-}}=0.97
$$

Computing $\left[\mathrm{HCO}_{3}^{-}\right]$as $\mathrm{mg} \cdot \mathrm{l}^{-1} \mathrm{a}_{\mathrm{HCO}_{3}^{-}}$is replaced by $\mathrm{c}_{\mathrm{HCO}_{3}^{-}}$. The systematic error thus introduced is concequently about 3 per cent. As the electrometrical pHmeasurements rather give $\mathrm{a}_{\mathrm{H}}{ }^{+}$than $\mathrm{c}_{\mathrm{H}}{ }^{+}$, and as the activity coefficient of $\mathrm{CO}_{2}$ is equal to 1 , the equation valied for Grane Langsø gets the following form

$$
\frac{10^{-\mathrm{paH}} \cdot \mathrm{c}_{\mathrm{HCO}_{3}^{-}} \cdot 0.97}{\mathrm{c}_{\mathrm{CO}_{2}+\mathrm{CO}_{2} \mathrm{aq}}}=K_{\mathrm{CO}_{2}}
$$

The uncertainty (standard deviation) on the pH -calculations in Grane Langsø probably amounts to $\pm 0.1$, that is $\pm 26$ per cent on $\mathrm{c}_{\mathrm{H}^{+}}\left(10^{0.1}=1.26\right)$. The standard
deviation on the total $\mathrm{CO}_{2}$ values commonly met with in Grane Langs $\varnothing$, viz. about $1 \mathrm{mg} \cdot \mathrm{l}^{-1}$, is about $\pm 7$ per cent. Assuming that the uncertainties on $\mathrm{c}_{\mathrm{CO}_{2}+\mathrm{CO}_{2} \mathrm{aq}}$ and $\mathrm{c}_{\text {total } \mathrm{CO}_{2}}$ are of the same order of magnitude, the uncertainty on the quantity of $\mathrm{HCO}_{3}^{-}$. $1^{-1}$ approaches 35 per cent. This estimate implies a content of about 1 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$.

The above mentioned analysis from August 1950 was performed on surface water. In the bottom water the $\mathrm{CO}_{2}$ concentration rises to at most 0.000338 at the end of the summer stagnation. The resulting increase of the $\mathrm{HCO}_{3}^{-}$concentration is, however, not accompanied by any appreciable increase of the ionic strenght, since no measurements of the specific conductivity have surpassed the value 57 (see p. 32). This means that the ionic strength of all the water levels examined must lie near to 0.00065 in all seasons, and consequently the activity coefficient of $\mathrm{HCO}_{3}^{-}$comes near to 0.97 for the bottom water also.

## 10. The Carbon Dioxide

Fig. 9 indicates that Grane Langsø is a lake poor in $\mathrm{CO}_{2}$, as 86 per cent of the total number (477) of $\mathrm{CO}_{2}$ analyses lay between 0.27 and 1.74 mg total $\mathrm{CO}_{2} \cdot l^{-1}$. These figures correspond to molar concentrations between $6 \cdot 10^{-6}$ and $4 \cdot 10^{-5}$. The highest value ever measured amounted to 14.89 mg total $\mathrm{CO}_{2} \cdot \mathrm{I}^{-1}$ or the concentration 0.000338 . The yearly fluctuations of the $\mathrm{CO}_{2}$-quantities measured during three years are outlined in Table 18.

Table 18. The yearly fluctuations of the quantities of total $\mathrm{CO}_{2}$, as $\mathrm{mg} \cdot \mathrm{l}^{-1}$, in Grane Langsø.

| Period | Yearly extremes of $\mathrm{CO}_{2}$ | Fluctuation |
| :---: | :---: | :---: |
| March 1958 <br> - July 1958 | 0.71 (July 2nd, 6 m depth) 9.88 (April 5th, 11 m depth) | 9.17 |
| $\begin{aligned} & \text { August } 1958 . \\ & - \text { July } 1959 . \end{aligned}$ | 0.27 (July 21st, 6 m depth) 11.37 (February 8 th, 11 m depth) | 11.10 |
| $\begin{aligned} & \text { August } 1959 . \\ & \text { - July } 1960 \end{aligned}$ | 0.36 (July 27th, 4 m depth) <br> 13.07 (August 23rd, 11 m depth) | 12.71 |
| $\begin{aligned} & \text { August } 1960 . \\ & \text { - July } 1961 . \end{aligned}$ | 0.50 (June 15 th, $0-2 \mathrm{~m}$ depth) <br> 14.89 (August 28th, 11 m depth) | 14.39 |

Apart from the rather short period March-July 1958, the difference between the lowest and highest value of the year fluctuates between 11.10 and 14.39 mg total $\mathrm{CO}_{2} \cdot l^{-1}$, on an average 12.7 mg .

The difference between the extremes of the individual depth series can rise to at most $14.03 \mathrm{mg} \cdot \mathrm{l}^{-1}$ total $\mathrm{CO}_{2}$. A difference of this order has only been observed in late August, but considerable differences also occur in February, as shown in Table 19.


Fig. 9. The distribution of the values of total carbon dioxide in Grane Langs $\varnothing$. Note the logarithmic scale of the abscissa.

At the dates mentioned the 11 m layer always exhibited the largest $\mathrm{CO}_{2}$-values, and in nearly all other cases this also held true.

In the circulation periods the greatest differences within each vertical $\mathrm{CO}_{2}$-series on an average amounts to $0.09 \mathrm{mg} \cdot \mathrm{l}^{-1}$, a quantity of the same order of magnitude as the standard deviation on a single $\mathrm{CO}_{2}$-analysis, $0.07 \mathrm{mg} \cdot \mathrm{l}^{-1}$.

A detailed study of the vertical $\mathrm{CO}_{2}$-series in Figs. $10-11$ indicates that two distribution patterns are characteristic for Grane Langsø in the summer stagnation period:

Table 19. The greatest differences between the extreme values of total $\mathrm{CO}_{2}$ as $\mathrm{mg} \cdot \mathrm{l}^{-1}$ within the individual vertical series from 4 years.

| Winter stagnation period | Greatest difference | Summer stagnation period | Greatest <br> difference |
| :---: | :---: | :---: | :---: |
| April, 5, 1958 <br> February 8, 1959, <br> January 31, 1960 <br> February 12, 1961 | $\begin{aligned} 9.88-1.45 & =8.43 \\ 11.37-1.30 & =10.07 \\ 5.17-1.35 & =3.82 \\ 6.92-1.15 & =5.77 \end{aligned}$ | August $24,1958 \ldots \ldots$ August $23,1959 \ldots$ August $28,1960 \ldots$ July $9,1961 \ldots .$. | $\begin{aligned} 11.15-1.27 & =9.88 \\ 13.07-0.82 & =12.25 \\ 14.89-0.86 & =14.03 \\ 4.14-0.64 & =3.50 \end{aligned}$ |

(i) The $\mathrm{CO}_{2}$-distribution is uniform from the surface to 8 m depth, more rarely to 6 or 10 m depth; the $\mathrm{CO}_{2}$-quantities are then increasing in the $10-11 \mathrm{~m}$ layers, eventually $8-11 \mathrm{~m}$ layers, with the $\mathrm{CO}_{2}$-maximum always being placed in the 11 m layer. Examples: August 1, 1958 and August 23, 1959 (cf. Fig. 10).
(ii) The $\mathrm{CO}_{2}$-quantities are decreasing from the surface to a minimum at 6 m depth, more rarely at 4 or 8 m depth, after which the quantities are increasing towards the 11 m layer, where the $\mathrm{CO}_{2}$-maximum always is found. Examples: July 21, 1959 and June 18, 1958 (cf. Fig. 10).

The occurrence of a $\mathrm{CO}_{2}$-minimum in the 11 m layer is a very rare event indeed. Example: May 3, 1958. This minimum is probably a result of the photosynthetic activity of Nitella or Uroglena, at a moment when inconsiderable quantities of $\mathrm{CO}_{2}$ are entering the bottom water after the effective stirring of the lake during the vernal circulation in April.

The patterns of the winter stagnation period look somewhat different from those of the summer half.
(i) The $\mathrm{CO}_{2}$-quantities gradually increase towards a maximum at the subsurface depth of 11 meters. This pattern is rare. Examples: March 9, 1958 and April 5, 1958 (cf. Fig. 11).


Fig. 10. Patterns of the vertical distribution of total carbon dioxide in Grane Langsø during the summer stagnation period of 1959 .


Fig. 11. Patterns of the vertical distribution of total carbon dioxide in Grane Langso during the winter stagnation periods of 1958 and 1961.
(ii) A relative $\mathrm{CO}_{2}$ maximum is present immediately below the ice, while the absolute maximum lies at 11 m depth; a minimum, not very pronounced, is inserted at 4 or 6 m depth. Examples: February 8, 1959 and January 22, 1961 (cf. Fig. 11).
(iii) A uniform distribution to 4 m or 6 m depth, after which the $\mathrm{CO}_{2}$ quantities rise in the 6 m or 8 m layer; from this level the $\mathrm{CO}_{2}$ content is either increasing towards the bottom, or it remains nearly constant in the hypolimnion. Examples: February 12, 1961, and March 13, 1960 (cf. Figs. 11 and 23).

In the following descriptions of the temporal variations of total $\mathrm{CO}_{2}, \mathrm{pH}$, and $\mathrm{HCO}_{3}^{-}$, the occasions of the vernal turn-over and the autumnal turn-over have been used as starting-points instead of the calendar. These two events set in at well-defined moments, viz. when the thermocline touches the lake surface and the lake bottom, respectively (see p. 87). I think that the results will appear more clearly when the temporal course of the biological, chemical, and physical fluctuations in a lake is described from these crucial points in the annual cycle of the lake, rather than from the calendar.

In the tables on the temporal variations of $\mathrm{CO}_{2}, \mathrm{pH}$, phosphate, and iron, the symbol cive stands for the vernal circulation, cive being an abbreviation of circuitus vernales (circuitus here means "Durchwanderungen", which may be translated to transmigration of the water layers). The negative figures before cive denote the number of months of 30 days previous to cive, while the positive ones signify the number of months after cive. The autumnal circulation is symbolized by ciau (from circuitus autumnales), and the meaning of the associated figures is identical with that of the cive figures.

Fig. 12 shows the yearly fluctuations of the quantity of total $\mathrm{CO}_{2}$ below one square metre in the central part of Grane Langsø during four years. In Table 20 these computed results are arranged in relation to the moments of the two annual turn-overs. Table 21 gives a further account of the length of the circulation and stagnation periods, together with the moments of the turn-overs.

Nr. 2


Table 20. Total $\mathrm{CO}_{2}$, stated as $\mathrm{g} \cdot 11 \mathrm{~m}^{-3}$, in the central part of Grane Langs $\varnothing$.


Table 21. The moments of cive and ciau, and the duration of the four phases in the annual cycle of Grane Langsø.

|  | Winter <br> stagnation | cive | Spring <br> circulation | Summer <br> stagnation | ciau | Autumn <br> circulation |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $1958 \ldots$ | 100 days | about April 10 | 15 days | 128 days | about Sept. 1 | 122 days |
| $1959 \ldots$ | 58 days | about Febr. 27 | 32 days | 153 days | about Sept. 1 | 122 days |
| $1960 \ldots$ | 86 days | March 26 | 35 days | 122 days | about Sept. 1 | 122 days |
| $1961 \ldots$ | 35 days | Febr. 18 | 53 days | 102 days | about July 23 |  |

(1) The largest quantities of total $\mathrm{CO}_{2}$ during the winter stagnation periods occur in the month prior to the spring turn-over. If the period is prolonged, as was the case in 1958 , the amount was as high as nearly 36 g per 11 cubic meters or $36 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$. The quantities occurring in the month before cive of the other three years lay between 21 and $29 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$. The later $\mathrm{CO}_{2}$ values of the winter stagnation periods lie, however, between 24 and $27^{1} / 4 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$. The $\mathrm{CO}_{2}$ quantity at the end of the short winter stagnation period of 1961 ( 35 days) was nearly as large as that from the end of the long period of 1960 , which lasted for 86 days. The reason for this remarkable result may partly be that the quantity of total $\mathrm{CO}_{2}$ was no less than $18.5 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ at the end of the autumnal circulation period of 1960 , while it amounted to only $16.1 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ at the end of the corresponding period of 1959. In 1959 the $\mathrm{CO}_{2}$ quantity just before cive attained the value $27^{1} / 4 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$, after a quantity of as much as $19^{1 / 4 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}}$ at the end of the preceding autumnal circulation period.

In order to examine whether the rise in total $\mathrm{CO}_{2}$ during the winter stagnation period is constant or irregular, the daily increment has been computed; these average increments are listed in Table 22. The vertical dotted lines indicate the beginning of the winter stagnation periods. The small crosses denote the dates of analyses appro-

Table 22. The increase, on an average, of g total $\mathrm{CO}_{3} \cdot 11 \mathrm{~m}^{-3}$. day ${ }^{-1}$ during the winter stagnation periods of 1958-1961 in the middle of Grane Langsø.

| -3 |  | -2 |  |  |  |  |  | -1 |  |  | cive |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1958... | $?$ | $\times$ |  |  | ? |  |  |  | $\times$ |  | 0.27 | $\times$ | about April 10 |
| 1959... |  |  |  |  |  | 0.3 |  | $\times$ | $\begin{gathered} 1 \\ 0.13 \end{gathered}$ |  | $\times$ |  | about Febr. 27 |
| 1960... | 1 1 1 1 | $0.18$ | $\times$ | 0.10 | $\times$ | $0.27$ | $\times$ | $0.35$ |  | $\times$ | $-0.25 \times$ |  | March 26 |
| 1961... |  |  |  |  |  |  |  |  | $.32$ |  | $0.14$ | $\times$ | Febr. 18 |

priately arranged relative to cive. The value 0.32 of 1961 was computed assuming that the $\mathrm{CO}_{2}$ quantity of January 14th, 1961 is identical with that of December 28th, 1960, viz. $18^{1 / 2} \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$.

It appears from Table 22 that the daily increase of total $\mathrm{CO}_{2}$ during the winter stagnation period is irregular, and that the greatest daily increments, more than $0.3 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$, occurred in the second month before the vernal turn-over. In the month before cive the daily increment decreased, in one case to a negative value. In 1959 and 1961 , with short winter stagnation periods, values of $0.31-0.32 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ were found in the first part of the period, whereas the daily increment during the last part was only $0.13-0.14 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$. The long winter stagnation period of 1960 , however, started with rather small values, $0.18-0.10 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$. Nevertheless, in this case also the increment decreased strongly towards the end of the period, even to a negative value of $-0.25 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$.

These figures of the daily increment in total $\mathrm{CO}_{2}$, mostly computed from time intervals of 14 days, are mentioned here because the $\mathrm{CO}_{2}$ consumption due to photosynthesis of the algae and submerged vegetation is small during the winter stagnation period. The decreasing values of the last part of the period may be interpreted as a result of increasing photosynthesis, depending on the transparency of the ice-cover and, of course, the rising light intensity.
(2) A remarkable decline in the $\mathrm{CO}_{2}$ quantity takes place in the first month after the vernal turn-over. The lake now opened for complete circulation of its water volume probably liberates $\mathrm{CO}_{2}$ to the atmosphere (see p. 59), and the conditions for photosynthesis are growing better. In the spring of 1958 a decline of no less than 21.2 g total $\mathrm{CO}_{2} \cdot 11 \mathrm{~m}^{-3}$ in 28 days was obtained. In 1959 the decline amounted to $8.2 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ in 20 days, whereas in 1960 it was $7.5 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ in 14 days, and in $19616 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ also in 14 days.
(3) During the four summer stagnation periods investigated, the quantities of
total $\mathrm{CO}_{2}$ always rise. This increase is by no means constant: maxima alternate with minima. The highest values, from $9.3-20.7 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$, always occurred in the month previous to the autumnal turn-over. In the last part of the second month before ciau a minimum was found in 1958,1959 , and 1961 ; it amounted to $6.2-11.5 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$. This second minimum of the summer stagnation period was observed in the third month before ciau in $1960\left(7.7 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}\right)$.

The first minimum of the period mentioned was found in the fourth month before ciau in 1958,1960 , and 1961 . Quantities of total $\mathrm{CO}_{2}$ fell to $6.7-10.1 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$. In 1959 the first minimum, amounting to $13 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$, occurred already in the sixth month before ciau, or rather in the first month after the vernal turn-over.

The secondary maxima of total $\mathrm{CO}_{2}$ occurred in the fourth month before the autumnal turn-overs of 1959 and $1960\left(11.5-15.2 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}\right)$, in the second month prior to ciau, however, in $1958\left(12.1 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}\right)$, and in the third month before ciau in $1961\left(8.6 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}\right)$.

This alternation of maxima and minima of total $\mathrm{CO}_{2}$ is closely connected with the alternation of minima and maxima of the phytoplankton productivity. Like many other lakes, Grane Langsø exhibits two production maxima within the summer half. The monthly investigation of the primary production during the period August 1950 to July 1951 demonstrated a small maximum in April and a larger one in July or August (Nygaard 1955, p. 131). According to Table 20 and Fig. 12, the first $\mathrm{CO}_{2}$ minimum of Grane Langsø occurred in April or May, while the second one lay in June or July (cf. also the survey of the analyses p. 91-107). These $\mathrm{CO}_{2}$ minima are reasonably well synchronized with the maxima of productivity, during which a considerable consumption of $\mathrm{CO}_{2}$ take place.
(4) Shortly after the autumnal turn-over the $\mathrm{CO}_{2}$ quantities decrease. The fall amounts to $0.3-6.7 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$, thus being much smaller than that confined to the spring turn-over. In the autumnal circulation period a distinct $\mathrm{CO}_{2}$ minimum always occurred in October, the second month after ciau, where the $\mathrm{CO}_{2}$ values declined to $12.4-15.8 \mathrm{~g}$ $\cdot 11 \mathrm{~m}^{-3}$. From this moment the quantities of total $\mathrm{CO}_{2}$ increased to values of $16.9-$ $19.2 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ in the fourth month after ciau, December.

It will appear from Section 12 that low pH values might have occurred in the time between late November and late December (see p. 68). Within this period of 1950 the phosphate quantity increased fourfold (see Fig. 6 and p. 26). This fact seems to indicate a strong decomposition of dead plant material in the lake from late November to late December. This supposition is supported by the result from Table 23, which demonstrates the daily increment of $\mathrm{CO}_{2}$ during the autumnal circulation periods which were investigated.

It is evident that the daily increments of $\mathrm{CO}_{2}$ are considerable in the third month after ciau. In November decaying organic material no doubt liberates considerable quantities of $\mathrm{CO}_{2}$, besides electrolytes such as phosphate.

After beginning in late November, the decay continues during the winter stagnation period, in which the lake cannot be aerated effectively. As photosynthesis of

Table 23. The average increment of total $\mathrm{CO}_{2}$, as $\mathrm{g} \cdot 11 \mathrm{~m}^{-3} \cdot \mathrm{day}^{-1}$, during the autumnal circulation periods of 1958-60.

the phytoplankton below the ice-cover is very small, and the respiration of Nitella is far greater than its photosynthesis, the absolute $\mathrm{CO}_{2}$ maximum must consequently occur within the winter stagnation period, as will also appear from Table 20.

The photosynthesis of Nitella flexilis, growing in depths of about 11 meters, is undoubtedly affected by variations in the population density of the phytoplankton. As seen from the survey of the analyses on p. 96, the transparency on August 24th, 1958 , surpassed 11 meters. This high transparency is due to a marked decrease of the plankton population. The $\mathrm{CO}_{2}$ quantity coincidently increased from $11.5 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ on August 1st to $20.7 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$ on August 24 th. This rise is not due merely to the large $\mathrm{CO}_{2}$ accumulation in the hypolimnion, as the epilimnion also increased its $\mathrm{CO}_{2}$ content considerably. The epilimnic rise is probably a result of the small $\mathrm{CO}_{2}$ consumption relative to the quantities of $\mathrm{CO}_{2}$ liberated by the decay of many dead plankton organisms from the subsiding maximum in early August. A relatively strong photosynthesis of Nitella is then conditioned by the improved light-conditions at the lake bottom.

On the contrary, the great Uroglena-maximum on July 27th, 1960, when the transparency of 4 meters was exceptionally low, must have inhibited the growth of Nitella, causing a smaller $\mathrm{CO}_{2}$ consumption than usual and consequently a larger content of $\mathrm{CO}_{2}$ in the bottom water.

It is likely that Nitella occasionally is able to counterbalance the changes in $\mathrm{CO}_{2}$ caused by the phytoplankton.

In the period from April to July, during which light is abundant, Nitella and the phytoplankton collaborate effectively in consuming $\mathrm{CO}_{2}$ from the 11 m layer, as the primary production of the phytoplankton on bright days can attain its greatest values at a subsurface depth of 11 meters.

During the month before ciau, as a rule August, when the temperature of the bottom water is rising and light intensities falling, the release of $\mathrm{CO}_{2}$ from the bottom sediments is evidently far greater than the consumption of $\mathrm{CO}_{2}$ by Nitella. This conclusion is based on the fact that the secondary $\mathrm{CO}_{2}$-maximum of Grane Langsø always was found in the month before ciau. If this month exceptionally is identicai wlth July, when light conditions for photosynthesis are still optimal, a secondary $\mathrm{CO}_{2}$ maximum of moderate size will result: only $9.3 \mathrm{~g} \cdot 11 \mathrm{~m}^{-3}$, as in 1961 .

The occurrence of two annual $\mathrm{CO}_{2}$-maxima in the 11 m -water is another matter.

The $\mathrm{CO}_{2}$-fluctuations of this water-layer are of a great interest for the productivity of the bottomplant Nitella. The absolute $\mathrm{CO}_{2}$-maximum ( $4.14-14.89 \mathrm{mg}$ total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ ) usually lay in -1 . ciau (late August). In the very windy and cool summer of 1961 it was exceptionally established already in early July, being of a moderate size (4.14 $\mathrm{mg} \cdot \mathrm{l}^{-1}$ ) on account of the vigorous water circulation. The secondary $\mathrm{CO}_{2}$-maximum ( $7.15-11.37 \mathrm{mg}$ total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ ) of the 11 m -water occurred in -2. or -1 . cive (JanuaryFebruary, rarely in April), apart from the year 1961, when the -1 . cive-maximum was greater than the -1 . ciau-maximum.

As will be shown in Section 14, the low-lying thermocline is liable to move slowly upwards during the winter stagnation period, reaching the lake surface at the onset of the vernal circulation (cf. Fig. 24). Centripetal chemical currents and the heat content of the bottom deposits can probably give rise to convective currents between the bottom and this low-lying thermocline. If so, the quantity of $\mathrm{CO}_{2}$ liberated from the bottom deposits is dispersed in a steadily increasing volume of water, and the $\mathrm{CO}_{2}$-maximum of the 11 m -water is consequently not observed at the end of this period, but somewhat earlier.

In the summer stagnation period, however, the convection-producing factors act from the lake surface down to the thermocline, which is gradually lowered. Consequently a continuous accumulation of $\mathrm{CO}_{2}$ takes place in a steadily decreasing volume of hypolimnic water. Under these conditions the $\mathrm{CO}_{2}$-maximum of the 11 m -water occurs at the end of the summer stagnation period.

In papers to come dealing with the productivity of Nitella flexilis, the oxygen patterns of Grane Langs $\varnothing$, and the phytoplankton productivity, the problems mentioned will be reconsidered.

Krogh und Lange (1931, p. 33) have determined the quantity of total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ in the hydrogen-carbonate lake Fures $\varnothing$, probably by the same method as that employed here. They found values fluctuating around $100 \mathrm{mg} \cdot \mathrm{l}^{-1}$ for the surface water, which are high values compared with the corresponding ones from Grane Langs $\varnothing$ which vary around only 1 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$.

Considering the minimal solubility of calcite, $12.7 \mathrm{mg} \mathrm{CaCO} 3 \cdot \mathrm{l}^{-1}$ (containing $5.1 \mathrm{mg} \mathrm{Ca}{ }^{++} \cdot \mathrm{l}^{-1}$ ) at $25^{\circ} \mathrm{C}$, in water which is in equilibrium with a $\mathrm{CO}_{2}$-pressure of about $5 \cdot 10^{-7}$ atmosphere Hutchinson remarks ". . . that unless at least 5 mg per liter Ca is present in a natural water, calcitic shells will tend to dissolve, whatever the $\mathrm{CO}_{2}$-pressure may be." (1957, p. 662). As Grane Langsø contains only $1.8-3.6 \mathrm{mg}$ $\mathrm{Ca}^{++} \cdot \mathrm{l}^{-1}$, the $\mathrm{CO}_{2}$ of its water must always be aggressive. The dead calcitic shells of Astacus and Pisidium are consequently liable to dissolve rather quickly. A dead specimen of Astacus lying on shallow water disintegrates within some days.

## 11. The $\mathrm{CO}_{2}$ Exchange between the Lake Surface and the Atmosphere

As will be seen from Section $10, \mathrm{CO}_{2}$ is a factor exhibiting considerable yearly fluctuations. Now the problem is: does the $\mathrm{CO}_{2}$ move into the lake surface from the atmosphere, providing an enrichment of the gas in the lake, or is $\mathrm{CO}_{2}$ lost from the lake, or do both events alternate within a year?

In order to determine the exchange direction at any season, it is first necessary to know the quantities of free $\mathrm{CO}_{2}$ absorbed in distilled water which is in equilibrium with the atmosphere at the various temperatures met with in nature. These quantities should then be compared with those of free $\mathrm{CO}_{2}$ in the surface water of the lake.

As the solubility of $\mathrm{CO}_{2}$ in aqueous solutions of electrolytes must depend on their ionic strength, this question should also be considered before a solution of the problem is possible.

The figures of Table 79 in Hutchinson's work (1957, p. 654) have been used for the construction of Fig. 13. These figures are assumed to represent the quantities of total $\mathrm{CO}_{2}$ in distilled water. It is possible, however, to compute the concentration of free $\mathrm{CO}_{2}$ on the basis of the Henderson-Hasselbalch equation

$$
\frac{\mathrm{c}_{\mathrm{H}^{+}} \cdot \mathrm{c}_{\mathrm{HCO}_{3}^{-}}}{\mathrm{c}_{\mathrm{CO}_{2}}}=\mathrm{K}_{\mathrm{CO}_{2}}
$$

where $\mathrm{c}_{\mathrm{CO}_{2}}$ is the concentration of free $\mathrm{CO}_{2}$. The ionization constant of $\mathrm{CO}_{2} \mathrm{aq} \mathrm{K}_{1}$ is about $10^{-4}$, and so much greater than that of the hydrogen-carbonate ion, $\mathrm{K}_{2}=$ about $10^{-10}$, and the dissociation constant of water, $\mathrm{K}_{\mathrm{w}}=$ about $10^{-14}$. The increment of $\left[\mathrm{H}^{+}\right]$due to the processes $\mathrm{HCO}_{3}^{-} \rightleftarrows \mathrm{H}^{+}+\mathrm{CO}_{3}^{--}$and $\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{H}^{+}+\mathrm{OH}^{-}$is consequently negligible and $\mathrm{c}_{\mathrm{H}^{+}}$is practically identical with $\mathrm{c}_{\mathrm{HCO}_{3}^{-}}$. Therefore

$$
\left(\mathrm{c}_{\mathrm{H}^{+}}\right)^{2}=\mathrm{K}_{\mathrm{CO}_{2}} \cdot \mathrm{c}_{\mathrm{CO}_{2}}=\left(\mathrm{c}_{\mathrm{HCO}_{3}^{-}}\right)^{2} .
$$

As $\mathrm{c}_{\text {total } \mathrm{CO}_{2}}=\mathrm{c}_{\mathrm{CO}_{2}}+\mathrm{c}_{\mathrm{HCO}}{ }^{-}$we get

$$
\begin{equation*}
\left(\mathrm{c}_{\mathrm{CO}_{2}}\right)^{2}-\left(2 \mathrm{c}_{\text {total } \mathrm{CO}_{2}}+\mathrm{K}_{\mathrm{CO}_{2}}\right) \cdot \mathrm{c}_{\mathrm{CO}_{2}}+\left(\mathrm{c}_{\text {total } \mathrm{CO}_{2}}\right)^{2}=0 \tag{5}
\end{equation*}
$$

On Fig. 13 total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}, \mathrm{pH}$, and free $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ can be read for all temperatures between $0^{\circ}$ and $25^{\circ} \mathrm{C}$ and the ionic strength $=0$.

In order to approach the next question, the solubility of $\mathrm{CO}_{2}$ in electrolytes, Fig. 14 has beeen drawn. It is based on the measurements given by Chr. Bohr (1899, p. 504-505). At the large NaCl concentration of 3.41 , the absorption coefficient $\alpha$ of $\mathrm{CO}_{2}$ is less than 50 per cent of that for destilled water; this also holds true at $0^{\circ} \mathrm{C}$ and $20^{\circ} \mathrm{C}$.

As previously mentioned the ionic strength of Grane Langsø is about 0.00065 (see p. 46). The ionic strenght is defined by

$$
\mu=\frac{1}{2} \sum c_{i} \cdot z_{i}^{2}
$$



Fig. 13. The saturation values of $\mathrm{CO}_{2}$ in distilled water at various temperatures (thick graph), and the corresponding values of free $\mathrm{CO}_{2}$ (thin graph) and pH (dotted line). Ordinates: $\mathrm{mg} \mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ and pH -units.


Fig. 14. The absorption coefficient $(\alpha)$ of $\mathrm{CO}_{2}$ at various concentrations of aqueous NaCl solutions.
and for a uni-univalent electrolyte such as $\mathrm{NaCl} \mu$ must be equal to $c$. A NaCl -solution of identical ionic strength to that of Grane Langs $\sigma$ must consequently be of the concentration 0.00065 .

If we make the approximation of assuming linearity of the graphs between $c=0$ and $c=1.17, \alpha$ can be computed for a NaCl-solution of the ionic strength 0.00065 .

Temp. $0^{\circ}$ C. $\alpha$ decreases $1.713-1.234=0.479$ when the concentration increase 1.17. For an alteration in concentration of $0.00065 \alpha$ must therefore change $\frac{0.479}{1.17}$. $0.00065 \approx 0.0003$.

Temp. 20 C. $\alpha$ decreases $0.878-0.664=0.214$ when the concentration increases 1.17. For an alteration in concentration of $0.00065 \alpha$ must concequently change $\frac{0.214}{1.17} \cdot 0.00065 \approx 0.0001$.

Corrections of this order of size are probably much smaller than the uncertainty on the third decimal of $\alpha$. Therefore we may safely assume that the solubilities of $\mathrm{CO}_{2}$ in the water of Grane Langs $\varnothing$ and in distilled water are virtually identical.

Figs. 15-16 permit a comparison, at intermediate temperatures, of the free $\mathrm{CO}_{2}$ in surface water of Grane Langsø with that of distilled water in equilibrium with the atmosphere.

In 1958 , when normally only monthly analyses were performed, the surface water may have been supersaturated with $\mathrm{CO}_{2}$ during the whole year.

In 1959 , when monthly analyses were made in the first half, but fortnightly ones in the second half, two minima occurred, one in the second month (April) after cive, the other in the fifth month (July) after cive. The surface water was undersaturated with $\mathrm{CO}_{2}$ only in July.

In 1960, when analyses were made twice a month, supersaturation likewise prevailed. The surface water exhibited undersaturation in two periods, however: the first and second months (April-May) after cive, and the fifth month (July) after cive.

In 1961, when two series of $\mathrm{CO}_{2}$-analyses were performed monthly until the end of July, the surface water was super-saturated apart from two periods in which undersaturation prevailed: the second and third month (April) after cive, and the fourth month (June) after cive. The abnormally early time, June, for the second $\mathrm{CO}_{2}{ }^{-}$ minimum may be due to interaction of the mild spring and the windy summer of 1961. Total circulation took place in even July, an exceptional occurrence within the six summers in which vertical temperature distributions of this wind-sheltered lake were followed.

Generally, the surface water of Grane Langso is supersaturated with $\mathrm{CO}_{2}$ for the whole year; in two periods, however, the lake can be undersaturated: April with possibly May, and July with possibly June. The lake thus liberates $\mathrm{CO}_{2}$ to the atmosphere during the greater part of the year.

It is hardly possible to compute how much $\mathrm{CO}_{2}$ moves into or out from the lake surface within a definite space of time, i. a. because the lake does not make up a closed system. Admission of $\mathrm{CO}_{2}$ continually takes place, partly direct by precipitation, partly indirect by rain water filting through the soil of the surrounding coniferous plantations.

It is evident that the $\mathrm{CO}_{2}$-fluctuations which are confined to lake surface are


Fig. 15. The thick graphs represent the monthly or fortnightly values of free $\mathrm{CO}_{2}$ in the surface water of Grane Langsø in 1958-59. The thin graphs indicate the saturation values of free $\mathrm{CO}_{2}$ in distilled water, when in equilibrium with the atmospheric $\mathrm{CO}_{2}$ pressure under thermal conditions exactly identical to those met with in the lake. Ordinates in mg free $\mathrm{CO}_{2} \cdot 1^{-1}$.


Fig. 16. Representation as in Fig. 15 of the conditions during 1960-61.
dependent on biological factors, as well as physical and meteorological ones. Biological processes such as photosynthesis and respiration, decay included, deeply influence the standing stock of $\mathrm{CO}_{2}$ in the lake. The physically determined and regular change between stagnation periods, when $\mathrm{CO}_{2}$ is allowed to accumulate in the bottom water, and periods of circulation, when the $\mathrm{CO}_{2}$ of the bottom water is brought up to i. a. the lake surface, must cause great fluctuations of $\mathrm{CO}_{2}$, as shown on Figs. 10-11. Finally, the precipitation yields an irregular $\mathrm{CO}_{2}$ supply to the lake, but the rain water filtering through the soil of the surrounding plantations must contain much more $\mathrm{CO}_{2}$ per litre, before it runs into the lake.

A feature common to many temperate lakes is the two yearly maxima in the standing stock of plankton organisms, one in April-May, the other in July-August. On the whole this means that the primary production, and with it the consumption of $\mathrm{CO}_{2}$, are largest in the two periods mentioned.

As found earlier by Nygatrd (1955, p. 131), Grane Langsø exhibited two maxima in its gross production within 1950-51, when it was only examined monthly. The first, small maximum occurred in April; the second one, considerably larger, took place in August. I am under the impression that something similar occurred during the three years 1958-61. The matter cannot be decided, however, until the calculations of the ${ }^{14} \mathrm{C}$-data are available.

The $\mathrm{CO}_{2}$-tension of lake Furesø has been determined by Krogh (1904, p. 384) and Brøndsted und Wesenberg-Lund (1912, p. 450). According to Brøndsted’s determinations, the $\mathrm{CO}_{2}$-tension of the surface water was below the atmospheric value $3.3 \cdot 10^{-4}$ in March-May and July 1909. In the remaining months the $\mathrm{CO}_{2}{ }^{-}$ tension of the surface water lay between 4 and $12.5 \cdot 10^{-4}$.

Krogh and Lange (1931) determined the $\mathrm{CO}_{2}$-tension in lake Furesø at intervals within the years 1929 and 1930. Unfortunately no determinations were made in July and August. Tab. 2 of their paper (1931, p. 33) demonstrates that for surface water an equilibrium with the atmospheric $\mathrm{CO}_{2}$ or a slight undersaturation of $\mathrm{CO}_{2}$ was present in March, April, and May, the $\mathrm{CO}_{2}$-tension being $0.00024-0.00031$ in these spring months. In autumn and winter the surface values surpass the equilibrium value, 0.00033 , the $\mathrm{CO}_{2}$ tension here amounting to $0.00039-0.00060$. As will appear from the information given above, the investigation of Grane Langsø has confirmed and extended Krogh and Lange's results from Fureso.

The two authors write ( 1931, p. 32) ".... $\mathrm{CO}_{2}$ wird somit gewöhnlich von der Oberfläche abgegeben und ermöglicht eine entsprechende Ablagerung von Calciumkarbonat." In connection with this it may be remarked that any liberation of $\mathrm{CaCO}_{3}$ is likely to occur only in the spring and high summer, when i.a. the equilibrium- $\mathrm{CO}_{2}$ of the carbon dioxide system is being exhausted by the vigorous photosynthesis of the phytoplankton; in these two periods the lake probably absorbs $\mathrm{CO}_{2}$ from the atmosphere.

A hard water lake such as Furesø and a very soft water lake such as Grane Langsø thus seem to behave similarly as regards the $\mathrm{CO}_{2}$ exchange between lake and
atmosphere. The diffusion of $\mathrm{CO}_{2}$ from the lake surface to the atmosphere and the supply of $\mathrm{CO}_{2}$ from the ground water probably balance over a long period. A lake may thus be considered as a device by which $\mathrm{CO}_{2}$ returns to the atmosphere, after having been fixed photosynthetically by the land vegetation, and gradually liberated by the decay of dead organisms, partly to the atmosphere, partly to the ground water running into the lake.

## 12. The Hydrogen Ion Concentration

During the period 1950-1961, 545 electrometric pH determinations were carried out on water samples from Grane Langs $\sigma$. The greatest number of pH measurements lay between 5.6 and 5.7. A critical examination of this material has rendered it probable that some of the pH determinations, expecially those from the bottom water, are not reliable.

The $\mathrm{CO}_{2}$ content of the lake water from Grane Langs $\varnothing$ usually exceeds the quantity of $\mathrm{CO}_{2}$ (about $0.56-0.59 \mathrm{mg} \cdot \mathrm{l}^{-1}$ ) of distilled water which is in equilibrium with the atmospheric $\mathrm{CO}_{2}$ at $18-20^{\circ} \mathrm{C}$. The result must be a $\mathrm{CO}_{2}$ loss by diffusion during some of the pH determinations, which consequently yield values which are too high. Now the question arises whether an essential difference can be ascertained between, on one hand, the pH value computed on the assumption that pH is merely determined by the $\mathrm{CO}_{2}$ concentration of the lake water markedly poor in electrolytes, and, on the other hand, the corresponding pH value measured electrometrically at about $18-20^{\circ} \mathrm{C}$, when the temperature of the lake water itself was about $18-20^{\circ} \mathrm{C}$ and the $\mathrm{CO}_{2}$ content was approximately in equilibrium with the atmospheric $\mathrm{CO}_{2}$. If these two pH values turn out to be nearly identical, the hydrogen ion concentration of Grane Langs $\varnothing$ is mainly determined by the $\mathrm{CO}_{2}$ content of the lake water.

The $\mathrm{CO}_{2}$ quantities of Table 79 in Hutchinson's work of 1957 are assumed to represent mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$, thus also including the hydrogen-carbonate $\mathrm{CO}_{2}$. It is evident that the values of total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ from Grane Langsø include the hydrogen carbonate $\mathrm{CO}_{2}$, since the carbon dioxide was distilled off at a pH value far below 4.0.

During the period October 1960 to July 1961 two new glass electrodes were employed, viz. Radiometer' G 200 B in a siliconed state in order to obtain a quickly adjustable pH -meter. In the same period precision buffer solutions were used for the adjustment of the instrument (cf. p. 19).

The calculation of pH was made by means of the following equations (cf. p. 57):

$$
\begin{gather*}
\left(\mathrm{c}_{\text {free } \mathrm{CO}_{2}}\right)^{2}-\left(2 \mathrm{c}_{\text {total } \mathrm{CO}_{2}}+\mathrm{K}_{\mathrm{CO}_{2}}\right) \mathrm{c}_{\text {free } \mathrm{CO}_{2}}+\left(\mathrm{c}_{\text {total } \mathrm{CO}_{2}}\right)^{2}=0 \\
\mathrm{pH}=\frac{1}{2} \mathrm{pK}_{\mathrm{CO}_{2}}-\frac{1}{2} \log \mathrm{c}_{\text {free } \mathrm{CO}_{2}} . \tag{6}
\end{gather*}
$$

With the aid of equation (5) on p. 57 it is also possible to compute pH directly from the content of total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ :

Table 24. A comparison of the pH values measured and the corresponding ones computed from Grane Langsø in June-July 1961.

| Depths | Temp. | $\begin{gathered} \mathrm{pH} \\ \text { measured } \end{gathered}$ | $\begin{gathered} \mathrm{pH} \\ \text { computed } \end{gathered}$ | $\triangle \mathrm{pH}$ | Grane <br> Langsø mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | Distilled water in equilibrium with the atmospheric $\mathrm{CO}_{2}, \mathrm{mg}$ total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | $\triangle \mathrm{CO}_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| June 15 |  |  |  |  |  |  |  |
| 0 m . . . . . | 17.15 | 5.51 | 5.71 | $-0.20$ | 0.50 | 0.60 | $-0.10$ |
| 2 m . | 17.0 | 5.50 | 5.71 | $-0.21$ | 0.50 | 0.60 | $-0.10$ |
| 4 - | 16.9 | 5.50 | 5.70 | $-0.20$ | 0.57 | 0.60 | $-0.03$ |
| 6 - | 16.0 | 4.53 | 5.70 | $-0.17$ | 0.54 | 0.62 | -0.08 |
| 8 - | 15.6 | 5.63 | 5.67 | $-0.04$ | 0.61 | 0.63 | $-0.02$ |
| $10-$ | 14.95 | 5.59 | 5.61 | $-0.02$ | 0.78 | 0.65 | $+0.13$ |
| 11 -.. | 14.85 | 5.56 | 5.54 | $+0.02$ | 1.06 | 0.65 | +0.41 |
| July 9 |  |  |  |  |  |  |  |
| $0 \mathrm{~m} . . .$. | 17.2 | 5.68 | 5.63 | $+0.05$ | 0.73 | 0.60 | $+0.13$ |
| 2 - | 17.1 | 5.69 | 5.66 | $+0.03$ | 0.64 | 0.60 | $+0.04$ |
| 4 - | 17.1 | 5.68 | 5.63 | $+0.05$ | 0.72 | 0.60 | $+0.12$ |
| 6 - | 17.1 | 5.68 | 5.66 | $+0.02$ | 0.65 | 0.60 | $+0.05$ |
| 8 - | 17.05 | 5.68 | 5.63 | $+0.05$ | 0.72 | 0.60 | $+0.12$ |
| $10-$ | 17.05 | 5.68 | 5.64 | $+0.04$ | 0.69 | 0.60 | $+0.09$ |
| 11 - | 16.3 | 5.48 | 5.23 | $+0.25$ | 4.14 | 0.62 | $+3.52$ |
| July 23 |  |  |  |  |  |  |  |
| 0 m . . | 17.65 | 5.65 | 5.64 | $+0.01$ | 0.70 | 0.59 | $+0.11$ |
| 2 - | 17.55 | 5.64 | 5.66 | $-0.02$ | 0.64 | 0.59 | $+0.05$ |
| 4 - | 17.55 | 5.63 | 5.66 | $-0.03$ | 0.64 | 0.59 | $+0.05$ |
| 6 - | 17.55 | 5.63 | 5.66 | $-0.03$ | 0.64 | 0.59 | $+0.05$ |
| 8 - | 17.45 | 5.65 | 5.62 | $+0.03$ | 0.75 | 0.59 | $+0.16$ |
| $10-$ | 17.2 | 5.60 | 5.49 | $+0.11$ | 1.42 | 0.60 | $+0.82$ |
| 11-.. | 17.2 | 5.59 | 5.45 | $+0.14$ | 1.67 | 0.60 | +1.07 |

$$
\begin{gather*}
\left(\mathrm{c}_{\mathrm{H}^{+}}\right)^{2}=\mathrm{K}_{\mathrm{CO}_{2}} \cdot \mathrm{c}_{\mathrm{CO}_{2}} ; \quad \mathrm{c}_{\text {total } \mathrm{CO}_{2}}=\mathrm{c}_{\mathrm{H}^{+}}+\mathrm{c}_{\mathrm{CO}_{2}} \\
\left(\mathrm{c}_{\mathrm{H}^{+}}\right)^{2}+\mathrm{K}_{\mathrm{CO}_{2}} \cdot \mathrm{c}_{\mathrm{H}^{+}}-\mathrm{K}_{\mathrm{CO}_{2}} \cdot \mathrm{c}_{\text {total } \mathrm{CO}_{2}}=0  \tag{7}\\
\mathrm{c}_{\mathrm{H}^{+}}=-\frac{1}{2} \mathrm{~K}_{\mathrm{CO}_{2}}+\sqrt{\left(\frac{1}{2} \mathrm{~K}_{\mathrm{CO}_{2}}\right)^{2}+\mathrm{K}_{\mathrm{CO}_{2}} \cdot \mathrm{c}_{\text {total } \mathrm{CO}_{2}} .}
\end{gather*}
$$

In the cool and windy summer of 1961 the temperature of the laboratory room used for pH determination was about $18^{\circ} \mathrm{C}$, thus nearly identical with that of the lake water. In the following description only the results from water samples measuring at least $16^{\circ} \mathrm{C}$ are considered.

Table 24 demonstrates that on June 15 the water layers of $0-6 \mathrm{~m}$ subsurface depths contained smaller quantities of $\mathrm{CO}_{2}$ than does distilled water in equilibrium
with the atmosphere at the same temperature. Therefore it is assumed that some $\mathrm{CO}_{2}$ has diffused from their air into the lake water, thus making it more acid. This assumption fits the facts, the pH values measured being $0.17-0.21$ units smaller than the calculated ones.

On July 9 the $\mathrm{CO}_{2}$ values of Grane Langs $\varnothing$ were, on the other hand, slightly higher than the corresponding ones of distilled water in equilibrium with 0.033 per cent $\mathrm{CO}_{2}$ of the atmosphere. Assuming that the lake water during the pH determination has liberated some $\mathrm{CO}_{2}$ to the air, the pH must have increased somewhat. There is also in this case accordance between theory and practice, the pH -values measured being $0.02-0.05$ units higher than the computed ones.

The bottom water, however, was relatively rich in $\mathrm{CO}_{2}$. During the pH determination some loss of $\mathrm{CO}_{2}$ by diffusion to the air must have taken place. The pH value measured was 0.25 unit higher than the computed one.

Also on July 23 the lake water from $0-8 \mathrm{~m}$ subsurface depths contained slightly greater $\mathrm{CO}_{2}$ concentrations than does distilled water in equilibrium with the atmosphere. In this case the pH values measured lay from -0.03 to +0.03 units higher than the computed ones. The water from 10 m and 11 m subsurface depths was somewhat richer in $\mathrm{CO}_{2}$ than distilled water in equilibrium with 0.033 per cent $\mathrm{CO}_{2}$. The diffusion of $\mathrm{CO}_{2}$ during the pH determination may have increased pH with $0.11-0.14$ units compared to the pH values calculated.

Table 24 thus makes it probable that the diffusion of $\mathrm{CO}_{2}$ plays a certain part during the pH determination of the very soft water of Grane Langs $\varnothing$. All things considered a good agreement exists under summer conditions between the pH values measured and the computed ones, provided that the pH determinations are made at temperatures nearly identical with those of the lake, and that the $\mathrm{CO}_{2}$ of the lake water approximately equilibrates with the atmospheric $\mathrm{CO}_{2}$.

The conclusion of these comparisons is that pH of Grane Langso seems in all essentials to be determined by the $\mathrm{CO}_{2}$ concentration of the lake water.

The calculation of pH implies an ionic strength of the solution approaching nil. The ionic strength of Grane Langs $\varnothing$ amounts to about 0.00065 , however, and it is possible that i.a. groundwater supply or metabolic products originating from the many organisms of the lake, succeeding each others, may to some degree influence pH . This supposition is founded on the following facts.

During the autumnal circulation of $1960, \mathrm{pH}$-measurements were undertaken at the temperatures actually met with in the lake. The volumes of the buffer solution and the water samples from Grane Langs $\varnothing$ were chosen to be to $60-100 \mathrm{ml}$ instead of the 5 ml normally used, in order to keep their temperatures constant at e.g. $4^{\circ} \pm$ $0.1^{\circ} \mathrm{C}$ during the standardization and determinations. Correction were made, according to the instruction and operating manual of the pH -meter used, for temperatures deviating from $20^{\circ} \mathrm{C}$ and for any difference between the reading- pH and buffer- pH .

In the period October 9th to December 28th, the computed pH values fluctuated within the limits 5.50 and 5.56 , thus varying at most 0.06 units. The values measured,

Table 25. A comparison of the pH -values measured and computed, their differences $(\Delta \mathrm{pH})$, the quantity of total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ at the various levels of Grane Langs $\varnothing$, the quantity of total $\mathrm{CO}_{2}$ of distilled water in equilibrium with the atmospheric $\mathrm{CO}_{2}$ at the corresponding temperatures, and finally the differences ( $4 \mathrm{CO}_{2}$ ) between the two last quantities.

| Depths | Temp. | pH measured | $\mathrm{pH}$ <br> computed | $\Delta \mathrm{pH}$ | Grane Langsø, mg total $\mathrm{CO}_{2} \cdot 1^{-1}$ | Distilled water in equilibrium with the atmospheric $\mathrm{CO}_{2}, \mathrm{mg}$ total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | $\triangle \mathrm{CO}_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| October 9, 1960 |  |  |  |  |  |  |  |
| 0 m . | 13.05 | 5.72 | 5.52 | $+0.20$ | 1.28 | 0.69 | $+0.59$ |
| 2 - | 13.05 | 5.70 | 5.51 | $+0.19$ | 1.30 | 0.69 | $+0.61$ |
| 4 - | 13.05 | 5.72 | 5.52 | $+0.20$ | 1.28 | 0.69 | $+0.59$ |
| 6 - | 13.05 | 5.72 | 5.52 | $+0.20$ | 1.25 | 0.69 | $+0.56$ |
| 8 - | 13.05 | 5.71 | 5.51 | $+0.20$ | 1.30 | 0.69 | $+0.61$ |
| $10-$ | 13.05 | 5.70 | 5.51 | $+0.19$ | 1.33 | 0.69 | $+0.64$ |
| $11-\ldots$ | 13.05 | 5.71 | 5.51 | $+0.20$ | 1.32 | 0.69 | $+0.63$ |
| October 19, 1960 |  |  |  |  |  |  |  |
| 0 m . . | 10.85 | 5.67 | 5.55 | $+0.12$ | 1.17 | 0.75 | $+0.42$ |
| 2 - | 10.75 | 5.66 | 5.55 | $+0.11$ | 1.19 | 0.75 | $+0.44$ |
| 4 - | 10.7 | 5.68 | 5.55 | $+0.13$ | 1.16 | 0.75 | $+0.41$ |
| 6 - | 10.7 | 5.66 | 5.56 | $+0.10$ | 1.14 | 0.75 | $+0.39$ |
| 8 - | 10.7 | 5.68 | 5.56 | $+0.12$ | 1.14 | 0.75 | $+0.39$ |
| $10-$ | 10.65 | 5.69 | 5.55 | $+0.14$ | 1.18 | 0.75 | $+0.43$ |
| $11-\ldots$. | 10.65 | 5.68 | 5.55 | $+0.13$ | 1.15 | 0.75 | $+0.40$ |

November 6, 1960

| 0 m . . . . . . . | 8.45 | 5.59 | 5.54 | $+0.05$ | 1.30 | 0.80 | $+0.50$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | 8.45 | 5.60 | 5.53 | $+0.07$ | 1.35 | 0.80 | $+0.55$ |
| 4 - | 8.45 | 5.59 | 5.54 | $+0.05$ | 1.29 | 0.80 | $+0.49$ |
| 6 - | 8.45 | 5.59 | 5.53 | $+0.06$ | 1.32 | 0.80 | $+0.52$ |
| 8 - | 8.45 | 5.60 | 5.54 | $+0.06$ | 1.29 | 0.80 | $+0.49$ |
| $10-$ | 8.45 | 5.59 | 5.53 | $+0.06$ | 1.32 | 0.80 | $+0.52$ |
| 11 - | 8.45 | 5.59 | 5.53 | $+0.06$ | 1.37 | 0.60 | $+0.57$ |
| November 20, 1960 |  |  |  |  |  |  |  |
| 0 m . | 6.35 | 5.44 | 5.52 | $-0.08$ | 1.46 | 0.88 | $+0.58$ |
| 2 - | 6.3 | 5.44 | 5.52 | $-0.08$ | 1.49 | 0.88 | $+0.61$ |
| 4 - | 6.2 | 5.42 | 5.51 | $-0.09$ | 1.51 | 0.88 | $+0.63$ |
| 6 - | 6.15 | 5.43 | 5.51 | $-0.08$ | 1.54 | 0.88 | $+0.66$ |
| 8 - | 6.15 | 5.43 | 5.51 | $-0.08$ | 1.51 | 0.88 | $+0.63$ |
| $10-$ | 6.15 | 5.42 | 5.51 | $-0.09$ | 1.55 | 0.88 | $+0.67$ |
| 11-....... | 6.15 | 5.42 | 5.51 | $-0.09$ | 1.52 | 0.88 | $+0.64$ |

Table 25 (continued).

| Depths | Temp. | $\begin{gathered} \mathrm{pH} \\ \text { measured } \end{gathered}$ | $\begin{gathered} \mathrm{pH} \\ \text { computed } \end{gathered}$ | $\Delta \mathrm{pH}$ | Grane Langsø, mg total $\mathrm{CO}_{2} \cdot$ - $^{-1}$ | Distilled water in equilibrium with the atmospheric $\mathrm{CO}_{2}, \mathrm{mg}$ total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | $\triangle \mathrm{CO}_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| December 11, 1960 |  |  |  |  |  |  |  |
| $0 \mathrm{~m} . . .$. | 4 | 5.60 | 5.51 | $+0.09$ | 1.53 | 0.94 | $+0.59$ |
| 2 - | 4 | 5.60 | 5.51 | $+0.09$ | 1.55 | 0.94 | +0.61 |
| 4 - | 4 | 5.61 | 5.51 | $+0.10$ | 1.52 | 0.94 | $+0.58$ |
| 6 - | 4 | 5.59 | 5.51 | $+0.08$ | 1.54 | 0.94 | $+0.60$ |
| 8 - | 4 | 5.59 | 5.50 | $+0.09$ | 1.56 | 0.94 | +0.62 |
| $10-$ | 4 | 5.59 | 5.50 | $+0.09$ | 1.58 | 0.94 | $+0.64$ |
| 11 - | 4 | 5.58 | 5.51 | $+0.07$ | 1.50 | 0.94 | $+0.56$ |
| December 28, 1960 |  |  |  |  |  |  |  |
| $0 \mathrm{~m} . . . .$. | 3.3 | 5.63 | 5.50 | $+0.13$ | 1.70 | 0.94 | $+0.76$ |
| 2 - | 3.3 | 5.63 | 5.50 | $+0.13$ | 1.69 | 0.94 | $+0.75$ |
| 4 - | 3.3 | 5.62 | 5.50 | $+0.12$ | 1.67 | 0.94 | $+0.73$ |
| 6 - | 3.3 | 5.62 | 5.50 | $+0.12$ | 1.70 | 0.94 | $+0.76$ |
| 8 - | 3.3 | 5.62 | 5.50 | $+0.12$ | 1.67 | 0.94 | $+0.73$ |
| $10-$ | 3.35 | 5.63 | 5.50 | $+0.13$ | 1.67 | 0.94 | $+0.73$ |
| 11 - | 3.35 | 5.62 | 5.50 | $+0.12$ | 1.67 | 0.94 | $+0.73$ |

Table 26. Average values of the columns 5 and 8 in the preceding table.

| Date | $\Delta \mathrm{pH}$ | $\triangle \mathrm{CO}_{2}$ |
| :---: | :---: | :---: |
| October 9 | $+0.20$ | $+0.60$ |
| October 19 | $+0.12$ | $+0.40$ |
| November 6 | $+0.06$ | $+0.50$ |
| November 20 | $-0.08$ | $+0.65$ |
| December 11. | $+0.09$ | $+0.60$ |
| December 28 | $+0.12$ | $+0.75$ |

on the contrary, fluctuated from 5.42 on November 20 th to 5.72 on October 9th, thus varying over 0.30 units.

As the $\mathrm{CO}_{2}$ values from the autumn of 1960 always surpassed the corresponding ones of distilled water, a $\mathrm{CO}_{2}$ loss by diffusion to the air is supposed to take place during the pH determinations, $\Delta \mathrm{CO}_{2}$ always being positive. It is consequently to be expected that the pH values measured are higher than the computed ones. According to Table 26, however, the average values measured decreased from October 9th towards a marked pH minimum on November 20th, after which the pH values again increased.

This seems to show that acid-reacting substances, possibly formed by the dacay of parts of the submerged vegetation, were liberated during the late autumn of 1960. Now pH determinations undertaken with water very poor in electrolytes can be rather inaccurate, on account of i.a. the large difference in ionic strength between the lake water and the buffer solution. It is consequently difficult to comment on the pH fluctuations in the autumn of 1960. In this connection I wish to remark, however, that a similar pH minimum, viz. pH 5.44 , was measured in late November 1959.

Even if the components of the $\mathrm{CO}_{2}$ system play an important role in determining pH , other substances such as ammonia, formed by decomposition of the proteins contained in dead plankton organisms and hydrophytes, occasionally must interfere with the $\mathrm{CO}_{2}$ system. Even such small $\mathrm{NH}_{3}$ quantities as 0.01 mg per litre distilled water can raise the pH by a few hundreths, if the quantity of free $\mathrm{CO}_{2}$ amounts to about $1 \mathrm{mg} \cdot \mathrm{l}^{-1}$.

Domogalla, Fred and Peterson (1926, p. 371-372, Figs. 1-2) found that the bottom water of Lake Mendota obtained a $\mathrm{NH}_{3}$ maximum in -1 . to -2 . cive and another in -1 . ciau. The surface water likewise exhibited two annual $\mathrm{NH}_{3}$ maxima, one in cive +1 . and the other in ciau +1 . after admixture with the large quantities of $\mathrm{NH}_{3}$ in the bottom water introduced by the turnovers.

Similar results were obtained by Kusnezow (1959, Abb. 53 p. 163) in Tschornoje See. The two lakes mentioned are eutrophic, the Russian one being very rich in $\mathrm{H}_{2} \mathrm{~S}$. Grane Langs $\varnothing$, which may be termed oligotrophic, is an acid lake, however. As extremely few determination of ammonia have been made in this lake (cf. Table 9, p. 32), my own results from the $\mathrm{NH}_{3}$ measurements in the likewise acid but humic lake Gribsø, which may be characterized as mesotrophic, are given in Table 26 bis. The analytic methods for a quantitative determination of $\mathrm{NH}_{3}$ and $\mathrm{NO}_{3}^{-}$are given on p. 32 .

In the bottom water of lake Gribsø, also, one $\mathrm{NH}_{3}$ maximum lay in -1. ciau and the other in -1 . to -2 . cive, the values being respectively $1.20 \mathrm{mg} \cdot \mathrm{l}^{-1}$ and $0.6-0.7$ $\mathrm{mg} \cdot \mathrm{l}^{-1}$. In Grane Langsø the quantities of ammonia in the bottom water probably never attain these figures, because the rather high oxygen values of its bottom water favour the nitrification of ammonia.

Lake Gribsø. Summer stagnation (August 1949): 0.6 per cent $\mathrm{O}_{2}$ in 11 m . Winter stagnation (February 1950): 44 per cent $\mathrm{O}_{2}$ in 11 m .

Grane Langs $\varnothing$. Summer stagnation (August 1958 and 1959): 33-62 per cent oxygen saturation in 11 m . Winter stagnation (February-March 1958, 1959, and 1960): $51-71$ per cent oxygen saturation in 11 m .

In Gribsø, however, the oxygen saturation and with it the nitrification were extremely small during summer stagnation; during winter stagnation considerable oxygen concentrations in the bottom water favoured a vigorous nitrification at the expense of ammonia, as shown in Table 26 bis.

The rather considerable oxygen saturation values in the bottom water of Grane Langsø make it probable that large quantities of ammonia should not be expected there during the stagnation periods.

Table 26 bis. The yearly fluctuations of ammonia and nitrate in lake Gribso. $\mathrm{NH}_{3}-\mathrm{N}$ in the period of $1949-50$.

|  | ciau |  |  |  |  |  |  |  | cive |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \text { July } \\ 6 \end{gathered}$ | Aug. 3 | Sep. 3 | Oct. 8 | Nov. 5 | Dec. 3 | Dec. 28 | $\begin{gathered} \text { Jan. } \\ 28 \end{gathered}$ | Feb. 25 | Mar. 25 | $\begin{gathered} \text { Apr. } \\ 8 \end{gathered}$ | May $4$ | June 3 |
| 0 m | 0.15 | 0.20 | 0.25 | 0.24 | 0.20 | 0.25 | 0.29 | 0.40 | 0.15 | 0.23 | 0.30 | 0.28 | 0.25 |
| 1 - | 0.15 | 0.20 | 0.25 | 0.24 | 0.20 | 0.25 | 0.29 | 0.45 | 0.28 | 0.23 | 0.30 | 0.30 | 0.24 |
| 2 - | 0.15 | 0.15 | 0.20 | 0.24 | 0.20 | 0.25 | 0.29 | 0.48 | 0.28 | 0.23 | 0.30 | 0.30 | 0.23 |
| 3 | 0.10 | 0.15 | 0.30 | 0.24 | 0.20 | 0.25 | 0.29 | 0.45 | 0.28 | 0.23 | 0.30 | 0.28 | 0.22 |
| 4 - | 0.10 | 0.20 | 0.30 | 0.24 | 0.20 | 0.25 | 0.29 | 0.45 | 0.28 | 0.23 | 0.30 | 0.28 | 0.21 |
| 5 | 0.10 | 0.25 | 0.30 | 0.24 | 0.20 | 0.25 | 0.29 | 0.48 | 0.28 | 0.23 | 0.35 | 0.28 | 0.20 |
| 6 - | 0.10 | 0.20 | 0.30 | 0.24 | 0.20 | 0.25 | 0.29 | 0.45 | 0.30 | 0.23 | 0.35 | 0.25 | 0.22 |
| 7 - | 0.10 | 0.20 | 0.20 | 0.27 | 0.20 | 0.25 | 0.29 | 0.40 | 0.30 | 0.23 | 0.35 | 0.25 | 0.22 |
| 8 - | 0.10 | 0.20 | 0.20 | 0.30 | 0.20 | 0.25 | 0.29 | 0.45 | 0.35 | 0.23 | 0.35 | 0.25 | 0.22 |
| 9 - | 0.10 | 0.30 | 0.35 | 0.85 | 0.20 | 0.25 | 0.29 | 0.50 | 0.35 | 0.23 | 0.35 | 0.28 | 0.22 |
| $10-$ | 0.20 | 0.35 | 0.45 | 1.00 | 0.20 | 0.25 | 0.29 | 0.50 | 0.40 | 0.23 | 0.35 | 0.28 | 0.22 |
| 11 - | 0.20 | 0.45 | 0.55 | 1.20 | 0.30 | 0.25 | 0.29 | 0.70 | 0.60 | 0.23 | 0.35 | 0.25 | 0.25 |
|  |  |  |  | $3-$ | in 1 | per | d of | 949 |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | July 6 | Aug. <br> 3 | Sep. <br> 3 | Oct. 8 | Nov. 5 | Dec. <br> 3 | Dec. 28 | Jan. 28 | Feb. 25 | Mar. 25 | Apr. | $\begin{gathered} \text { May } \\ 4 \end{gathered}$ | June 3 |
| 0 m | 0.005 | 0.005 | 0 | 0.005 | 0 | 0.02 | 0.045 | 0.045 | 0.070 | 0.120 | 0.03 | 0 | 0 |
| 1 - | 0.005 | 0 | 0 | 0 | 0 | 0.01 | 0.045 | 0.040 | 0.053 | 0.115 | 0.02 | 0 | 0 |
| 2 - | 0.005 | 0 | 0 | 0 | 0 | 0.015 | 0.045 | 0.035 | 0.050 | 0.115 | 0.02 | 0 | 0 |
| 3 - | 0.005 | 0 | 0 | 0 | 0 | 0.01 | 0.045 | 0.032 | 0.054 | 0.115 | 0.01 | 0 | 0 |
| 4 - | 0.005 | 0 | 0 | 0 | 0 | 0.01 | 0.045 | 0.040 | 0.075 | 0.115 | 0.02 | 0 | 0 |
| 5 - | 0.005 | 0 | 0.005 | 0 | 0.005 | 0.01 | 0.045 | 0.055 | 0.105 | 0.115 | 0.02 | 0 | 0 |
| 6 - | 0.01 | 0 | 0.005 | 0 | 0 | 0.01 | 0.045 | 0.060 | 0.120 | 0.120 | 0.02 | 0 | 0 |
| 7 - | 0.02 | 0.03 | 0.005 | 0 | 0 | 0.01 | 0.045 | 0.070 | 0.150 | 0.120 | 0.025 | 0 | 0.005 |
| 8 - | 0.05 | 0.035 | 0 | 0.005 | 0 | 0.015 | 0.045 | 0.075 | 0.200 | 0.115 | 0.030 | 0.005 | 0.005 |
| 9 - | 0.04 | 0.005 | 0 | 0 | 0 | 0.01 | 0.045 | 0.080 | 0.570 | 0.115 | 0.035 | 0.025 | 0.02 |
| $10-$ | 0.02 | 0 | 0 | 0 | 0 | 0.01 | 0.045 | 0.320 | 1.00 | 0.115 | 0.035 | 0.04 | 0.02 |
| 11 - | 0.005 | 0 | 0 | 0 | 0 | 0.005 | 0.045 | 1.70 | 1.35 | 0.115 | 0.035 | 0.043 | 0.02 |

In order to examine the correctness of this assumption I paid a visit to Grane Langsø on March 27th, 1964, with Mr. Aage Rebsdorf, Master of Science, to whom I am indebted for valuable discussions on the subject in question. At this moment the lake was covered with ice, 11 cm thick. In the Silkeborg Laboratory Mr. Rebsdorf made the analyses of ammonia (cf. Mackereth 1963) the uncertainty of which does not surpass $0.005 \mathrm{mg} \mathrm{NH}_{3}-\mathrm{N} \cdot \mathrm{l}^{-1}$. He further determined pH by means of Radiometer's pH -meter 22 , using the precision buffer $6.88\left(20^{\circ} \mathrm{C}\right)$ for adjustment, while I made the analyses of total carbon dioxide. The following results were obtained.

The quantities of ammonia did not surpass $0.1 \mathrm{mg} N H_{3}-N \cdot l^{-1}$, as might have been expected. The pH values, however, turned out surprisingly high.


It is not possible to compute the pH of the Grane Langs $\varnothing$ water, considering $\mathrm{CO}_{2}$ and $\mathrm{NH}_{3}$ as well. It is possible, however, to calculate the pH of distilled water which contains the same quantities of $\mathrm{CO}_{2}$ and $\mathrm{NH}_{3}$ as did Grane Langsø on March 27th, 1964. The values obtained in this way lie between 5.48 and 5.83 , while the values computed by the $\mathrm{CO}_{2}$ figures alone, vary between 5.23 and 5.64 . At the end of the winter stagnation period the ammonia or rather the concentration of $\mathrm{NH}_{4}^{+}$in Grane Langsø is thus able to increase pH of distilled water with $0.09-0.25$ unit. In this connection it should be mentioned, however, that the nitrification of $\mathrm{NH}_{3}$ must result in an acidification of the water. The low pH values measured in late November (cf. p. 66 and 68) may be a result of the nitrification of the quantities of $\mathrm{NH}_{3}$ liberated during the autumnal decay of the vegetation (cf. p. 26). Only regular determinations of the vertical distribution of $\mathrm{NH}_{3}$ and $\mathrm{NO}_{3}^{-}$in Grane Langs $\varnothing$ can decide the matter.

Comparing the calculated and measured pH values from March 27, 1964, it is evident that either the values measured are unreliable, or alkaline substances other than ammonia must have been present in the water. pH determinations in Grane Langsø obviously represent a difficult task. Mr. Rebsdorf has made series of electrometrical pH measurements on distilled water containing much more $\mathrm{CO}_{2}$ than the water of Grane Langsø ever did. He also made pH determinations on $\mathrm{CO}_{2}$ water highly undersaturated in relation to the atmospheric $\mathrm{CO}_{2}$ pressure. These experiments have shown that pH is altered by only a few hundreths during a determination made according to the procedure described on p. 19 .

Recalling the standard deviation $\pm 0.07$ per cent on values of total $\mathrm{CO}_{2}$ lying around $1 \mathrm{mg} \cdot \mathrm{l}^{-1}$ (c.f. p. 21), the uncertainty of pH calculated by the equations (6) or (7) can be determined to a few hundreths. Various metabolic products liberated by the bacterial decomposition of dead organisms in the lake undoubtedly influence the $\mathrm{CO}_{2}$ system perceptibly on some occasions, as mentioned above. Therefore $p H$ is stated with one decimal only in the Survey of the Analyses (p.91-107). In addition for the period October 1960 to July 1961 the pH values measured by means of precision buffer solutions and two new glass electrodes are given in brackets in the Survey, unless they are stated in the text.

Fig. 17 demonstrates that Grane Langso is an acid lake, as pH values above 6


Fig. 17. The distribution of the pH values calculated from Grane Langsø. Note the logarithmic scale of the abscissa.
never occurred in the central part of the lake. The extremes are 4.9 and 5.9 , computed respectively from August 28 th, 1960, at a depth of 11 m , and July 21st, 1959, at a depth of 6 m . The greatest number of pH values lies within the interval of 5.4-5.7, 87 per cent of the 545 calculations falling within this region. The greatest number of pH values measured electrometrically lay within the interval of 5.6-5.7.

As the quantities of $\mathrm{HCO}_{3}^{-}$lie between 0.1 and $0.7 \mathrm{mg} \cdot \mathrm{l}^{-1}$, corresponding to $\mathrm{HCO}_{3}^{-}$alkalinities of only $0.002-0.01 \mathrm{mval} \cdot \mathrm{l}^{-1}$, Grane Langs $\varnothing$ must be characterized as a weakly buffered lake. One would expect a water of this type to exhibit great pH fluctuations. This is, however, not true as evident from Table 27.

The yearly pH fluctuations exhibited identical values in each of the 3 years of investigation, viz. 0.9 pH unit (according to the electrometrical pH measurements 0.87 pH unit). In the very shallow water between the hydrophytes of the littoral zone, the pH fluctuations during the summer half are assumed to be considerably greater.

During the circulation periods the pH differences at the various levels are 0 or a few hundreths. In the stagnation periods considerable differences occur simultaneously within the single vertical pH series. The largest difference was calculated

Table 27. The yearly fluctuations of pH in the central part of Grane Langs $\varnothing$.

| Periods | Yearly extremes of pH | Fluctuation |
| :---: | :---: | :---: |
| August 1958. | 5.0 (August) | 0.9 |
| - July 1959 | 5.9 (July) |  |
| August 1959. | 5.0 (August) | 0.9 |
| - July 1960 | 5.9 (July) |  |
| August 1960. | 4.9 (August) | 0.9 |
| - July 1961 | 5.8 (April and June) |  |

on July 27 th, 1960 , when pH was 5.9 and 5.1 in the subsurface depths of 4 m and 11 m , respectively. The hydrogen ion concentration at 11 m was concequently quite 6 times as great as that at 4 m .

A detailed study of the Survey of the Analyses on p. 91 reveals several patterns of the vertical pH distribution in Grane Langsø during the summer and winter stagnation periods.

For the summer stagnation period it is possible to distinguish between two types (cf. Fig. 18):
(i) pH is almost constant from the surface to a subsurface depth of 6 m or 8 m , after which pH is falling to a minimum at a depth of 11 meters. This clinograde pH type always occur at the end of August, just before ciau. It is, however, also commonly met with in June. Under certain conditions, such as low transparency (July 27th, 1960) or vigorous water circulation due to a windy period (July 9th, 1961), the clinograde pH curve is also found in July.
(ii) pH is nearly constant from the surface to 4 m or 6 m depth, while a pH


Fig. 18. Patterns of the vertical pH distribution in Grane Langsø during the summer stagnation periods of 1958,1959 , and 1960.


Fig. 19. Patterns of the vertical pH distribution in Grane Langso during the winter stagnation period of 1959.
maximum is lying in a subsurface depth of 6 m or 8 m , after which the pH values decrease to a minimum at 11 m . This positive heterograde pH type is characteristic of July. It also occurs in the first half of May (May 14th, 1960) and, more rarely, in June.

The vertical pH distribution of the winter stagnation period is similar to that of the summer stagnation period, (cf. Fig. 19). The type of February 8th, is very rare, however; only one further example, from January 22nd, 1961, is known. The pH-type in winter is nearly always clinograde. The slope of these clinograde hibernal pH graphs is considerably steeper than that of the aestival graphs.

The two patterns of vertical pH distribution are probably due to the interaction of the $\mathrm{CO}_{2}$ consumers and the ordinary $\mathrm{CO}_{2}$ producing factors. The $\mathrm{CO}_{2}$-consumers are the phytoplankton and the hydrophytes, especially Nitella growing at a subsurface depth of 11 meters. The ${ }^{14} \mathrm{C}$-determinations of primary production by the plankton algae have shown that within the period March-July the greatest daily photosynthesis can occur at all levels from $0-11 \mathrm{~m}$, depending on the illumination during the experimental day and the quantitative vertical distribution of the plankton-organisms. The maximum productivity is often found in a subsurface depth of $4-6 \mathrm{~m}$. The photosynthesis of Nitella flexilis considerably surpasses its respiration already in late March.

The vigorous $\mathrm{CO}_{2}$ uptake during photosynthesis in the summer stagnation period with intense light must have the effect of increasing pH , especially in the depths of $4-6 \mathrm{~m}$. When covered with ice the lake exhibits an extremely small photosynthesis activity, relatively considerable only in the uppermost water-layers and then only in March.

As it may be difficult from the Survey of the Analyses on p. 91-107 to get an idea of the seasonal pH variations during the three years' investigations, the average pH has been computed as a simple arithmetic average of the 7 pH values of each column. pH being a logarithmic function of $\left[\mathrm{H}^{+}\right]$, such a calculation is incorrect, of course. A comparison with the results obtained by the adequate method of calculation

$$
\left[\mathrm{H}^{+}\right]=\frac{2\left(\bar{x}_{0-2}+\bar{x}_{2-4}+\bar{x}_{4-6}+\bar{x}_{6-8}+\bar{x}_{8-10}\right)+\bar{x}_{10-11}}{11} ; \quad \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]
$$

where $\bar{x}_{0-2}$ stands for the average of $\left[\mathrm{H}^{+}\right]$in 0 m and 2 m , etc., demonstrates the differences to be only a few hundreths.

On February 8th, 1959 , the mutual differences between the pH values from the various levels amounted to 0.5 pH unit. Only 7 of the 70 vertical pH series exhibit differences as big as $0.5-0.8$ units within the single series. The remaining pH series were much more uniform. The arithmetic average of February 8th, 1959, was pH 5.42 , thus 0.03 smaller than pH calculated in accordance with the expression above for $\left[\mathrm{H}^{+}\right]$, which gave the result pH 5.45 . During the circulation periods the differences are smaller than 0.01 pH unit. Therefore Fig. 20 has been drawn on the basis of the arithmetic means of the individual columns.

Fig. 20 shows that two yearly $p H$ maxima occur in the central part of Grane Langsø, one with pH values between 5.6 and 5.75 in the first or second month after cive (April, rarely in May), the other with pH -values between 5.55 and 5.7 in the fourth month, rarely the fifth one after cive (July, exceptionally in June). These maxima are no doubt connected with the photosynthetic activity of the phytoplankton, an assumption to be returned to in a future paper.

The lowest $p H$ values, $5.35-5.45$, of the three years' investigations lay in the month before cive, which was normally February and rarely April. The secondary pH minimum, $5.5-5.6$, as a rule occurred in the third month after cive (May). During the long period of autumnal circulation, lasting for at least 4 months, pH was rather constant, nearly always fluctuating from about 5.5 to 5.55 .

In order to see whether a remarkable lake as Grane Langso differs from other Danish waters concerning its annual pH fluctuations, monthly electrometrical pH determinations in 1950-51 from lake Gribso, the turf-pit Kattehale Mose, and the 5 m deep pond Frederiksborg Slotssø are given in the Tables 28, 29, and 30. Lake Gribs $\varnothing$ was furthermore subjected to a detailed pH investigation in 1949-50.

It is evident from Figs. 18-19 and the review on p. $72-73$ that the pH graphs of the winter stagnation period normally were clinograde in Grane Langs $\varnothing$, whereas positive or alkaline heterograde graphs and clinograde graphs characterized the lake in the summer stagnation period. The likewise acid but humic lake Gribsø exhibits another pH type in both stagnation periods, as demonstrated by Table 28 (cf. Aberg and Rodhe 1942, p. 192; Hutchinson 1957, p. 604).



Fig. 20. The yearly fluctuations of pH in Grane Langsø. An individual pH value represents the arithmetic mean of the 7 calculated values from a vertical series. Circulation periods are indicated by oppositely directed arrows, ice-periods by horizontal hatched columns.

As regards the yearly pH fluctuations of the bottom water, lake Gribso is characterized by showing its highest pH value, 6.45 , in -1 . ciau (October) and so at the end of summer stagnation. At the autumnal overturn, normally in the first half of November, a marked fall of pH took place, after which pH gradually declined to the smallest value of the year, 4.45 , occurring in -1 . cive (February) and so during winter stagnation. This means an annual pH-amplitude of no less than 2 pH-units. A secondary maximum, pH 6.25 , was observed in -4 . ciau (August), and a secondary minimum, pH 4.85 , occurred in cive +3 . (May-June).

The pH fluctuations of the surface water of Gribse, 0.4 pH units, were far smaller than those of the bottom water. The highest value of $1949-50, \mathrm{pH} 5.35$, occurred in

Table 28. pH -fluctuations of Lake Gribsø in 1949-50.


Table 28 continued ( $1950-51$ ).

|  |  |  |  | -1 ci |  |  |  |  |  |  |  |  |  | 4 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | June 15 | $\begin{gathered} \text { July } \\ 28 \end{gathered}$ | Aug. 3 | Oct. 18 | Nov. 13 | Dec. <br> 12 | $\begin{gathered} \text { Jan. } \\ 15 \end{gathered}$ | $\begin{gathered} \text { Feb. } \\ 14 \end{gathered}$ | Mar. 8 | Apr. <br> 10 | May <br> 10 | June 11 | July 9 |  |
| 0 - | 5.20 | 5.25 | 5.25 | 5.27 | 5.26 | 4.98 | 4.80 | 4.92 | 4.77 | 4.62 | 4.68 | 4.82 | 4.79 |  |
| 1 - | 5.15 | 5.25 | 5.25 | 5.25 | 5.23 | 4.98 | 4.87 | 4.93 | 4.68 | 4.60 | 4.71 | 4.81 | 4.85 |  |
| 2 - | 5.15 | 5.25 | 5.25 | 5.28 | 5.20 | 4.97 | 4.71 | 4.72 | 4.72 | 4.61 | 4.72 | 4.82 | 4.90 |  |
| 3 - | 5.15 | 5.15 | 5.20 | 5.30 | 5.20 | 4.98 | 4.57 | 4.54 | 4.58 | 4.60 | 4.63 | 4.82 | 4.91 |  |
| 4 - | 5.10 | 5.15 | 5.20 | 5.23 | 5.21 |  |  |  |  | 4.58 | 4.48 | 4.59 | 4.61 |  |
| 5 - | 5.05 | 4.95 | 5.10 |  | 5.22 |  |  | 4.69 |  | 4.59 | 4.46 | 4.50 |  |  |
| 6 - | 5.00 | 4.95 | 5.00 |  | 5.21 |  |  |  |  | 4.62 | 4.62 | 4.49 | 4.50 |  |
| 7 - | 4.95 | 5.05 | 5.10 |  | 5.23 |  |  | 4.65 |  | 4.60 | 4.51 | 4.51 |  |  |
| 8 - | 4.90 | 5.05 | 5.70 |  | 5.23 |  |  |  |  | 4.60 | 4.58 | 4.53 | 4.56 |  |
| 9 - | 4.90 | 5.10 | 5.70 |  | 5.25 |  |  | 4.20 |  | 4.61 | 4.59 | 4.52 | 4.70 |  |
| $10-$ | 4.90 | 5.65 | 5.85 |  | 5.24 |  |  | 4.32 |  | 4.58 | 4.56 | 4.63 | 4.87 |  |
| 11 - | 5.00 | 5.95 | 5.85 |  | 5.21 |  |  | 4.44 |  | 4.60 | 4.75 | 4.67 | 5.00 |  |
| average | 5.04 | 5.23 | 5.37 |  | 5.22 |  |  | 4.60 |  | 4.60 | 4.61 | 4.64 | 4.77 |  |

Table 29. pH fluctuations of Kattehale Mose in 1950-51.

-5 . ciau (June-July, possibly identical with cive +3 . of 1949 ); the lowest one, pH 4.95, occurred in cive +1 . (March).

In the period $1950-51$ the absolute pH maximum, 5.25 , was observed in the long period from July to November. The secondary maximum, pH 4.82, occurred in cive +3 . (June). The smallest pH value, 4.62 , was measured in cive +1 . (April) also in 1950-51.

Gribsø grew more and more alkaline from June to October 1949, the arithmetic pH mean increasing from 5.22 to 5.59 (cf. Fig. 21). The average then declined to the absolute minimum, pH 4.85 , in March. This arithmic mean is, of course, far more influenced by the pH values of the bottom water than by those of the surface water. Gribsø in its entirety was more acid, $\mathrm{pH} 4.60-4.77$, in spring and early summer of 1951 than in the same period of 1950 , when pH varied between 5.0 and 5.2 .

The vertical distribution of $p H$ in Gribsø is, during summer stagnation, quite different from that in Grane Langsø. At the beginning of the two stagnation periods

Table 30. Frederiksborg Slotssø, pH fluctuations in 1950-51.


Table 30 continued.

|  | cive |  |  | $+1$ |  | $+2$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Apr. <br> 3 | Apr. $14$ | Apr. <br> 25 | $\begin{gathered} \text { May } \\ 3 \end{gathered}$ | $\begin{gathered} \text { May } \\ 15 \end{gathered}$ | $\begin{gathered} \text { May } \\ 26 \end{gathered}$ | $\begin{gathered} \text { June } \\ 4 \end{gathered}$ | June 18 | July 2 |
| 0.1 m . | 7.48 | 8.37 | 9.12 | 8.93 | 9.01 | 9.10 | 9.37 | 9.55 | 9.32 |
| 0.5 - | 7.49 | 8.37 | 9.11 | 8.92 | 9.02 | 9.10 | 9.42 | 9.54 | 9.32 |
| 1 m . | 7.48 | 8.36 | 9.11 | 8.87 | 9.02 | 9.10 | 9.32 | 9.45 | 9.32 |
| 2 - | 7.42 | 8.36 | 9.10 | 8.78 | 9.01 | 8.96 | 8.56 | 9.18 | 9.32 |
| 3 - | 7.32 | 8.34 | 8.96 | 8.67 | 9.02 | 8.57 | 8.22 | 8.68 | 9.24 |
| 4 - | 7.09 | 8.34 |  | 7.86 |  |  | 7.88 |  |  |
| 5 - | 6.80 | 8.35 |  | 7.57 |  |  | 7.39 |  |  |

the pH graph of Gribsø is always clinograde, but then grows gradually negative or acid heterograde. It is noteworthy that the water layer exhibiting the lowest pH value is also shifted upwards during summer and winter stagnation. $\AA$ berg and Rodhe (1942, p. 223) have pointed out that the smallest value of the vertical pH series from lake Skärshultsjön is shifted upwards during summer stagnation. This slightly acid lake exhibits a specific conductivity nearly identical with that of Grane Langsø, but its water is brown like that of Gribsø. The specific conductivity of the surface water of Gribsø fluctuated around 130 reciprocal megohms (cf. Berg and Clemens Petersen 1956, p. 139). On January 28th, 1950, it amounted, however, to 273 reciprocal megohms for the 11 m layer.

Krogh and Lange's pH determinations from lake Furesø (1931, p. 33) and those made by Nygatrd (cf. Berg et al. 1958, p. 102) do not allow reliable conclusions, either on the shape of the pH graphs in the stagnation periods, or on the occurrence of the maxima and minima of pH .

Sigurd Olsen made regular pH determinations in the permanently alkaline and large ponds Lyngby $\mathrm{S}_{\varnothing}$ and Bagsværd $\mathrm{S}_{\varnothing}$ (1955, p. 89-90). The highest values occurred in July or August, whereas somewhat smaller ones were measured in April or June. The deepest pH minimum was observed in November or December; a secondary minimum occurred in March.


Jun. July Aug. Sep. Oct. Nov. Dec. Jan. Feb. Mar. Apr. May Jun. July Aug.
Fig. 21. The yearly fluctuations of pH in lake Gribsø. An individual pH value represents the arithmetic mean of the 12 measurements from a vertical series. The onset of the autumnal and vernal circulation is indicated by oppositely directed arrows. The lake was icebound from about January 7 th to March 15 th, 1950.

Nygatrd examined how pH fluctuated in the surface water of 14 North Zealandic ponds (1938, p. 542). The majority of the alkaline and moderately acid ponds exhibited two annual pH maxima, one in July or August, the other in April or May. The lowest pH values usually were observed in October-November or FebruaryMarch. A rise of pH occurred in all the ponds except one, shortly after the ice had been broken up.

The results of these two investigations on the yearly pH fluctuations agree very well with the results obtained from Grane Langs. A pH minimum in late November, due to acid-reacting substances other than $\mathrm{CO}_{2} \mathrm{aq}$, may be proved in Grane Langso by reliable methods for measuring pH (cf. p. 68).

The results from Grane Langsø, Gribsø, Kattehale Mose, and Frederiksborg Slotssø are outlined in Table 31. Besides the Danish waters, the North American Lake Mendota, Wisconsin, is also treated. Juday, Fred, and Wilson (1924) made fortnightly pH determinations in this lake by a colorimetric method throughout three years. Considering the measurements from the first two years, where the samples were taken at depths of $0,5,10,15,20$, and 22 m , I suppose that the great majority of the pH graphs may have been clinograde. A positive heterograde vertical distribution of pH seems to be very rare; it occurred on March 14th, 1922.

It seems to be a characteristic feature for Grane Langsø that its surface water

Table 31. The occurrence of maxima and minima of pH in various waters.

|  |  | Surface | Water | Bottom | Water |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | pH-maxima | pH-minima | pH-maxima | pH-minima |
| Lake <br> Grane <br> Lang- <br> sø | $\left\lvert\, \begin{gathered} \text { March } 1958 \\ \text { - July } 1958 \end{gathered}\right.$ |  |  |  | -1. cive (April) |
|  | August 1958 - July 1959 | -2. ciau (July) <br> cive +1. (March) |  | \|cive +1. (March) | -1. ciau (Aug.) <br> -1. cive (Febr.) |
|  | $\left\{\begin{array}{l} \text { August } 1959 \\ - \text { July } 1960 \end{array}\right.$ | $\begin{array}{\|l\|} \hline-2 . \text { ciau (July) } \\ \hline \text { cive }+1 . \text { (April) } \\ \hline \end{array}$ | $\frac{\mid \text { cive }+1 . \text { (March) } \mid}{\text { ciau }+1 . \text { (Sept.) }}$ | cive +1. (April) | $\begin{array}{\|c\|} \hline-1 . \text { ciau (Aug.) } \\ \hline-2 . \text { to }-1 . \text { cive } \\ \text { (Febr.-March) } \\ \hline \end{array}$ |
|  | - August 1960 | $\frac{-2 . \text { ciau (June) }}{\text { cive }+3 .(\text { April) }}$ | cive +1. (Febr.) | cive +2. (April) | -1. ciau (Aug.) <br> (Jan. - February) |
| Lake <br> Grib- <br> sø | $\text { ( June } 1949-1 \text { June } 1950$ | $\begin{aligned} & \hline-5 . \text { ciau }=\text { cive }+3 . \\ & \text { (June-July) } \end{aligned}$ | cive +1. (March) | -1 . ciau (Oct.); <br> -4. ciau (August) | $\mid-1$. cive (Febr.) <br> cive +3 . (May- <br> June). |
|  | $\begin{aligned} & \text { July } 1950- \\ & \text { July } 1951 \end{aligned}$ | cive +3 . (June) | cive + 1. (April) |  |  |
| Lake Mendota | $\left\lvert\, \begin{aligned} & \text { August } 1919 \\ & \text {-August } 1920\end{aligned}\right.$ | -3 . ciau to ciau +3 . <br> (Aug. to Febr.); <br> cive +2 . and +3 . <br> (June and July). | ```-1. cive (March); cive +4. (July- August).``` | $\begin{aligned} & \text { ciau }+1 \text {. } \text { (Nov.); } \\ & \hline \text { cive }+1 . \text { (April) } \end{aligned}$ |  |
|  | $\left\{\begin{array}{l} \text { Sept. } 1920 \\ \text { - Oct. } 1921 \end{array}\right.$ | -3. ciau to ciau (Aug. to Oct.); <br> -2 . cive and -1 . cive (Jan. and Febr) | ciau to ciau +2 . <br> (Nov. to Jan.); cive to cive +4 . <br> (March to July). | ciau +1. and +2. <br> (Nov.-Jan.) $;$ <br> cive +1. (March- <br> April) | $\begin{array}{\|c\|} \hline-1 . \text { ciau (Sept.) } \\ \hline-2 . \text { and }-1 \text {. cive } \\ \text { (February) } \\ \hline \end{array}$ |
| Katte- <br> hale <br> Mose | $\left\{\begin{array}{l}\text { July 1950- } \\ \text { July } 1951\end{array}\right.$ | -1. ciau (Sept.); ciau +3 . (Dec.). | cive +1. and +2. <br> (April and May) <br> ciau +2 (Nov.). | $\begin{aligned} & \text { ciau }+3 \text {. (Dec.) } \\ & -3 \text {. ciau (July) } \end{aligned}$ | $\begin{aligned} & -2 . \text { cive (Febr.) } \\ & \text { ciau }+2 \text {. (Nov.) } \end{aligned}$ |
| Frede- <br> riks- <br> borg <br> Slots- <br> sø | $\text { \| } \begin{aligned} & \text { July } 1950- \\ & \text { July } 1951 \end{aligned}$ | cive +3 . (June <br> -1 . ciau (August). | - 2. cive (March). |  | -1. cive (April) |

usually develops two yearly pH maxima, lying in -2 . ciau (July or June) and cive +1 . (March or April). An annual pH -minimum is likewise situated in cive +1 . (February or March), in which feature it is similar to lake Gribs $\varnothing$. A pH maximum often seems to occur in cive +3 . In Gribsø; the same is observed in Grane Langsø. In the case of Lake Mendota, it is difficult to recognize general features as to the occurrence of maxima and minima confined to its surface water.

Regarding the bottom water Grane Langs $\varnothing$ is characterized by having a pH maximum in cive +1 . (March or April); this also happens in Lake Mendota. The pH minima occurred in -1 . cive (January-April) and -1. ciau (August). In these points Grane Langsø highly resembles Lake Mendota, but also in lake Gribsø, Kattehale Mose, and Frederiksborg Slotssø the minima can occur in -1 . or -2 . cive.

It seems to be a recurrent event in the eutrophic and permanently alkaline Lake Mendota for one of the two yearly pH maxima of its bottom water to occur in ciau +1 . (November), an event never observed in the continuously acid lakes Grane Langsø and Gribsø.

The survey of Table 31 may be simplified as follows:

## Surface waters

The pH-maxima most frequently occurred in the second month before ciau, but also possibly the first one. Maxima were further observed in the third month after cive.

## Bottom waters

The $p H$ maxima most frequently lay in the first month after cive.

The pH minima were most often observed in the first month after cive.
-

The $p H$ minima generally were found in the first month before cive, possibly the second one. Minima were also observed in the first month before ciau.

## 13. The Hydrogen Carbonate Ion

The quantities of $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ have been calculated with the aid of the equation on p. 57:

$$
\log c_{\mathrm{HCO}}^{\overline{3}}, ~=-\mathrm{pH}
$$

If the uncertainty of the pH calculations as estimated is $\pm 0.1$ unit, the uncertainty of the $\mathrm{HCO}_{3}^{-}$quantities approximates 35 per cent, as shown on p. 47. The $\mathrm{HCO}_{3}^{-}$values stated in Survey of the Analyses on p. 91 are given with one decimal place.

As pH has not always been measured electrometrically by a safe method I


Fig. 22. The distribution of the results from the calculation of the hydrogen-carbonate ion in Grane Langsø. Note the logarithmic scale of the abscissa.
think it not being advisable to treat the subject $\mathrm{HCO}_{3}^{-}$in such detail as that of carbon dioxide.

As previously mentioned the alkalinity of Grane Langsø must be very small, since the titration values approached nil (cf. p. 17). This conclusions has been entirely confirmed by the results obtained with the aid of Krogh and Rehberg's method for determining total carbon dioxide. About 94 per cent of the total number of $\mathrm{HCO}_{3}^{-}$ calculations (492) from Grane Langsø lay between 0.1 and $0.3 \mathrm{mg} \mathrm{HCO}-{ }_{3}^{-} \cdot l^{-1}$ (cf. Fig. 22), corresponding to alkalinity values between 0.002 and $0.005 \mathrm{mval} \cdot \mathrm{l}^{-1}$. The highest value ever calculated amounted to $0.7 \mathrm{mg} \cdot \mathrm{l}^{-1}$ or an alkalinity of $0.01 \mathrm{mval} \cdot \mathrm{l}^{-1}$.

The titration alkalinity of water from the hydrogen-carbonate lake Fures $\varnothing$ varies around 2.6 mval $\cdot \mathrm{l}^{-1}$ according to Brønsted and Wesenberg-Lund (1912, p. 448). Krogh und Lange (1931, p. 33) and Jonasson and Mathiesen (1959, p. 159) found values about $2.3 \mathrm{mval} \cdot \mathrm{l}^{-1}$. The alkalinity values of Grane Langs $\varnothing$, stated as hydrogencarbonate ion concentration, amount to about $0.0025 \mathrm{mval} \cdot \mathrm{l}^{-1}$, thus nearly one thousand times smaller than those of lake Furesø.

The yearly fluctuations of the ion in question during a period of 3 years are given in Table 32.

The difference between the lowest and highest value of the individual years thus fluctuates only between 0.5 and $0.6 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$, being on an average 0.6 mg .

The greatest difference between the extremes within a single vertical series amounts to about $0.5 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$, as shown in Table 33 . The amplitudes of the various

Table 32. The yearly fluctuations of the quantities of $\mathrm{HCO}_{3}^{-}$, stated as $\mathrm{mg} \cdot \mathrm{l}^{-1}$, in Grane Langsø.

| Period | Yearly extremes of $\mathrm{HCO}_{3}^{-}$ | Fluctuation |
| :---: | :---: | :---: |
| March 1958 <br> - July 1958 | $\begin{aligned} & 0.1\left\{\begin{array}{l} (\text { May 26th, 2 m, 6 m, 8 m) } \\ \begin{array}{l} \text { (June 18th, } 8 \mathrm{~m}) \\ (\text { July 2nd, } 6 \mathrm{~m}) \end{array} \\ 0.5 \quad \text { (April 5th, } 11 \mathrm{~m}) \end{array}\right. \end{aligned}$ | 0.4 |
| $\begin{aligned} & \text { August } 1958 \\ & \text { - July } 1959 \end{aligned}$ | 0.1 (July 21st, 6 m ) <br> 0.6 (August 24th, 11 m ) | 0.5 |
| $\begin{aligned} & \text { August } 1959 \\ & \text { - July } 1960 \end{aligned}$ | $\begin{aligned} & 0.1\left\{\begin{array}{l} \left(\begin{array}{l} \text { May } 14 \mathrm{th}, 6 \mathrm{~m}) \\ (\text { July } 27 \mathrm{th}, 4 \mathrm{~m}) \end{array}\right. \\ 0.7 \end{array} \text { (August 23rd, } 11 \mathrm{~m}\right. \text { ) } \end{aligned}$ | 0.6 |
| August 1960 <br> - July 1961 | $\begin{aligned} & 0.1\left\{\begin{array}{l} \left(\begin{array}{l} \text { April 23rd, } 8-10 \mathrm{~m}) \\ (\text { June } 15 \mathrm{th}, 0-6 \mathrm{~m}) \end{array}\right. \\ 0.7 \end{array} \text { (August 28th, } 11 \mathrm{~m}\right) \end{aligned}$ | 0.6 |

Table 33. The greatest annual amplitudes, stated as $\mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$, within the single vertical series of Grane Langsø.

| Winter stagnation <br> period | Greatest <br> difference | Summer stagnation <br> period | Greatest <br> difference |
| :--- | :---: | :---: | :---: |
| April 5 th, $1958 \ldots \ldots \ldots \ldots$ | $0.5-0.2=0.3$ | August 24 th, $1958 \ldots \ldots$ | $0.6-0.2=0.4$ |
| February 8 th, $1959 \ldots \ldots \ldots$ | $0.5-0.2=0.3$ | August 23 rd, $1959 \ldots \ldots$ | $0.7-0.2=0.5$ |
| January 31 st, $1960 \ldots \ldots \ldots$ | $0.3-0.2=0.1$ | August 28 th, $1960 \ldots \ldots$ | $0.7-0.2=0.5$ |
| February 12th, $1961 \ldots \ldots \ldots$ | $0.4-0.2=0.2$ | July 9 th, $1961 \ldots \ldots \ldots$ | $0.4-0.1=0.3$ |

years are about 0.1 to $0.3 \mathrm{mg} \cdot \mathrm{l}^{-1}$ in the winter stagnation period, and about 0.3 to $0.5 \mathrm{mg} \cdot \mathrm{l}^{-1}$ in the summer stagnation period.

The vertical distribution of $\mathrm{HCO}_{3}^{-}$was orthograde, of course, in the circulation periods, and always inverse clinograde in the winter stagnation period. In the summer stagnation period the vertical distribution was either negative heterograde, the minimum occurring in subsurface depths of $4 \mathrm{~m}, 6 \mathrm{~m}$, or 8 m , or inverse clinograde, the latter being always observed at the end of the period (August). The negative heterograde distribution, often established in June and July, is connected with the relatively strong photosynthetic activity of the plankton algae in the subsurface depths mentioned.

## 14. The Movement of a Winter Thermocline

After a detailed examination of the thermal conditions and the stratification of total carbon dioxide during the winter stagnation period of 1960 (see p. 101 and Fig. 11), it is suggested that a thermocline has moved upwards to the ice from the deeper levels in Grane Langsø. Fig. 23 should illustrate this assumption.



Fig. 23. Above: the vertical distribution of total $\mathrm{CO}_{2}$ in Grane Langso during the ice-period of 1960. Below: the thermal conditions in this pe-
riod. The figures to the left of the graphs represent values of $\frac{d \theta}{d z}$, the temperature difference between two levels divided by the distance in

The lake was nearly homogeneous as to temperature and total $\mathrm{CO}_{2}$ before the ice-cover. At the beginning of January 1960 the lake had frozen over. On January 17 th an upper thermocline, $\frac{d \theta_{z}}{d z}=0.65$, between 0 and 2 m , and a lower thermocline, $\frac{d \theta_{z}}{d z}=0.50$, between 6 and 8 m , were established.

During the two following months $\frac{d \theta_{z}}{d z}$ of the upper thermocline steadily increased up to 1.60 on March 13th. Regarding the lower-thermocline, the $\frac{d \theta_{z}}{d z}$ values of the $6-8 \mathrm{~m}$ level decreased to 0 on March 13th, whereas the $\frac{d \theta_{z}}{d z}$ values of the $4-6 \mathrm{~m}$ level were steadily increasing from 0.05 in January to 0.20 on March 13 th. These facts demonstrate a shift upwards of the lower thermocline. Unfortunately no observations were possible between March 13th and 26th, when the lake became open. Temperature measurements of previous years seem, however, to indicate a further raising of the lower thermocline at the end of the ice-cover.

Table 34 indicates an increase of the $\frac{d \theta_{z}}{d z}$ value for the $0-1 \mathrm{~m}$ layer from 1.6 to 2.0 in March-April 1958, while the corresponding value for the $1-2 \mathrm{~m}$ layer simultaneously decreases from 1.1 to 0.4 .

Table 34. The position of the thermoclines in Grane Langsø at the end of the winter stagnation period in 1958 and 1951.

| $z$ | March 9, 1958 Ice 10 cm thick |  |  | April 5, 1958 <br> Ice 20 cm thick |  |  | March 29, 1951 Ice 15 cm thick |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\theta_{z}$ | $\frac{d \theta_{z}}{d z}$ | mg $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ | $\theta z$ | $\frac{d \theta_{z}}{d z}$ | mg $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ | $\theta z$ | $\frac{d \theta z}{d z}$ | $\begin{gathered} \mathrm{mg} \\ \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1} \end{gathered}$ |
| $0 \mathrm{~m} \ldots \ldots \ldots \ldots$ | $0.2^{\circ}$ | 1.6 | 0.2 | $1.1^{\circ}$ | 2.0 | 0.2 | $1.3^{\circ}$ | 3.2 |  |
| $1-\ldots \ldots \ldots$ | $1.8^{\circ}$ |  |  | $3.1{ }^{\circ}$ | 0.4 |  | $4.5^{\circ}$ | $0$ |  |
| $2-\ldots \ldots \ldots$ | $2.9^{\circ}$ | 1.1 | 0.2 | $3.5^{\circ}$ |  | 0.2 | $4.5^{\circ}$ |  |  |
| $3-\ldots \ldots \ldots$ | $3.1^{\circ}$ | 0.2 |  | $3.7^{\circ}$ | 0.2 |  | $4.4{ }^{\circ}$ | $0.1$ |  |
| $4-\ldots \ldots \ldots$ | $3.3^{\circ}$ | 0.2 | 0.2 | $3.7^{\circ}$ | $0$ | 0.2 | $4.4^{\circ}$ | $0$ |  |
| $5-\ldots \ldots$. |  | 0.1 |  | $3.8^{\circ}$ | 0.1 |  | $4.4{ }^{\circ}$ | $0$ | unknown |
| 6-.......... | $3.5{ }^{\circ}$ |  | 0.2 | $4.0^{\circ}$ | 0 | 0.3 |  | 0 |  |
| $7-\ldots \ldots$. |  | 0.2 |  |  |  |  | $4.4{ }^{\circ}$ |  |  |
| $8-\ldots \ldots .$. | $3.9{ }^{\circ}$ |  | 0.3 | $4.0^{\circ}$ |  | 0.3 |  | 0 |  |
| 9-......... |  | 0.1 |  |  | 0.05 |  | $4.4^{\circ}$ | $0$ |  |
| 10-....... | $4.1^{\circ}$ | 0 | 0.3 | $4.1^{\circ}$ | 0.25 | 0.3 | $4.4{ }^{\circ}$ |  |  |
| 11 - | $4.1^{\circ}$ |  | 0.4 | $4.35{ }^{\circ}$ |  | 0.5 | 5.0*) | 0.75 |  |

*) in 10.8 m depth.

Conditions on March 29th, 1951, represent the final stage just before the tender ice was breaking up. Here the $\frac{d \theta_{z}}{d z}$ value for the $0-1 \mathrm{~m}$ layer is large, 3.2 , while the $1-2 \mathrm{~m}$ value has decreased to 0 , indicating that the lower thermocline has now joined with the upper thermocline.

The solar radiation on March 29th, 1951, and the preceding days contributed to the heating to $4.5^{\circ} \mathrm{C}$ of the $1-2 \mathrm{~m}$ water layer below the ice. Heat given off from the bottom sediments can create vertical currents; how high up in the lake they will reach depends on their densities. The third way in which the water volume below the ice is warmed up is referred to by Hutchinson (1957, p. 454 and 456). Centripetal melt water currents from the ice margin run on mild days across the sloping lake bottom, taking up electrolytes and so increasing in density.

On the bright days around March 29th, 1951, a zone about 10 m broad of icefree water was formed each afternoon along the margin of Grane Langsø; next morning this zone had frozen over again. On the data in question the water from 10.8 m measured $5^{\circ} \mathrm{C}$. This water from about 0.7 m above the lake bottom must have a greater density than the water from $10 \mathrm{~m}\left(4.4^{\circ} \mathrm{C}\right)$, in spite of its higher temperature.

Temperatures of more than $4^{\circ} \mathrm{C}$ below ice have been observed in the 11 m layer of Grane Langsø in $1951\left(5^{\circ} \mathrm{C}\right), 1958\left(4.35^{\circ} \mathrm{C}\right), 1959\left(4.4^{\circ} \mathrm{C}\right)$, and $1960\left(4.3^{\circ} \mathrm{C}\right)$.

As one $\mathrm{mg} \mathrm{HCO}=3 \cdot{ }^{-1}$ increases the density of distilled water by 0.0000018 , it is possible to calculate the density changes from distilled water, caused by the $\mathrm{HCO}_{3}^{-}$ quantities met with on April 5th, 1958 (Hutchinson 1957, p. 676 and 204-205).

Table 35 gives the reader an idea of the density changes of the Grane Langsø water, caused exclusively by $\mathrm{HCO}_{3}^{-}$at the end of the winter stagnation. It is evident that ions other than $\mathrm{HCO}_{3}^{-}$have been liberated from the bottom deposits to the 10 m and 11 m layers in greater quantities than to the other water layers. As the concentrations of the other ions are unknown for the series of April 5th, 1958, it is not possible to comment on the real densities at the various levels of Grane Langs $\varnothing$, except that all the figures must be larger than those stated in Table 35. It is possible that the

Table 35. The density increase from distilled water, caused by the quantities of $\mathrm{HCO}_{3}^{-}$in Grane Langsø on April 5th, 1958.

| depth | temp. | density of pure water | $\mathrm{mg} \mathrm{HCO}-{ }_{3}^{-} \cdot \mathrm{l}^{-1}$ | $\begin{aligned} & \text { density of pure water } \\ & +\mathrm{HCO}_{3}^{-} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |
| 0 m . | 1.1 | 0.9999315 | 0.2 | 0.9999319 |
| 2 - | 3.5 | 0.9999981 | 0.2 | 0.9999985 |
| 4 - | 3.7 | 0.9999994 | 0.2 | 0.9999998 |
| 6 - | 4.0 | 1.0000000 | 0.3 | 1.0000005 |
| 8 - | 4.0 | 1.0000000 | 0.3 | 1.0000005 |
| $10-$ | 4.1 | 0.9999999 | 0.3 | 1.0000004 |
| 11 - | 4.35 | 0.9999989 | 0.5 | 0.9999998 |



Fig. 24. The movements of the low-lying thermoclines in Grane Langsø. The pairs of vertical arrows stand for the circulation periods. The short horizontal lines represent the average depths of the thermoclines. The broken lines indicate the probable movements of the thermoclines.
increase of the $\frac{d \theta_{z}}{d z}$ values for the $10-11 \mathrm{~m}$ layer from 0 to 0.75 (see Table 34) are due to "chemical density currents".

The information given above makes it probable, that if the duration of the icecover is 2-4 months, a lower thermocline above the lake bottom will gradually move upwards, finally reaching the primary (upper) thermocline immediately below the ice, and then disappear at the onset of the vernal circulation.

The best possible way to prove the correctness of this hypothesis is to use thermistor thermometers in connection with recorders, which continually register the temperatures of the various levels in a period prior to the breaking up of the ice.

In order to give a survey of the movements of the thermoclines in Grane Langsø, Table $36-37$ have been made. Fig. 24 is a diagram based on Table 37, thus demonstrating how, on an average, the lower thermocline behaves during the winter stagnation period, and how the thermocline of the summer stagnation period proceeds.

The preparation of Table 37 and the diagram Fig. 24 presented some problems. The duration of the ice-cover in the five best investigated winters is from about 35 days to about 110 days, on an average about 80 days. In the preparation of Table 36 and 37 the winter stagnation period is considered to last from early January to late March. ${ }^{1}$ The vernal circulation normally occurs at the transition from March to April, after which the summer stagnation period extends to the end of August. The exceptional series from April 5th, 1958, when the lake was icebound, is disregarded. Also the temperature series measured in February and March, when the lake was

[^0]Table 36. The depths of the thermoclines in Grane Langso.

|  | From January 1st to January 15th: no observations. |
| :---: | :---: |
| January. | 17.i.1960: 6-8 m. 18.i.1959: $8-10 \mathrm{~m}$. 22.i.1961: $10-11 \mathrm{~m} .26 . \mathrm{i} .1958: 10-11 \mathrm{~m} .31 . \mathrm{i} .1960: 6-8 \mathrm{~m}$. |
| February. | 8.ii.1959: 6-8 m. 12.ii.1961: $8-10 \mathrm{~m}$. 14.ii.1960: $2-4 \mathrm{~m}$. 23.ii.1951: $1-2 \mathrm{~m}$. 28.ii.1960: $6-8 \mathrm{~m}$. |
| March. | 9.iii.1958: 1-2 m. 13.iii.1960: 4-6m. 29.iii.1951: $0-1 \mathrm{~m}$. 27.iii.1964: $0-1 \mathrm{~m}$. |
| April. | 5.iv.1953: 2-6 m. 9.iv.1961: $2-4 \mathrm{~m} .10 . \mathrm{iv} .1960: 0 \mathrm{~m} .20 . \mathrm{iv} .1962: 2-4 \mathrm{~m} .21 . \mathrm{iv} .1951: 1-3 \mathrm{~m}$. 21.iv.1957: 1-2 m. 23.iv.1961: 6-8 m. 24.iv.1960: $0 \mathrm{~m} .25 . i v .1959: 4-6 \mathrm{~m}$. |
| May. | 3.v.1958: 6-8 m. 6.v.1957: 0 m. 7.v.1961: 8-10 m. 14.v. 1960: 4-6 m. 16.v.1959: 6-8 m. 17.v.1957: $1-2 \mathrm{~m}$ and 5-6 m. 21.v.1961: $8-10 \mathrm{~m} .23 . \mathrm{v} .1951: 6-7 \mathrm{~m} .26 . \mathrm{v} .1958: 8-10 \mathrm{~m} .29 . \mathrm{v}$. 1957: 5-6 m. 29.v.1960: 6-8 m. |
| June. | 4.vi.1961: $10-11 \mathrm{~m}$ and $2-4 \mathrm{~m}$. 10.vi.1959: 6-8 m. 15.vi.1960: 6-8 m. 15.vi.1961: 4-6 m and 8-10 m. 16.vi.1957: 2-3 m and 7-8 m. 18.vi.1958: 6-8 m. 26.vi.1951: 6-7m. 28.vi.1960: 6-8 m. |
| July. | 2.vii.1958: 6-8 m. 5.vii. 1957: 7-8 m. 6.vii. $1959: 8-10 \mathrm{~m} .9$. vii. $1961: 10-11 \mathrm{~m}$. 7.vii. $1955: 5-6 \mathrm{~m}$ and $8-9 \mathrm{~m}$. 15.vii.1954: 8-9 m. 15.vii.1958: 6-8 m. 18.vii.1955: 5-6 m. 20.vii.1951: 7-9 m. 20.vii.1957: 7-8 m. 21.vii.1959: 8-10 m. 23.vii.1961: 8-10 m. 24.vii.1962: 8-10 m. 27.vii.1960 : 8-10 m. 31.vii.1954: 8-9 m. |
| August. | 1.viii.1958: 8-10 m. 4.vii.1957: $10-11 \mathrm{~m}$. 8.vii. $1950: 10-11 \mathrm{~m} .9$.vii. $1960: 8-10 \mathrm{~m}$. 10 .viii. 1959: 8-10 m. 23.viii.1959: 10-11 m. 24.viii.1958: 10-11 m. 28.viii. 1960: 10-11 m. |

ice-free and isothermal, are left out of account. If two thermoclines occurred simultaneously, only the low-lying one is included in the calculation of the figures in Table 37.

The diagram Fig. 24 indicates a rather rapid shiftning of the lowlying winter thermocline from the bottom water to the lake surface. This movement should ordinarily be finished within about 3 months. The summer thermocline, however, has about 5 months to move from the surface to the lake bottom. The fall of the thermocline is very rapid in April-May, but slow in June-July, after which the fall again becomes rather rapid.

The thermocline of June-July as a rule lies in a subsurface depth of 8 to 8.5 m . In these two summer months a rather stable stratification occurs in the lake. The material is too scanty to decide whether or not a temporary stratification is present at the change from February to March in a subsurface depth of 3.5 to 4 m .

Table 37. The average depths of the low-lying thermoclines in Grane Langso.

| January | First half : | ? | latter half: | 8.9 m |
| :---: | :---: | :---: | :---: | :---: |
| February | First half : | 6.3 m | latter half: | 4.3 |
| March | First half : | 3.3 - | latter half: | 0.5 - |
| April | First half: | 2.3 - | latter half: | 3.1 - |
| May | First half: | 5.3 | latter half: | 7.1 - |
| June | First half : | 8.4 - | latter half: | 7.0 - (?) |
| July . . | First half : | 8.3 - | latter half: | 8.2 - |
| August | First half : | 9.6 - | latter half: | 10.5 |

## 15. Summary

The Danish Lobelia-lake Grane Langsø, lying on stratified drift, covers an area of 11.38 ha and has a maximum depth of 11.5 m . The transparency fluctuates between 4 m and at least 11.5 m .

This tunnel-valley lake has no visible affluents and effluents. Section 3 represents a preliminary study of the water balance of Grane Langsø. An attempt has been made to determine the flow of the sub-lacustrine inlet by means of the chloride content of the air and precipitation.

With the aid of Krogh and Rehberg' method the total $\mathrm{CO}_{2}$ quantity has been measured fortnightly or monthly in seven levels of the lake for more than three years. The standard deviation on a single determination is 0.07 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$.

Grane Langsø is poor in $\mathrm{CO}_{2}$, values generally varying between 0.27 and 1.71 $\mathrm{mg} \cdot \mathrm{l}^{-1}$; the absolute extremes were 0.27 and $14.89 \mathrm{mg} \cdot \mathrm{l}^{-1}$.

The lake is moderately acid with pH-values usually fluctuating between 5.4 and 5.7 ; the absolute pH -extremes were 4.9 and 5.9 . Comparisons with pH measurements from Gribsø are made.

A critical examination of the electrometric pH measurements has rendered it probable that some of the determinations are not reliable owing to the loss or uptake of $\mathrm{CO}_{2}$ by diffusion during the measurement. A comparison between the pH values computed on the assumption that pH is in all essentials determined by the $\mathrm{CO}_{2}$ concentration of the lake water, and the pH values being measured when the temperature and the $\mathrm{CO}_{2}$ tension of the lake water correspond to the temperature of the laboratory room and the $\mathrm{CO}_{2}$ pressure there, revealed a good agreement. The pH values of Grane Langsø, given in this paper, are computed from the quantities of total $\mathrm{CO}_{2} \cdot l^{-1}$.

As the activity coefficient of $\mathrm{HCO}_{3}^{-}$proved to come very close to 0.97 , the unmodified Henderson-Hasselbalch equation was employed for computation of the $\mathrm{HCO}_{3}^{-}$quantities. They normally lay between 0.1 and $0.3 \mathrm{mg} \cdot \mathrm{l}^{-1}$; the absolute extremes were 0.1 and $0.7 \mathrm{mg} \cdot \mathrm{l}^{-1}$. The $\mathrm{HCO}_{3}^{-}$alkalinity thus lies as low as $0.002-0.005$; the greatest alkalinity ever calculated was $0.01 \mathrm{mval} \cdot \mathrm{l}^{-1}$.

The occurrence of the maxima and minima of these and other factors has been described relative to the two crucial points in the annual cycle of a lake: the moments of the vernal turnover (here called cive) and the autumnal turn-over (designed ciau).

Grane Langsø usually liberates $\mathrm{CO}_{2}$ to the atmosphere apart from the periods of April-May and July-August, when the lake generally absorbs some $\mathrm{CO}_{2}$ from the atmosphere.

Phosphate has been determined monthly within one year for five levels of the lake. Grane Langs $\varnothing$ also turned out to be poor in phosphate-phosphorus, as no determination attained the value $0.01 \mathrm{mg} \cdot \mathrm{l}^{-1}$.

The results of the phosphate and iron determinations from Grane Langsø are compared with the corresponding ones from lake Gribso and other Danish waters.

The specific conductivity varied little about 50 reciprocal megohms (extremes 48 and 57), and the ionic strength was as low as about $0.00065 ; 0.94-0.98$ mval ions $\cdot 1^{-1}$ were found. Grane Langs $\varnothing$ is a sodium chloride lake, the ionic diagram of which highly resembles that of seawater. The equivalent percentages of $\mathrm{SO}_{4}^{--}$and especially $\mathrm{Ca}^{++}$is far greater, however, than the corresponding ones of seawater. A comparison between the ionic composition of the lake water and that estimated for the precipitation falling over the lake, renders it probable that Grane Langsø contains rainwater in a somewhat concentrated state, but with an extra supply of chloride, which possibly originates from selective vegetation capture of the large NaCl -condensation nuclei from the air.

The causes of the strongly decreasing $\mathrm{Ca}^{++}$content of lake Gribso during the Subatlantic Period are reconsidered in the light of W. Ohle's discovery of the effect of "Laubdy" in removing $\mathrm{Ca}^{++}$and $\mathrm{HCO}_{3}^{-}$from lake water.

The hypothesis is advanced that in Grane Langsø, which normally is ice-covered for a few months, a thermocline is moving upwards during the winter stagnation period from the deepest parts of the lake to the ice-cover. This thermocline reaches the lake surface at the onset of the vernal turn-over.

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## 17. Survey of the Analyses



| 0.2 m | $0.4{ }^{\circ} \mathrm{C}$ |  |  |  | $\mathrm{O}_{2}$-saturation $93 \%$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 m | $1.75{ }^{\circ} \mathrm{C}$ | $0.01 \mathrm{mg} \mathrm{Fe}{ }^{++} \cdot \mathrm{l}^{-1}$ |  |  |  |  |
| 2 - | $2.7^{\circ} \mathrm{C}$ |  |  |  |  |  |
| 3 - | $3.2{ }^{\circ} \mathrm{C}$ | 0.01 | - | - | - | $92 \%$ |
| 5 - | $3.8{ }^{\circ} \mathrm{C}$ | 0.01 | - | - | - | $90^{\circ} / 0$ |
| 7 - | $4.25^{\circ} \mathrm{C}$ | 0.01 | - | - | - | $77 \%$ |
| $10-$ | $4.3{ }^{\circ} \mathrm{C}$ | 0.03 | - | $\rightarrow$ | - | 73.5 \% |

March 29, 1951. Ice 15 cm thick.

| 0.15 m . | $1.3{ }^{\circ} \mathrm{C}$ | 4 m | $4.4{ }^{\circ} \mathrm{C}$ | 10 m | $4.4{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 m | $4.5{ }^{\circ} \mathrm{C}$ | 5 - | $4.4{ }^{\circ} \mathrm{C}$ | 10.8 m | $5.0^{\circ} \mathrm{C}$ |
| 2 - | $4.5{ }^{\circ} \mathrm{C}$ | 7 - | $4.4{ }^{\circ} \mathrm{C}$ |  |  |
| 3 - | $4.4{ }^{\circ} \mathrm{C}$ | 9 - | $4.4{ }^{\circ} \mathrm{C}$ |  |  |
| April 21, 1951. |  |  |  |  |  |
| 0 m . | $6.9{ }^{\circ} \mathrm{C}$ | 5 m | $6.2{ }^{\circ} \mathrm{C}$ | 11 m | $5.8^{\circ} \mathrm{C}$ |
| 1 - | $7.0^{\circ} \mathrm{C}$ | 7 - | $6.2{ }^{\circ} \mathrm{C}$ |  |  |
| $3-$ | $6.45{ }^{\circ} \mathrm{C}$ | 10 - | $5.8{ }^{\circ} \mathrm{C}$ |  |  |
| May 23, 1951. |  |  |  |  |  |
| 1 m . | $14.45{ }^{\circ} \mathrm{C}$ | 5 m | $12.95{ }^{\circ} \mathrm{C}$ | 9 m | $7.6{ }^{\circ} \mathrm{C}$ |
| 2 - | $14.1^{\circ} \mathrm{C}$ | 6 - | $11.65{ }^{\circ} \mathrm{C}$ | $10-$ | $7.5^{\circ} \mathrm{C}$ |
| $3-$ | $14.0^{\circ} \mathrm{C}$ | 7 - | $9.05{ }^{\circ} \mathrm{C}$ | 11 - | $7.7{ }^{\circ} \mathrm{C}$ |
| 4 - | $13.9^{\circ} \mathrm{C}$ | 8 | $7.9^{\circ} \mathrm{C}$ |  |  |

June 26, 1951. Transparency 10.25 m at 17.30 hours.

| 1 m | $17.5{ }^{\circ} \mathrm{C}$ | 6 m | $17.2^{\circ} \mathrm{C}$ | 9 m | $11.3{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 3 | $17.5{ }^{\circ} \mathrm{C}$ | 7 - | $14.5{ }^{\circ} \mathrm{C}$ | $10-$ | $11.05^{\circ} \mathrm{C}$ |
| 5 | $17.25^{\circ} \mathrm{C}$ | 8 - | $12.4{ }^{\circ} \mathrm{C}$ | 11 - | $10.9^{\circ} \mathrm{C}$ |
| July 20, 1951. Transparency 10.25 m at 17.00 on July 26 th . |  |  |  |  |  |
| 1 m | $17.3{ }^{\circ} \mathrm{C}$ | 6 m | $17.05^{\circ} \mathrm{C}$ | 9 m | $13.4{ }^{\circ} \mathrm{C}$ |
| 3 | $17.25^{\circ} \mathrm{C}$ | 7 - | $17.0^{\circ} \mathrm{C}$ | 10 - | $12.9^{\circ} \mathrm{C}$ |
| 5 | $17.1^{\circ} \mathrm{C}$ | 8 - | $15.2^{\circ} \mathrm{C}$ | 11 - | $12.8{ }^{\circ} \mathrm{C}$ |



July 15-19, 1954.

| 1 m | $17.9{ }^{\circ} \mathrm{C}$ | oxygen saturation | $102 \%$ |
| :---: | :---: | :---: | :---: |
| 3 - | $17.8^{\circ} \mathrm{C}$ |  |  |
| 5 - | $17.6^{\circ} \mathrm{C}$ |  |  |
| 6 - | $17.4{ }^{\circ} \mathrm{C}$ |  |  |
| 7 - | $16.7^{\circ} \mathrm{C}$ | oxygen saturation | $102 \%$ |
| 8 - | $15.0^{\circ} \mathrm{C}$ | - - | $109 \%$ |
| 9 - | $12.9{ }^{\circ} \mathrm{C}$ | - - | $107 \%$ |
| $10-$ | $12.2{ }^{\circ} \mathrm{C}$ |  |  |
| 11 - | $11.8^{\circ} \mathrm{C}$ | - - | $90^{\circ} \%$ |

July 31, 1954.

| 1 m | $17.3{ }^{\circ} \mathrm{C}$ | 8 m | $16.7^{\circ} \mathrm{C}$ | 10 m | $12.9{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 7 | $16.9^{\circ} \mathrm{C}$ | 9 | $13.9^{\circ} \mathrm{C}$ | 11 | $12.4{ }^{\circ} \mathrm{C}$ |

August 3rd, 1954. Transparency 11 m .

| 0 m | $19.1^{\circ} \mathrm{C}$ | 4 m | $17.3{ }^{\circ} \mathrm{C}$ | 8 m | $13.3{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $19.2{ }^{\circ} \mathrm{C}$ | 5 - | $16.6^{\circ} \mathrm{C}$ | 9 - | $12.1^{\circ} \mathrm{C}$ |
| 2 | $18.8^{\circ} \mathrm{C}$ | 6 - | $15.1{ }^{\circ} \mathrm{C}$ | 10 | $11.7^{\circ} \mathrm{C}$ |
| $3-$ | $18.0^{\circ} \mathrm{C}$ | 7 - | $14.4{ }^{\circ} \mathrm{C}$ | 11 | $11.8^{\circ} \mathrm{C}$ |

July 18, 1955.
$0 \mathrm{~m} \ldots \ldots . \operatorname{coc} \quad 23.0^{\circ} \mathrm{C} \quad$ oxygen saturation $102^{\circ} /$
$1-\ldots . . .22 .65^{\circ} \mathrm{C} \quad$ - $\quad$ - $101 \%$

$3-\ldots . \operatorname{c} . \operatorname{c} 22.4^{\circ} \mathrm{C} \quad-\quad 100 \%$

$5-\ldots \ldots 19.1^{\circ} \mathrm{C}$ - $-108 \%$

| $3^{\circ} \mathrm{C}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |

$7-\ldots \ldots 15.9^{\circ} \mathrm{C}$ - $\quad$ - $109 \%$
$8-\ldots \ldots \ldots 14.6^{\circ} \mathrm{C} \quad-\quad$ - $112 \%$

$11-\ldots \ldots . . .$.
$11.8 \mathrm{~m} \ldots .{ }^{\circ}$

October 20, 1956.
$1 \mathrm{~m} \ldots \ldots . . .{ }^{2} .{ }^{\circ} \mathrm{C}$
$11-\ldots \ldots . .$.

December 1, 1956.
$1 \mathrm{~m} \ldots . . .{ }^{\circ} . .$.
$11-\ldots \ldots . \ldots .4^{\circ} \mathrm{C}$
February 3, 1957.

| $1 \mathrm{~m} \ldots \ldots \ldots$ | $2.3^{\circ} \mathrm{C}$ |
| ---: | :--- | :--- |
| $5-\ldots \ldots \ldots$ | $2.35^{\circ} \mathrm{C}$ |
| $11-\ldots \ldots \ldots$ | $2.4^{\circ} \mathrm{C}$ |

November 11, 1956.

| $1 \mathrm{~m} \ldots \ldots \ldots$ | $6.9^{\circ} \mathrm{C}$ |
| ---: | :--- |
| $11-\ldots \ldots$. | $6.9^{\circ} \mathrm{C}$ |

December 30, 1956.
$1 \mathrm{~m} \ldots . .{ }^{2} .{ }^{\circ} \mathrm{C}$.
$11-\ldots \ldots \ldots . .2 .1^{\circ} \mathrm{C}$


April 7, $195 \%$.

| $1 \mathrm{~m} \ldots \ldots \ldots$ | $6.65^{\circ} \mathrm{C}$ |
| :---: | :--- | :--- |
| $5-\ldots \ldots \ldots$ | $6.3^{\circ} \mathrm{C}$ |
| $11-\ldots \ldots$ | $5.1^{\circ} \mathrm{C}$ |

Ice 8 cm thick on March 3, 1957.
April 21, 1957.

| 1 m | $8.1{ }^{\circ} \mathrm{C}$ | 5 m | $7.5{ }^{\circ} \mathrm{C}$ | 9 m | $7.4{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $7.7{ }^{\circ} \mathrm{C}$ | 6 - | $7.5{ }^{\circ} \mathrm{C}$ | 10 - | $7.2{ }^{\circ} \mathrm{C}$ |
| 3 - | $7.6{ }^{\circ} \mathrm{C}$ | 7 - | $7.5^{\circ} \mathrm{C}$ | 11 - | $7.1^{\circ} \mathrm{C}$ |
| 4 - | $7.5^{\circ} \mathrm{C}$ | 8 - | $7.5{ }^{\circ} \mathrm{C}$ |  |  |
| May 6, 1957. |  |  |  |  |  |
| 1 m | $8.7{ }^{\circ} \mathrm{C}$ | 6 m | $8.7^{\circ} \mathrm{C}$ | 10 m | $8.7{ }^{\circ} \mathrm{C}$ |
| $3-$ | $8.7^{\circ} \mathrm{C}$ | 7 - | $8.7^{\circ} \mathrm{C}$ | 11 - | $8.7^{\circ} \mathrm{C}$ |
| 4 | $8.7{ }^{\circ} \mathrm{C}$ | 8 - | $8.7^{\circ} \mathrm{C}$ |  |  |
| 5 - | $8.7^{\circ} \mathrm{C}$ | 9 - | $8.7^{\circ} \mathrm{C}$ |  |  |

May 17. 1957.

| 1 m | $13.1{ }^{\circ} \mathrm{C}$ | 5 m | $11.1{ }^{\circ} \mathrm{C}$ | 9 m | $10.0^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | $11.9{ }^{\circ} \mathrm{C}$ | 6 - | $10.55^{\circ} \mathrm{C}$ | $10-$ | $10.0^{\circ} \mathrm{C}$ |
| 3 | $11.7^{\circ} \mathrm{C}$ | 7 - | $10.4^{\circ} \mathrm{C}$ | 11 - | $9.9{ }^{\circ} \mathrm{C}$ |
| 4 | $11.6^{\circ} \mathrm{C}$ | 8 - | $10.1^{\circ} \mathrm{C}$ |  |  |

May 29, 1957.

| 1 m | $13.4{ }^{\circ} \mathrm{C}$ | 5 m | $13.4{ }^{\circ} \mathrm{C}$ | 9 m | $10.8^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | $13.4{ }^{\circ} \mathrm{C}$ | 6 - | $12.3{ }^{\circ} \mathrm{C}$ | $10-$ | $10.8^{\circ} \mathrm{C}$ |
| 3 - | $13.4{ }^{\circ} \mathrm{C}$ | 7 - | $11.3{ }^{\circ} \mathrm{C}$ | 11 - | $10.5^{\circ} \mathrm{C}$ |
| 4 | $13.4{ }^{\circ} \mathrm{C}$ | 8 - | $11.1^{\circ} \mathrm{C}$ |  |  |
| June 16, 1957. |  |  |  |  |  |
| 1 m . | $19.4{ }^{\circ} \mathrm{C}$ | 5 m | $16.7^{\circ} \mathrm{C}$ | 9 m | $14.8{ }^{\circ} \mathrm{C}$ |
| 2 | $19.0^{\circ} \mathrm{C}$ | 6 - | $16.5{ }^{\circ} \mathrm{C}$ | $10-$ | $14.4{ }^{\circ} \mathrm{C}$ |
| 3 | $17.45{ }^{\circ} \mathrm{C}$ | 7 - | $16.3^{\circ} \mathrm{C}$ | 11 - | $14.15{ }^{\circ} \mathrm{C}$ |
| 4 - | $16.95^{\circ} \mathrm{C}$ | 8 - | $15.3{ }^{\circ} \mathrm{C}$ |  |  |

July 5, 1957.

| 0 m | $19.5{ }^{\circ} \mathrm{C}$ | 4 m | $19.6{ }^{\circ} \mathrm{C}$ | 8 m | $17.1^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $19.5{ }^{\circ} \mathrm{C}$ | 5 - | $18.75^{\circ} \mathrm{C}$ | 9 - | $16.65^{\circ} \mathrm{C}$ |
| 2 - | $19.6{ }^{\circ} \mathrm{C}$ | 6 - | $18.4^{\circ} \mathrm{C}$ | $10-$ | $15.9^{\circ} \mathrm{C}$ |
| 3 | $19.4{ }^{\circ} \mathrm{C}$ | 7 - | $18.05^{\circ} \mathrm{C}$ | 11 - | $15.9^{\circ} \mathrm{C}$ |
| July 20, 1957. |  |  |  |  |  |
| 1 m | $20.0^{\circ} \mathrm{C}$ | 5 m | $19.9{ }^{\circ} \mathrm{C}$ | 9 m | $17.4{ }^{\circ} \mathrm{C}$ |
| 2 | $20.1^{\circ} \mathrm{C}$ | 6 - | $19.7^{\circ} \mathrm{C}$ | $10-$ | $17.25^{\circ} \mathrm{C}$ |
| 3 - | $20.0^{\circ} \mathrm{C}$ | 7 - | $19.5{ }^{\circ} \mathrm{C}$ | 11 - | $17.0^{\circ} \mathrm{C}$ |
| 4 | $20.0^{\circ} \mathrm{C}$ | 8 - | $18.1^{\circ} \mathrm{C}$ |  |  |

August 4, 1957.

| 1 m | $19.3{ }^{\circ} \mathrm{C}$ | 6 m | $18.6^{\circ} \mathrm{C}$ | 9 m | $18.4{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 3 | $19.1^{\circ} \mathrm{C}$ | 7 | $18.6{ }^{\circ} \mathrm{C}$ | 10 m | $18.15^{\circ} \mathrm{C}$ |
| 5 | $18.8^{\circ} \mathrm{C}$ | 8 | $18.6{ }^{\circ} \mathrm{C}$ | 11 - | $17.1^{\circ} \mathrm{C}$ |

September 1, 1957.

| 1 m | $17.2{ }^{\circ} \mathrm{C}$ | 5 m | $16.9{ }^{\circ} \mathrm{C}$ | 9 m | $16.8^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | $17.2{ }^{\circ} \mathrm{C}$ | 6 - | $16.9^{\circ} \mathrm{C}$ | 10 - | $16.8^{\circ} \mathrm{C}$ |
| 3 | $17.2{ }^{\circ} \mathrm{C}$ | 7 | $16.85^{\circ} \mathrm{C}$ | 11 - | $16.8^{\circ} \mathrm{C}$ |
| 4 | $17.1^{\circ} \mathrm{C}$ | 8 | $16.8{ }^{\circ} \mathrm{C}$ |  |  |

September 21, 1957.

| 1 m | $14.6{ }^{\circ} \mathrm{C}$ | 8 m | $14.6{ }^{\circ} \mathrm{C}$ | 10 m | $14.5{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 5 | $14.6{ }^{\circ} \mathrm{C}$ | 9 - | $14.5{ }^{\circ} \mathrm{C}$ | 11 | $14.5{ }^{\circ} \mathrm{C}$ |

October 17, 1957.


December 29, 1957.
The southernmost part of the lake covered with ice. Transparency more than 11.5 m .


January 26, 1958. Ice 10 cm thick, covered with 5 cm snow.

| 0.1 m . | $0.55{ }^{\circ} \mathrm{C}$ | 4 m | $2.4{ }^{\circ} \mathrm{C}$ | 10 m | $3.3{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 m | $1.9{ }^{\circ} \mathrm{C}$ | 6 - | $2.85{ }^{\circ} \mathrm{C}$ | 11 - | $3.9{ }^{\circ} \mathrm{C}$ |
| 2 - | $2.1{ }^{\circ} \mathrm{C}$ | 8 - | $2.9{ }^{\circ} \mathrm{C}$ |  |  |

March 9, 1958 . Ice 10 cm thick.

| 0.1 m . | $0.2{ }^{\circ} \mathrm{C}$ | pH 5.6 | 1.37 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 m | $1.8{ }^{\circ} \mathrm{C}$ |  |  |  |  |  |  |  |  |  |  |
| 2 | $2.9{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.41 | - | - | - | - | 0.2 | - | - | - |
| 3 - | $3.1{ }^{\circ} \mathrm{C}$ |  |  |  |  |  |  |  |  |  |  |
| 4 | $3.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.59 | - | - | - | - | 0.2 | - | - | - |
| 6 | $3.5{ }^{\circ} \mathrm{C}$ | - 5.4 | 2.12 | - | - | - | - | 0.2 | - | - | - |
| 8 - | $3.9^{\circ} \mathrm{C}$ | - 5.3 | 3.83 | - | - | - | - | 0.3 | - | - | - |
| 10 | $4.1^{\circ} \mathrm{C}$ | - 5.3 | 4.38 | - | - | - | - | 0.3 | - | - | - |
| 11 - | $4.1{ }^{\circ} \mathrm{C}$ | - 5.2 | 5.18 | - | - | - | - | 0.4 | - | - | - |

April 5, 1958. Ice 20 cm thick.

| 0.2 m . | $1.1^{\circ} \mathrm{C}$ | pH 5.6 | 1.45 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 m | $3.1^{\circ} \mathrm{C}$ |  |  |  |  |  |  |  |  |  |  |
| 2 | $3.5{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.61 | - | - | - | - | 0.2 | - | - | - |
| 3 - | $3.7^{\circ} \mathrm{C}$ |  |  |  |  |  |  |  |  |  |  |
| 4 - | $3.7^{\circ} \mathrm{C}$ | - 5.4 | 2.50 | - | - | - | - | 0.2 | - | - | - |
| 5 | $3.8{ }^{\circ} \mathrm{C}$ |  |  |  |  |  |  |  |  |  |  |
| 6 | $4.0^{\circ} \mathrm{C}$ | - 5.3 | 3.25 | - | - | - | - | 0.3 | - | - | - |
| 8 | $4.0^{\circ} \mathrm{C}$ | - 5.3 | 3.48 | - | - | - | - | 0.3 | - | - | - |
| 10 | $4.1^{\circ} \mathrm{C}$ | - 5.2 | 5.05 | - | - | - | - | 0.3 | - | - | - |
| 11 | $4.35{ }^{\circ} \mathrm{C}$ | - 5.1 | 9.88 | - | - | - | - | 0.5 |  | - | - |

May 3, 1958.

| 0 m | $8.7^{\circ} \mathrm{C}$ | pH 5.5 | 1.37 mg total $\mathrm{CO}_{2} \cdot 1^{-1}$ |  |  |  |  | $0.2 \mathrm{mg} \mathrm{HCO}-{ }^{-} \cdot 1^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $8.7^{\circ} \mathrm{C}$ | - 5.5 | 1.36 | - | - | - | - | 0.2 | - | - | - |
| 4 - | $8.6{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.29 | - | - | - | - | 0.2 | - | - | - |
| 6 | $8.2^{\circ} \mathrm{C}$ | - 5.5 | 1.25 | - | - | - | - | 0.2 | - | - | - |
| 8 | $7.0^{\circ} \mathrm{C}$ | - 5.5 | 1.34 | - | - | - | - | 0.2 | - | - | - |
| $10-$ | $6.7^{\circ} \mathrm{C}$ | - 5.5 | 1.35 | - | - | - | - | 0.2 | - | - | - |
| 11 | $6.4{ }^{\circ} \mathrm{C}$ | 5.6 | 1.16 | - | - | - | - | 0.2 |  | - |  |

May 26, 1958.

| 0 m | $12.7^{\circ} \mathrm{C}$ | pH 5.6 | 0.80 m | mg t | tal | $\mathrm{CO}_{2} \cdot 1^{-1}$ |  | 0.1 n |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $12.7^{\circ} \mathrm{C}$ | - 5.6 | 0.75 | - | - | - - |  | 0.1 | - | - - |
| 4 | $12.2{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.86 | - | - | - - |  | 0.1 | - | - - |
| 6 | $11.8^{\circ} \mathrm{C}$ | - 5.6 | 0.79 | - | - | - - |  | 0.1 | - | - |
| 8 - | $10.6^{\circ} \mathrm{C}$ | - 5.6 | 0.84 | - | - | - - |  | 0.1 | - | - - |
| $10-$ | $9.0^{\circ} \mathrm{C}$ | - 5.6 | 1.10 | - | - | - - |  | 0.2 | - | - - |
| 11 - | $8.3^{\circ} \mathrm{C}$ | - 5.4 | 2.28 | - | - | - - |  | 0.2 | - | - - |
| June |  |  |  |  |  |  |  |  |  |  |
| 0 m | $17.8{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.10 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| 2 - | $17.7^{\circ} \mathrm{C}$ | - 5.5 | 1.02 | - | - | - - |  | 0.2 | - | - - |
| 4 - | $17.5^{\circ} \mathrm{C}$ | - 5.6 | 0.92 | - | - | - - |  | 0.2 | - | - - |
| 6 - | $16.0^{\circ} \mathrm{C}$ | - 5.6 | 0.88 | - | - | - - |  | 0.2 | E | - |


| 8 m | $13.15{ }^{\circ} \mathrm{C}$ | pH 5.6 | 0.73 | mg total | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.1 mg | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 10 - | $11.3^{\circ} \mathrm{C}$ |  | 1.23 | - - | - | 0.2 - | - |
| 11 - | $10.7^{\circ} \mathrm{C}$ | 5.5 | 1.27 | - - | - - | 0.2 | - - |
| July 2, 1958. |  |  |  |  |  |  |  |
| 0 m | $21.2{ }^{\circ} \mathrm{C}$ | pH 5.6 | 0.80 | mg total | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.2 mg | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |
| 2 - | $20.4{ }^{\circ} \mathrm{C}$ | 5.6 | 0.89 | - - | - - | 0.2 | - - |
| 4 - | $18.7^{\circ} \mathrm{C}$ | 5.6 | 0.87 | - - | - - | 0.2 | - - |
| 6 | $18.0^{\circ} \mathrm{C}$ | 5.6 | 0.71 | - - | - - | 0.1 | - - |
| 8 | $13.85^{\circ} \mathrm{C}$ | 5.5 | 1.11 | - - | - - | 0.2 | - - |
| $10-$ | $13.2{ }^{\circ} \mathrm{C}$ | 5.5 | 1.42 | - - | - - | 0.2 | - - |
| 11 - | $12.6{ }^{\circ} \mathrm{C}$ | - 5.4 | 1.69 | - - | - - | 0.2 | - - |
| July 15, 1958. |  |  |  |  |  |  |  |
| 0 m | $20.75{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.00 | mg total | $\mathrm{CO}_{2} \cdot 1^{-1}$ | 0.2 mg | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |
| 2 - | $19.4{ }^{\circ} \mathrm{C}$ | - 5.5 | 0.93 | - - | - - | 0.2 | - - |
| 4 | $19.25^{\circ} \mathrm{C}$ | - 5.5 | 1.03 | - - | - - | 0.2 | - - |
| 6 - | $19.1{ }^{\circ} \mathrm{C}$ | 5.5 | 1.01 | - - | - - | 0.2 | - - |
| 8 - | $15.2{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.86 | - - | - - | 0.2 | - - |
| 10 - | $13.0{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.48 | - - | - - | 0.2 | - - |
| 11 - | $12.8{ }^{\circ} \mathrm{C}$ | - 5.4 | 2.39 | - - | - - | 0.3 | - - |


| 0 m | $17.5^{\circ} \mathrm{C}$ | pH 5.6 |
| :---: | :---: | :---: |
| 2 - | $17.5^{\circ} \mathrm{C}$ |  |
| 4 - | $17.4{ }^{\circ} \mathrm{C}$ | 5.6 |
| 6 | $17.3^{\circ} \mathrm{C}$ | 5.6 |
| 7 | $17.2^{\circ} \mathrm{C}$ |  |
| 8 - | $17.15^{\circ} \mathrm{C}$ | 5.6 |
| 9 | $17.0^{\circ} \mathrm{C}$ |  |
| $10-$ | $15.9^{\circ} \mathrm{C}$ | 5. |
| 11 | $14.7{ }^{\circ} \mathrm{C}$ | 5.3 |

August 24, 1958. Transparency more than 11 m .


September 28, 1958.

| 0 m | $15.25^{\circ} \mathrm{C}$ | pH 5.5 | 1.47 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  | $0.2 \mathrm{mg} \mathrm{HCO}{ }_{3}^{-} \cdot 1^{-1}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $15.25^{\circ} \mathrm{C}$ | 5.5 | 1.45 | - | - | - - | 0.2 | - | - |
| 4 | $15.25^{\circ} \mathrm{C}$ | - 5.5 | 1.50 | - | - | - - | 0.2 | - | - - |
| 6 | $15.25^{\circ} \mathrm{C}$ | - 5.5 | 1.45 | - | - | - - | 0.2 | - | - - |
| 8 | $15.25^{\circ} \mathrm{C}$ | 5.5 | 1.56 | - | - | - - | 0.2 | - | - - |
| $10-$ | $15.25^{\circ} \mathrm{C}$ | 5.5 | 1.58 | - | - | - - | 0.2 | - | - - |
| 11 - | $15.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.49 |  | - | - - | 0.2 |  |  |

October 23, 1958.

| 0 m | $11.1{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.48 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  | $0.2 \mathrm{mg} \mathrm{HCO}{ }_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $11.1{ }^{\circ} \mathrm{C}$ | 5.5 | 1.45 | - - | - - | 0.2 | - | - |
| 4. | $11.1^{\circ} \mathrm{C}$ | - 5.5 | 1.43 | - - | - - | 0.2 | - | - - |
| 6 - | $11.1^{\circ} \mathrm{C}$ | - 5.5 | 1.40 | - - | - - | 0.2 | - | - - |
| 8 | $11.1^{\circ} \mathrm{C}$ | - 5.5 | 1.44 | - - | - - | 0.2 | - | - - |
| $10-$ | $11.05^{\circ} \mathrm{C}$ | - 5.5 | 1.45 | - - | - - | 0.2 | - | - - |
| 11 - | $11.05^{\circ} \mathrm{C}$ | 5.5 | 1.39 | - - | - - | 0.2 | - | - - |
| November 23, 1958. |  |  |  |  |  |  |  |  |
| 0 m | $7.35{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.69 | mg total | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.2 m |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| 2 - | $7.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.68 | - - | - - | 0.2 | - | - - |
| 4 | $7.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.68 | - - | - - | 0.2 | - | - - |
| 6 | $7.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.69 | - - | - - | 0.2 | - | - - |
| 8 - | $7.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.71 | - - | - - | 0.2 | - | - - |
| $10-$ | $7.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.67 | - - | - - | 0.2 | - | - - |
| 11 - | $7.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.82 | - - | - - | 0.2 | - | - - |

December 29, 1958. Transparency more than 11.5 m .

| 0 m | $3.35{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.75 mg |  | total | $\mathrm{CO}_{2} \cdot \mathrm{I}^{-1}$ |  | $0.2 \mathrm{mg} \mathrm{HCO}-{ }^{-} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | $3.5{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.73 | - | - | - | - | 0.2 | - | - | - |
| 4 | $3.6{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.74 | - | - | - | - | 0.2 | - | - | - |
| 6 - | $3.7{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.72 | - | - | - | - | 0.2 | - | - | - |
| 8 | $3.75{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.80 | - | - | - | - | 0.2 | - | - | - |
| $10-$ | $3.85{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.75 | - | - | - | - | 0.2 | - | - | - |
| 11 - | $3.9{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.75 | - | - | - | - | 0.2 | - | - | - |

January 18, 1959. Ice 10 cm thick.

| 0.1 m | $0.2^{\circ} \mathrm{C}$ | pH 5.5 | 1.79 mg |  | total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  | $0.2 \mathrm{mg} \mathrm{HCO}{ }_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $2.9{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.64 | - | - | - - | 0.2 | - | - | - |
| 4 - | $3.1^{\circ} \mathrm{C}$ | - 5.5 | 1.71 | - | - | - - | 0.2 | - | - | - |
| 6 - | $3.35{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.79 | - | - | - - | 0.2 | - | - | - |
| 8 - | $3.4{ }^{\circ} \mathrm{C}$ | - 5.4 | 2.20 | - | - | - - | 0.2 | - | - | - |
| $10-$ | $3.75{ }^{\circ} \mathrm{C}$ | - 5.3 | 3.44 | - | - | - - | 0.3 | - | - | - |
| 11 - | $3.9{ }^{\circ} \mathrm{C}$ | - 5.2 | 5.78 | - | - | - - | 0.4 | - | - | - |

February 8, 1959. Ice 10 cm thick.

| 0.1 m . | $0.9{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.94 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |  | $0.2 \mathrm{mg} \mathrm{HCO}{ }_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 m | $3.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.47 | - | - | - | - | 0.2 | - | - | - |
| 4 - | $3.4{ }^{\circ} \mathrm{C}$ | - 5.6 | 1.30 | - | - | - | - | 0.2 | - | - | - |
| 6 - | $3.45{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.63 | - | - | - | - | 0.2 | - | - | - |
| 8 - | $4.0^{\circ} \mathrm{C}$ | - 5.4 | 2.23 | - | - | - | - | 0.2 | - | - | - |
| 10 - | $4.1^{\circ} \mathrm{C}$ | - 5.3 | 4.24 | - | - | - | - | 0.3 | - | - | - |
| 11 - | $4.4{ }^{\circ} \mathrm{C}$ | - 5.1 | 11.37 | - | - | - | - | 0.5 | - | - | - |

March 1, 1959. The northernmost and southernmost part of the lake covered with thin ice.

| 0 m | $4.2{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.73 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $4.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.71 | - | - | - | - | 0.2 | - | - | - |
| 4 - | $4.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.77 | - | - | - | - | 0.2 | - | - | - |
| 6 - | $4.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.70 | - | - | - | - | 0.2 | - | - | - |
| 8 - | $4.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.73 | - | - | - | - | 0.2 | - | - | - |
| $10-$ | $4.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.77 | - | - | - | - | 0.2 | - | - | - |
| 11 - | $4.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.69 | - | - | - | - | 0.2 | - | - | - |
| Biol. Skr. Dan.Vid. Selsk. 14, no. 2. |  |  |  |  |  |  |  | 7 |  |  |  |

March 26, 1959.


June 10, 1959. Transparency 11 m .

| 0 m | $16.75{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.04 mg total $\mathrm{CO}_{2} \cdot 1^{-1}$ |  |  |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $16.75{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.05 | - | - | - - | 0.2 | - | - | - |
| 4 - | $16.7^{\circ} \mathrm{C}$ | - 5.5 | 1.02 | - | - | - - | 0.2 | - | - | - |
| 6 - | $16.6^{\circ} \mathrm{C}$ | - 5.5 | 1.04 | - | - | - - | 0.2 | - | - | - |
| 8 - | $12.6{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.98 | - | - | - - | 0.2 | - | - | - |
| $10-$ | $11.0{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.51 | - | - | - - | 0.2 | - | - | - |
| 11 - | $10.9^{\circ} \mathrm{C}$ | - 5.4 | 2.02 | - | - | - - | 0.2 | - | - | - |

July 6, 1959.

| 0 m | $19.4{ }^{\circ} \mathrm{C}$ | pH 5.6 | 0.78 mg total $\mathrm{CO}_{2} \mathrm{l} \cdot{ }^{-1}$ |  |  |  | $0.2 \mathrm{mg} \mathrm{HCO}-{ }^{-} \cdot 1^{-1}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $18.6{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.73 | - | - | - - | 0.2 | S | - |
| 4 - | $18.2^{\circ} \mathrm{C}$ | - 5.6 | 0.70 | - | - | - - | 0.1 | - | - - |
| 6 - | $18.1^{\circ} \mathrm{C}$ | - 5.6 | 0.69 | - | - | - - | 0.1 | - | - - |
| 8 - | $17.6^{\circ} \mathrm{C}$ | - 5.6 | 0.86 | - | - | - - | 0.2 | - | - - |
| $10-$ | $14.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.41 | - | - | - - | 0.2 | - | - - |
| 11 - | $13.8{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.49 | - | - | - - | 0.2 | - | - - |
| July 21, 1959. |  |  |  |  |  |  |  |  |  |
| 0 m | $22.0{ }^{\circ} \mathrm{C}$ | pH 5.7 | 0.49 m | ng t | total | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.1 |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| 2 - | $20.95^{\circ} \mathrm{C}$ | - 5.7 | 0.46 | - | - | - - | 0.1 | - | - |
| $4-\ldots$ | $20 .{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.51 | - | - | - - | 0.1 | - | - |


| 6 m | $20.25^{\circ} \mathrm{C}$ | pH 5.9 | 0.27 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  | $0.1 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 8 | $19.45{ }^{\circ} \mathrm{C}$ | 5.8 | 0.39 | - | - | - | 0.1 | - | - | - |
| 10 - | $16.5{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.76 | - | - | - | 0.2 | - | - | - |
| 11 | $15.9^{\circ} \mathrm{C}$ | 5.3 | 2.70 | - | - | - | 0.3 | - | - | - |

August 10, 1959.


| 0 m |  |
| :---: | :---: |
|  |  |
|  |  |
|  |  |
|  |  |
| 10 | - |
| 11 |  |

$21.35^{\circ} \mathrm{C}$
$21.25^{\circ} \mathrm{C}$
$20.95^{\circ} \mathrm{C}$
$20.7^{\circ} \mathrm{C}$
$20.4^{\circ} \mathrm{C}$
$18.8^{\circ} \mathrm{C}$
$16.6^{\circ} \mathrm{C}$

|  |  |  |  |  |  |
| ---: | ---: | ---: | ---: | ---: | ---: |
| pH 5.6 | 0.84 mg | total $\mathrm{CO}_{2} \cdot 1^{-1}$ |  |  |  |
| -5.6 | 0.82 | - | - | - | - |
| -5.6 | 0.82 | - | - | - | - |
| -5.6 | 0.85 | - | - | - | - |
| -5.5 | 1.05 | - | - | - | - |
| -5.3 | 2.74 | - | - | - | - |
| -5.0 | 13.07 | - | - | - | - |

$0.2 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ 0.2 0.2 0.2

| 0.61 mg | total | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |
| :--- | :--- | :--- | :--- |
| 0.63 | - | - | - |
| 0.61 | - | - | - |
| 0.46 | - | - | - |
| 0.68 | - | - | - |
| 1.67 | - | - | - |
| 6.65 | - | - | - |

$0.1 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ pH 5.6 - 5.6

$$
0.6
$$

$$
0.1-
$$

$$
-5.6
$$

$$
-5.7
$$

$$
-5.6
$$

$$
-5.4
$$

6.65
0.1
$20.4^{\circ} \mathrm{C}$
$20.25^{\circ} \mathrm{C}$
$20.1^{\circ} \mathrm{C}$
$18.0^{\circ} \mathrm{C}$
$16.2^{\circ} \mathrm{C}$

- 5.1
0.2
pH 5.4
1.53 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$
$0.2 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$
September 6, 1959.

| $0 \mathrm{~m} \ldots \ldots \ldots \ldots$ | $19.25^{\circ} \mathrm{C}$ |
| ---: | :--- |
| $2-\ldots \ldots \ldots \ldots \ldots$ | $18.7^{\circ} \mathrm{C}$ |
| $4-\ldots \ldots \ldots \ldots$ | $18.55^{\circ} \mathrm{C}$ |
| $6-\ldots \ldots \ldots \ldots$ | $18.45^{\circ} \mathrm{C}$ |
| $8-\ldots \ldots \ldots \ldots$ | $18.4^{\circ} \mathrm{C}$ |
| $10-\ldots \ldots \ldots \ldots$ | $18.4^{\circ} \mathrm{C}$ |
| $11-\ldots \ldots \ldots \ldots$ | $18.35^{\circ} \mathrm{C}$ |

- 5.4
1.6
0.2 -
- 5.4
1.59
0.2
- 5.4
1.53 -
0.2
-5.4
$-\quad 5.4$
0.2

10 - ................................

- 5.4
1.51
0.2

September 20, 1959.

| $0 \mathrm{~m} \ldots \ldots \ldots \ldots$ | $16.9^{\circ} \mathrm{C}$ |
| ---: | :--- | :--- |
| $2-\ldots \ldots \ldots \ldots$ | $16.9^{\circ} \mathrm{C}$ |
| $4-\ldots \ldots \ldots \ldots$ | $16.9^{\circ} \mathrm{C}$ |
| $6-\ldots \ldots \ldots \ldots$ | $16.9^{\circ} \mathrm{C}$ |
| $8-\ldots \ldots \ldots \ldots$ | $16.85^{\circ} \mathrm{C}$ |
| $10-\ldots \ldots \ldots \ldots$ | $16.8^{\circ} \mathrm{C}$ |

pH 5.5
1.25 mg total $\mathrm{CO}_{2} \cdot 1^{-1}$
1.21
0.2

- 5.5
1.16 - - - -
0.2
- 5.5
1.22 -
0.2
- 5.5
- 5.5
1.26
0.2
$16.8^{\circ} \mathrm{C}$
$16.8^{\circ} \mathrm{C}$
- 5.5
1.16
0.2

11

October 4, 1959.
$0 m \ldots \ldots \ldots \ldots$
$2-\ldots \ldots \ldots \ldots \ldots$
$4-\ldots \ldots \ldots \ldots \ldots$
$6-\ldots \ldots \ldots \ldots \ldots$
$8-\ldots \ldots \ldots \ldots \ldots$
$14.8^{\circ} \mathrm{C}$
$14.75^{\circ} \mathrm{C}$
$14.75^{\circ} \mathrm{C}$
$14.7^{\circ} \mathrm{C}$
$14.7^{\circ} \mathrm{C}$
$14.7^{\circ} \mathrm{C}$
$14.7^{\circ} \mathrm{C}$

| pH 5.5 | 1.12 mg | total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |
| ---: | :--- | :--- | :--- | :--- |
| -5.5 | 1.08 | - | - | - |
| -5.5 | 1.07 | - | - | - |
| -5.5 | 1.14 | - | - | - |
| - | - |  |  |  |
| -5.5 | 1.14 | - | - | - |
| -5.5 | 1.22 | - | - | - |
| -5.5 | 1.27 | - | - | - |
| - | - |  |  |  |


| 0.2 mg | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |
| :---: | :---: |
| 0.2 - | - |
| 0.2 - | - - |
| 0.2 | - - |
| 0.2 - | - - |
| 0.2 - | - - |
| 0.2 - | - - |
|  | 7* |



December 29, 1959. Transparency more than 11.5 m . Beginning formation of ice.

| 0 m | $3.25^{\circ} \mathrm{C}$ | pH 5.5 | 1.49 | mg t | total | $\mathrm{CO}_{2} \cdot 1^{-1}$ | 0.2 I |  | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $3.4{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.46 | - | - | - | 0.2 | - | ${ }^{-1}$ |
| 4 - | $3.4{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.48 | - | - | - - | 0.2 | - | - |
| 6 - | $3.5{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.45 | - | - | - - | 0.2 | - | - |
| 8 - | $3.6{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.48 | - | - | - - | 0.2 | - | - - |
| $10-$ | $3.6{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.46 | - | - | - - | 0.2 | - | - - |
| 11 - | $3.65{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.45 | - | - | - - | 0.2 | - | - - |
| January 17, 1960. Ice 10 cm thick. |  |  |  |  |  |  |  |  |  |
| 0.1 m . | $0.2{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.82 m | mg t | total | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.2 I |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| 2 m | $1.5{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.65 | - | - | - - | 0.2 | - | - |
| 4 | $1.6{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.77 | - | - | - - | 0.2 | - | - - |
| 6 - | $1.7^{\circ} \mathrm{C}$ | - 5.5 | 1.63 | - | - | - - | 0.2 | - | - |
| 8 | $2.7^{\circ} \mathrm{C}$ | - 5.5 | 1.73 | - | - | - - | 0.2 | - | - - |
| 10 - | $2.7^{\circ} \mathrm{C}$ | - 5.5 | 1.78 | - | - | - - | 0.2 | - | - - |
| 11 - | $2.75{ }^{\circ} \mathrm{C}$ | - 5.5 | 2.04 | - | - | - - | 0.2 | - | - - |

January 31, 1960. Ice 10 cm thick.

| 0.1 m . | $0.2^{\circ} \mathrm{C}$ | pH 5.6 | 1.41 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 m | $1.6{ }^{\circ} \mathrm{C}$ | - 5.6 | 1.35 | - | - | - | - | 0.2 | - | - | - |
| 4 | $1.7^{\circ} \mathrm{C}$ | - 5.6 | 1.41 | - | - | - | - | 0.2 | - | - | - |
| 6 - | $1.8^{\circ} \mathrm{C}$ | - 5.5 | 1.54 | - | - | - | - | 0.2 | - | - | - |
| 8 - | $2.75{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.68 | - | - | - | - | 0.2 | - | - | - |
| $10-$ | $2.75{ }^{\circ} \mathrm{C}$ | - 5.4 | 3.00 | - | - | - | - | 0.3 | - | - | - |
| 11 - | $2.8^{\circ} \mathrm{C}$ | - 5.3 | 5.17 | - | - | - | - | 0.3 | - | - | - |

February 14, 1960 . Ice 16 cm thick.

| 0.16 m . | $0.65{ }^{\circ} \mathrm{C}$ | pH 5.5 |
| :---: | :---: | :---: |
| 2 m | $2.3{ }^{\circ} \mathrm{C}$ | - 5.5 |
| 4 - | $2.9{ }^{\circ} \mathrm{C}$ | - 5.5 |
| 6 | $3.15{ }^{\circ} \mathrm{C}$ | - 5.5 |
| 8 - | $3.6{ }^{\circ} \mathrm{C}$ | - 5.4 |
| $10-$ | $3.8{ }^{\circ} \mathrm{C}$ | - 5.3 |
| 11 - | $3.8{ }^{\circ} \mathrm{C}$ | - 5.3 |

February 28, 1960. Ice 22 cm thick.

| $0.22 \mathrm{~m} \ldots \ldots \ldots$ | $0.65^{\circ} \mathrm{C}$ | pH 5.6 |
| ---: | :--- | ---: |
| $2 \mathrm{~m} \ldots \ldots \ldots$ | $3.0^{\circ} \mathrm{C}$ | -5.5 |
| $4-\ldots \ldots \ldots$ | $3.25^{\circ} \mathrm{C}$ | -5.5 |
| $6-\ldots \ldots \ldots$ | $3.6^{\circ} \mathrm{C}$ | -5.5 |
| $8-\ldots \ldots \ldots$ | $4.1^{\circ} \mathrm{C}$ | -5.3 |
| $10-\ldots \ldots \ldots \ldots$ | $4.1^{\circ} \mathrm{C}$ | -5.3 |
| $11-\ldots \ldots \ldots$ | $4.1^{\circ} \mathrm{C}$ | -5.3 |



April 24, 1960.

| 0 m | $7.6^{\circ} \mathrm{C}$ | pH 5.7 | 0.64 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  | 0.1 mg |  | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $7.6{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.59 | - | - | - - | 0.1 |  | - - |
| 4 | $7.6^{\circ} \mathrm{C}$ | - 5.7 | 0.60 | - | - | - - | 0.1 | - | - - |
| 6 - | $7.6^{\circ} \mathrm{C}$ | 5.7 | 0.60 | - | - | - - | 0.1 | - | - - |
| 8 - | $7.6{ }^{\circ} \mathrm{C}$ | 5.7 | 0.71 | - | - | - - | 0.1 | - | - - |
| 10 - | $7.6^{\circ} \mathrm{C}$ | 5.7 | 0.68 | - | - | - - | 0.1 | - | - - |
| 11 - | $7.6^{\circ} \mathrm{C}$ | - 5.7 | 0.73 | - | - | - - | 0.1 | - | - - |
| May 14, 1960. |  |  |  |  |  |  |  |  |  |
| 0 m | $13.4{ }^{\circ} \mathrm{C}$ | pH 5.7 | 0.69 |  | tal | $\mathrm{CO}_{2} \cdot 1^{-1}$ | 0.1 |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| 2 - | $13.3{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.67 | - | - | - - | 0.1 | - | - - |
| 4 - | $12.6{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.68 | - | - | - - | 0.1 | - | - - |
| 6 - | $10.5{ }^{\circ} \mathrm{C}$ | - 5.8 | 0.42 | - | - | - - | 0.1 | - | - - |
| 8 - | $9.6{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.57 | - | - | - - | 0.1 | - | - - |
| 10 - | $9.3{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.67 | - | - | - - | 0.1 | - | - - |
| 11 - | $9.3{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.93 | - | - | - - | 0.2 | - | - - |
| May 29, 1960. |  |  |  |  |  |  |  |  |  |
| 0 m | $14.4{ }^{\circ} \mathrm{C}$ | pH 5.6 | 0.81 | mg t |  | $\mathrm{CO}_{2} \cdot 1^{-1}$ | 0.1 |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| 2 - | $14.2{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.77 | - | - | - - | 0.1 | - | - - |
| 4 - | $13.9{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.83 | - | - | - - | 0.1 | - | - - |
| 6 - | $13.0{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.73 | - | - | - - | 0.1 | - | - - |
| 8 - | $11.3{ }^{\circ} \mathrm{C}$ | - 5.6 | 1.10 | - | - | - - | 0.2 | - | - - |
| 10 - | $10.3{ }^{\circ} \mathrm{C}$ | - 5.4 | 1.90 | - | - | - - | 0.2 | - | - - |
| 11 - | $10.5{ }^{\circ} \mathrm{C}$ | - 5.4 | 2.03 | - | - | - - | 0.2 | - | - - |



| 0 m | $17.9^{\circ} \mathrm{C}$ | pH 5.7 | 0.65 mg total $\mathrm{CO}_{2} \cdot 1^{-1}$ |  |  |  | 0.1 mg |  | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $17.8^{\circ} \mathrm{C}$ | 5.7 | 0.58 | - | - | - - | 0.1 | - | - | - |
| 4 | $17.7^{\circ} \mathrm{C}$ | 5.7 | 0.60 | - | - | - - | 0.1 | - | - | - |
| 6 | $17.1{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.64 | - | - | - - | 0.1 | - | - | - |
| 8 - | $15.1{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.65 | - | - | - - | 0.1 | - | - | - |
| $10-$ | $14.5{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.84 | - | - | - - | 0.2 | - | - | - |
| 11 - | $13.3{ }^{\circ} \mathrm{C}$ | 5.4 | 1.79 | - | - | - - | 0.2 | - | - | - |

July 27, 1960. Transparency 4 m ; Uroglena-Maximum.


August 9, 1960.

| $0.1 \mathrm{~m} \ldots \ldots \ldots$ | $19.5^{\circ} \mathrm{C}$ |
| :---: | :---: |
| $2.1-\ldots \ldots \ldots$ | $19.3^{\circ} \mathrm{C}$ |
| $4.1-\ldots \ldots \ldots$ | $19.1^{\circ} \mathrm{C}$ |
| $6.1-\ldots \ldots \ldots$ | $18.8^{\circ} \mathrm{C}$ |
| $8.1-\ldots \ldots \ldots$ | $18.1^{\circ} \mathrm{C}$ |
| $10.1-\ldots \ldots \ldots$ | $16.6^{\circ} \mathrm{C}$ |
| $11.1-\ldots \ldots \ldots$ | $15.6^{\circ} \mathrm{C}$ |

## pH 5.6

- 5.6
- 5.6
0.68 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$
0.63
$0.1 \mathrm{mg} \mathrm{HCO} 3 \cdot 1^{-1}$
2.1
$19.3^{\circ} \mathrm{C}$
- 5.6
0.65 -
0.1
0.68
0.1
- 5.5
1.47
0.1
- 5.4
1.83
0.2
- 5.0
13.73
0.2

August 28, 1960.

| 0.05 m | $18.7^{\circ} \mathrm{C}$ |
| :---: | :---: |
| 2.05 | $18.6{ }^{\circ} \mathrm{C}$ |
| 4.05 - | $18.4{ }^{\circ} \mathrm{C}$ |
| 6.05 | $18.2^{\circ} \mathrm{C}$ |
| 8.05 | $18.0^{\circ} \mathrm{C}$ |
| 10.05 | $17.9^{\circ} \mathrm{C}$ |
| 11.05 - | $16.9^{\circ} \mathrm{C}$ |

pH 5.6
0.97 mg total $\mathrm{CO}_{2} \cdot \mathrm{I}^{-1}$
0.86
0.2

- 5.6
0.94
0.2
- 5.6
-     -         - 

1.02 - - - 0.2

- 5.5
1.02 -
0.2
- 5.5
1.32
0.2

September 11, 1960.

| 0.03 m | $16.8^{\circ} \mathrm{C}$ |
| :---: | :---: |
| 2.03 - | $16.8^{\circ} \mathrm{C}$ |
| 4.03 - | $16.75^{\circ} \mathrm{C}$ |
| 6.03 - | $16.7^{\circ} \mathrm{C}$ |
| $8.03-$ | $16.7^{\circ} \mathrm{C}$ |
| 10.03 - | $16.65^{\circ} \mathrm{C}$ |
| 11.03 - | $16.6{ }^{\circ} \mathrm{C}$ |

```
pH 5.5
```

1.03 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$
$0.2 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$
pH 5.5
0.98
0.2

- 5.5
0.98 - - -
0.2
0.93 - - - 0.2
1.03 - - 0.2
- 5.5
1.05
0.2
0.2
$1.42-$
0.2

September 25, 1960.

| $0 \mathrm{~m} \ldots \ldots \ldots \ldots$ | $16.1^{\circ} \mathrm{C}$ |
| :---: | :--- |
| $2-\ldots \ldots \ldots$ | $15.95^{\circ} \mathrm{C}$ |
| $4-\ldots \ldots \ldots$ | $15.95^{\circ} \mathrm{C}$ |
| $6-\ldots \ldots \ldots$ | $15.95^{\circ} \mathrm{C}$ |
| $8-\ldots \ldots \ldots$ | $15.9^{\circ} \mathrm{C}$ |
| $10-\ldots \ldots \ldots$ | $15.9^{\circ} \mathrm{C}$ |
| $11-\ldots \ldots \ldots$ | $15.9^{\circ} \mathrm{C}$ |

```
pH 5.5
```

1.04 mg total $\mathrm{CO}_{2} \cdot \mathrm{I}^{-1}$
$0.2 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$
1.06 - - -
0.2

- 5.5
1.06
0.6
1.04 - - - 0.2
1.04 -
0.2
0.2
1.04 - - - 0.2

October 9, 1960.

| 0 m | $13.05^{\circ} \mathrm{C}$ | pH 5.5 | 1.28 mg total $\mathrm{CO}_{2} \cdot 1^{-1}$ |  |  |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.95 m . | $13.05^{\circ} \mathrm{C}$ | - 5.5 | 1.30 | - | - | - | 0.2 | - | - - |
| 3.95 | $13.05^{\circ} \mathrm{C}$ | - 5.5 | 1.28 | - | - | - - | 0.2 | - | - - |
| 5.95 - | $13.05^{\circ} \mathrm{C}$ | - 5.5 | 1.25 | - | - | - - | 0.2 | - | - - |
| 7.95 - | $13.05^{\circ} \mathrm{C}$ | - 5.5 | 1.30 | - | - | - - | 0.2 | - | - - |
| 9.95 - | $13.05^{\circ} \mathrm{C}$ | - 5.5 | 1.33 | - | - | - - | 0.2 | - | - - |
| 10.95 - | $13.05^{\circ} \mathrm{C}$ | - 5.5 | 1.32 | - | - | - | 0.2 | - | - - |
| October 19, 1960. |  |  |  |  |  |  |  |  |  |
| 0 m | $10.85{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.17 m | mg t | total | $\mathrm{CO}_{2} \cdot 1^{-1}$ | 0.2 m |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |
| 1.96 m . | $10.75{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.19 | - | - | - - | 0.2 | - | - - |
| 3.96 - | $10.7^{\circ} \mathrm{C}$ | - 5.5 | 1.16 | - | - | - - | 0.2 | - | - |
| 5.96 - | $10.7^{\circ} \mathrm{C}$ | - 5.5 | 1.14 | - | - | - | 0.2 | - | - |
| 7.96 - | $10.7^{\circ} \mathrm{C}$ | - 5.5 | 1.14 | - | - | - - | 0.2 | - | - |
| 9.96 - | $10.65{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.18 | - | - | - - | 0.2 | - | - |
| 10.96-.... | $10.65{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.15 | - | - | - | 0.2 | - | - |


| November 6, 1960. |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.03 m . | $8.45{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.30 |  |  | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.2 |  | HCO |  |
| 2.03 | $8.45{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.35 | - | - | - - | 0.2 | - | - | , |
| 4.03 | $8.45{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.29 | - | - | - - | 0.2 | - | - | - |
| 6.03 | $8.45{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.32 | - | - | - - | 0.2 | - | - | - |
| 8.03 | $8.45{ }^{\circ} \mathrm{C}$ | 5.5 | 1.29 | - | - | - - | 0.2 | - | - | - |
| 10.03 | $8.45{ }^{\circ} \mathrm{C}$ | 5.5 | 1.32 | - | - | - - | 0.2 | - | - | - |
| 11.03 | $8.45{ }^{\circ} \mathrm{C}$ | 5.5 | 1.37 | - | - | - - | 0.2 | - | - | - |
| November 20, 1960. |  |  |  |  |  |  |  |  |  |  |
| $0.04 \mathrm{~m} . . . . . . . . .$. | $6.35{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.46 |  |  | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.2 |  | HCO |  |
| 2.04 - | $6.3^{\circ} \mathrm{C}$ | - 5.5 | 1.49 | - | - | - - | 0.2 | - | - | - |
| 4.04 - | $6.2^{\circ} \mathrm{C}$ | - 5.5 | 1.51 | - | - | - - | 0.2 | - | - | - |
| 6.04 - | $6.15{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.54 | - | - | - - | 0.2 | - | - | - |
| 8.04 | $6.15{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.51 | - | - | - - | 0.2 | - | - | - |
| 10.04 - | $6.15{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.55 | - | - | - - | 0.2 | - | - | - |
| 11.04 - | $6.15{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.52 | - | - | - - | 0.2 | - | - | - |
| December 11, 1960. |  |  |  |  |  |  |  |  |  |  |
| 0.11 m . | $4^{\circ} \mathrm{C}$ | pH 5.5 | 1.53 |  | otal | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.2 |  | HCO |  |
| 2.11 - | $4^{\circ} \mathrm{C}$ | - 5.5 | 1.55 | - | - | - - | 0.2 | - | - | - |
| 4.11 | $4^{\circ} \mathrm{C}$ | - 5.5 | 1.52 | - | - | - - | 0.2 | - | - | - |
| 6.11 - | $4^{\circ} \mathrm{C}$ | - 5.5 | 1.54 | - | - | - - | 0.2 | - | - | - |
| 8.11 | $4^{\circ} \mathrm{C}$ | - 5.5 | 1.56 | - | - | - - | 0.2 | - | - | - |
| 10.11 - | $4^{\circ} \mathrm{C}$ | - 5.5 | 1.58 | - | - | - - | 0.2 | - | - | - |
| 11.11 - | $4^{\circ} \mathrm{C}$ | - 5.5 | 1.50 | - | - | - - | 0.2 | - | - | - |
| December 28, 1960. |  |  |  |  |  |  |  |  |  |  |
| $0.14 \mathrm{~m} . .$. . | $3.3{ }^{\circ} \mathrm{C}$ | pH 5.5 | 1.70 |  |  | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.2 |  | HCO |  |
| 2.14 - | $3.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.69 | - | - | - - | 0.2 | - | - | - |
| 4.14 | $3.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.67 | - | - | - - | 0.2 | - | - | - |
| 6.14 | $3.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.70 | - | - | - - | 0.2 | - | - | - |
| 8.14 | $3.3{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.67 | - | - | - - | 0.2 | - | - | - |
| 10.14 - | $3.35{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.67 | - | - | - - | 0.2 | - | - | - |
| 11.14 - | $3.35{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.67 | - | - | - - | 0.2 | - | - | - |
| January 22, 1961. Ice 12 cm thick. |  |  |  |  |  |  |  |  |  |  |
| 0.14 m ..... | $0.5^{\circ} \mathrm{C}$ | pH $5.5(5,51)$ | 1.53 | mg t | otal | $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ | 0.2 |  | HCO |  |
| 2.14 - | $2.0{ }^{\circ} \mathrm{C}$ | - $5.6(5,52)$ | 1.19 | - | - | - - | 0.2 | - | - | - |
| 4.14 | $2.3{ }^{\circ} \mathrm{C}$ | - $5.6(5,53)$ | 1.15 | - | - | - - | 0.2 | - | - | - |
| 6.14 | $2.4{ }^{\circ} \mathrm{C}$ | - 5.6 (5.53) | 1.29 | - | - | - - | 0.2 | - | - | - |
| 8.14 | $2.7^{\circ} \mathrm{C}$ | - 5.5 (5.51) | 1.82 | - | - | - - | 0.2 | - | - | - |
| 10.14 - | $3.05{ }^{\circ} \mathrm{C}$ | - 5.3 (5.51) | 3.38 | - | - | - - | 0.3 | - | - | - |
| 11.14 - | $3.35{ }^{\circ} \mathrm{C}$ | - 5.2 (5.42) | 7.15 | - | - | - - | 0.4 | - | - | - |
| February 12, 1961. Ice 5 cm thick. |  |  |  |  |  |  |  |  |  |  |
| 0.15 m . | $1.1^{\circ} \mathrm{C}$ | pH 5.6 (5.20) | 1.19 | ng | tal | $\mathrm{CO}_{2} \cdot 1^{-1}$ | 0.2 |  | HCO |  |
| 2.15 | $3.1{ }^{\circ} \mathrm{C}$ | - 5.6 (5.45) | 1.21 | - | - | - - | 0.2 | - | - | - |
| 4.15 | $3.2{ }^{\circ} \mathrm{C}$ | - 5.6 (5.47) | 1.15 | - | - | - - | 0.2 | - | - | - |
| 6.15 | $3.3{ }^{\circ} \mathrm{C}$ | - 5.5 (5.46) | 1.43 | - | - | - - | 0.2 | - | - | - |
| 8.15 | $3.4{ }^{\circ} \mathrm{C}$ | - 5.4 (5.46) | 2.25 | - | - | - - | 0.2 | - | - | - |
| 10.15 | $3.9{ }^{\circ} \mathrm{C}$ | - 5.3 (5.47) | 4.85 | - | - | - - | 0.3 | - | - | - |
| 11.15 - | $4.0{ }^{\circ} \mathrm{C}$ | - 5.2 (5.42) | 6.92 | - | - | - - | 0.4 | - | - | - |

February 26, 1961.

| $0.16 \mathrm{~m} \ldots \ldots \ldots$ | $3.7^{\circ} \mathrm{C}$ |
| :---: | :--- |
| $2.16-\ldots \ldots$ | $4^{\circ} \mathrm{C}$ |
| $4.16-\ldots \ldots$ | $4^{\circ} \mathrm{C}$ |
| $6.16-\ldots \ldots$ | $4^{\circ} \mathrm{C}$ |
| $8.16-\ldots \ldots$ | $4^{\circ} \mathrm{C}$ |
| $10.16-\ldots \ldots \ldots$ | $4^{\circ} \mathrm{C}$ |
| $11.16-\ldots \ldots$ | $4^{\circ} \mathrm{C}$ |

March 12, 1961.

| $0.16 \mathrm{~m} \ldots \ldots$ | $5.4^{\circ} \mathrm{C}$ |
| :---: | ---: |
| $2.16-\ldots \ldots$ | $5.4^{\circ} \mathrm{C}$ |
| $4.16-\ldots \ldots$ | $5.4^{\circ} \mathrm{C}$ |
| $6.16-\ldots \ldots$. | $5.4^{\circ} \mathrm{C}$ |
| $8.16-\ldots \ldots$. | $5.4^{\circ} \mathrm{C}$ |
| $10.16-\ldots \ldots$ | $5.4^{\circ} \mathrm{C}$ |
| $11.16-\ldots \ldots$ | $5.4^{\circ} \mathrm{C}$ |

March 26, 1961.

| 0.16 m . . . | $6.2{ }^{\circ} \mathrm{C}$ |
| :---: | :---: |
| 2.16 - | $6.2{ }^{\circ} \mathrm{C}$ |
| 4.16 | $6.2{ }^{\circ} \mathrm{C}$ |
| 6.16 - | $6.2{ }^{\circ} \mathrm{C}$ |
| 8.16 - | $6.2{ }^{\circ} \mathrm{C}$ |
| 10.16 - | $6.2{ }^{\circ} \mathrm{C}$ |
| 11.16 - | $6.2{ }^{\circ} \mathrm{C}$ |
| April 9, 1961. |  |
| 0.19 m | $6.85{ }^{\circ} \mathrm{C}$ |
| 2.19 - | $6.75{ }^{\circ} \mathrm{C}$ |
| 4.19 - | $6.6{ }^{\circ} \mathrm{C}$ |
| 6.19 - | $6.5^{\circ} \mathrm{C}$ |
| 8.19 - | $6.4^{\circ} \mathrm{C}$ |
| 10.19 - | $6.3{ }^{\circ} \mathrm{C}$ |
| 11.19 | $6.25^{\circ} \mathrm{C}$ |

11.19 - . . . . . . . . . . $6.25^{\circ} \mathrm{C}$

| April $23,1961$. |  |
| :---: | :---: |
| $0.16 \mathrm{~m} \ldots \ldots \ldots$ | $10.15^{\circ} \mathrm{C}$ |
| $2.16-\ldots \ldots \ldots$ | $10.15^{\circ} \mathrm{C}$ |
| $4.16-\ldots \ldots \ldots$ | $10.0^{\circ} \mathrm{C}$ |
| $6.16-\ldots \ldots \ldots$ | $9.85^{\circ} \mathrm{C}$ |
| $8.16-\ldots \ldots \ldots$ | $8.85^{\circ} \mathrm{C}$ |
| $10.16-\ldots \ldots \ldots$ | $8.3^{\circ} \mathrm{C}$ |
| $11.16-\ldots \ldots$ | $8.1^{\circ} \mathrm{C}$ |

May 7, 1961.

| $0.13 \mathrm{~m} \ldots \ldots \ldots$ | $12.6^{\circ} \mathrm{C}$ |
| :---: | :--- |
| $2.13-\ldots \ldots \ldots$ | $12.55^{\circ} \mathrm{C}$ |
| $4.13-\ldots \ldots$ | $12.4^{\circ} \mathrm{C}$ |
| $6.13-\ldots \ldots$ | $12.1^{\circ} \mathrm{C}$ |
| $8.13-\ldots \ldots$ | $11.5^{\circ} \mathrm{C}$ |
| $10.13-\ldots \ldots \ldots$ | $10.3^{\circ} \mathrm{C}$ |
| $11.13-\ldots \ldots$ | $10.25^{\circ} \mathrm{C}$ |


| pH $5.7(5.62)$ | 0.87 mg total $\mathrm{CO}_{2} \cdot 1^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $-5.7(5.64)$ | $0.85-$ | - | - | - |
| $-5.7(5.63)$ | $0.81-$ | - | - | - |
| $-5.7(5.63)$ | $0.78-$ | - | - | - |
| $-5.7(5.62)$ | $0.81-$ | - | - | - |
| $-5.7(5.63)$ | 0.84 | - | - | - |
| - | - |  |  |  |
| $-5.7(5.64)$ | 0.80 | - | - | - |


| pH $5.7(5.51)$ | 0.78 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $-5.7(5.51)$ | $0.79-$ | - | - | - |
| $-5.7(5.51)$ | $0.79-$ | - | - | - |
| $-5.7(5.51)$ | $0.76-$ | - | - | - |
| $-5.7(5.49)$ | $0.78-$ | - | - | - |
| $-5.7(5.50)$ | $0.76-$ | - | - | - |
| $-5.7(5.46)$ | $0.80-$ | - | - | - |

$0.1 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$
0.1
0.1
0.1
0.1
0.1 -
$0.2 \mathrm{mg} \mathrm{HCO}-\mathrm{H}^{-1}$

| pH 5.5 (5.52) | 1.68 mg |  | total | $\mathrm{CO}_{2} \mathrm{l} \cdot{ }^{-1}$ |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| - 5.5 (5.51) | 1.61 | - | - | - | - | 0.2 | - | - | - |
| - 5.5 (5.50) | 1.61 | - | - | - | - | 0.2 | - | - | - |
| - 5.5 (5.50) | 1.64 | - | - | - | - | 0.2 | - | - | - |
| - 5.5 (5.50) | 1.69 | - | - | - | - | 0.2 | - | - | - |
| - 5.5 (5.51) | 1.62 | - | - | - | - | 0.2 | - | - | - |
| - 5.5 (5.50) | 1.60 | - | - | - | - | 0.2 | - | - | - |


| pH 5.6 (5.49) | 1.19 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |  | 0.2 mg |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| - 5.6 (5.50) | 1.15 | - | - | - | - | 0.2 | - | - | - |
| - 5.6 (5.49) | 1.11 | - | - | - | - | 0.2 | - | - | - |
| - 5.6 (5.48) | 1.11 | - | - | - | - | 0.2 | - | - | - |
| - 5.6 (5.48) | 1.16 | - | - | - | - | 0.2 | - | - | - |
| - 5.6 (5.49) | 1.16 | - | - | - | - | 0.2 | - | - | - |
| - 5.6 (5.49) | 1.10 | - | - | - | - | 0.2 | - | - | - |

$0.1 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$
0.1
0.1
0.1
0.1 -
0.1 -
0.1
0.1 -

| pH 5.7 (5.54) | 0.66 mg total $\mathrm{CO}_{2} \cdot 1^{-1}$ |  |  |  |  | 0.1 mg |  | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| - 5.7 (5.52) | 0.64 | - | - | - | - | 0.1 | - | - | - |
| - $5.7(5.51)$ | 0.61 | - | - | - | - | 0.1 | - | - | - |
| - 5.7 (5.53) | 0.60 | - | - | - | - | 0.1 | - | - | - |
| - 5.7 (5.55) | 0.56 | - | - | - | - | 0.1 | - | - | - |
| - 5.7 (5.52) | 0.60 | - | - | - | - | 0.1 | - | - | - |
| - 5.7 (5.48) | 0.71 | - | - | - | - | 0.1 | , | - | - |


| pH $5.6(5.50)$ | 0.82 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $-5.6(5.50)$ | $0.77-$ | - | - |  |
| $-5.7(5.48)$ | $0.65-$ | - | - | - |
| $-5.7(5.50)$ | $0.65-$ | - | - | - |
| $-5.7(5.50)$ | $0.69-$ | - | - | - |
| $-5.6(5.46)$ | $1.07-$ | - | - | - |
| $-5.5(5.45)$ | $1.22-$ | - | - | - |

$0.1 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{I}^{-1}$
0.1
0.1
0.1
0.1
0.2
0.2

May 21, 1961.

| $0.1 \mathrm{~m} \ldots \ldots \ldots$ | $13.6^{\circ} \mathrm{C}$ |
| :---: | :---: |
| $2.1-\ldots \ldots \ldots$ | $13.5^{\circ} \mathrm{C}$ |
| $4.1-\ldots \ldots \ldots$ | $13.4^{\circ} \mathrm{C}$ |
| $6.1-\ldots \ldots \ldots$ | $13.4^{\circ} \mathrm{C}$ |
| $8.1-\ldots \ldots \ldots$ | $13.0^{\circ} \mathrm{C}$ |
| $10.1-\ldots \ldots \ldots$ | $11.25^{\circ} \mathrm{C}$ |
| $11.1-\ldots \ldots \ldots$ | $10.95^{\circ} \mathrm{C}$ |


| pH $5.6(5.50)$ | 0.75 mg total $\mathrm{CO}_{2} \cdot 1^{-1}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $-5.6(5.48)$ | $0.73-$ | - | - | - |  |
| $-5.7(5.49)$ | $0.69-$ | - | - | - |  |
| $-5.7(5.50)$ | 0.71 | - | - | - | - |
| $-5.6(5.51)$ | 0.86 | - | - | - | - |
| $-5.6(5.46)$ | 0.82 | - | - | - | - |
| - | $5.5(5.45)$ | 1.20 | - | - | - |
| - |  |  |  |  |  |


| 0.1 mg | $\mathrm{HCO}_{3}^{-} \cdot 1^{-1}$ |  |
| :---: | :---: | :---: |
| 0.1 | - | - |
| 0.1 | - | - |
| 0.1 | - | - |
| 0.1 | - | - |
| 0.1 | - | - |
| 0.2 | - | - |
|  | - | - |

June 4, 1961.

| 0.07 m | $16.2{ }^{\circ} \mathrm{C}$ | pH 5.6 (5.50) | 0.67 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  | 0.1 mg |  | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.07 | $16.0^{\circ} \mathrm{C}$ | - 5.6 (5.51) | 0.66 | - | - | - - | 0.1 | - | - | - |
| 4.07 - | $14.9{ }^{\circ} \mathrm{C}$ | - 5.6 (5.51) | 0.73 | - | - | - - | 0.1 | - | - | - |
| 6.07 - | $14.5{ }^{\circ} \mathrm{C}$ | - 5.6 (5.53) | 0.73 | - | - | - - | 0.1 | - | - | - |
| 8.07 - | $14.25^{\circ} \mathrm{C}$ | - $5.6(5.53)$ | 0.75 | - | - | - - | 0.1 | - | - | - |
| 10.07 | $13.8{ }^{\circ} \mathrm{C}$ | - 5.6 (5.51) | 0.87 | - | - | - - | 0.2 | - | - | - |
| 11.07 - | $13.1^{\circ} \mathrm{C}$ | - 5.5 (5.47) | 1.12 | - | - | - | 0.2 | - | - | - |


| 0.03 m . | $17.15{ }^{\circ} \mathrm{C}$ |
| :---: | :---: |
| 2.03 | $17.0^{\circ} \mathrm{C}$ |
| 4.03 | $16.9^{\circ} \mathrm{C}$ |
| 6.03 | $16.0^{\circ} \mathrm{C}$ |
| $8.03-$ | $15.6^{\circ} \mathrm{C}$ |
| 10.03 - | $14.95^{\circ} \mathrm{C}$ |
| 11.03 | $14.85^{\circ} \mathrm{C}$ |


| pH 5.7 | 0.50 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |
| ---: | :--- | :--- | :--- | :--- |
| -5.7 | 0.50 | - | - | - |
| -5.7 | 0.57 | - | - | - |
| -5.7 | 0.54 | - | - | - |
| -5.7 | 0.61 | - | - | - |
| -5.6 | 0.78 | - | - | - |
| -5.5 | 1.06 | - | - | - |
| - |  |  |  |  |

$0.1 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{I}^{-1}$
0.1
0.1
0.1
0.1
0.1

| pH 5.6 | 0.73 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| -5.6 | $0.64-$ | - | - | - |
| -5.6 | $0.72-$ | - | - | - |
| -5.6 | $0.65-$ | - | - | - |
| -5.6 | $0.72-$ | - | - | - |
| -5.6 | 0.69 | - | - | - |
| -5.2 | $4.14-$ | - | - | - |

$0.1 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$
0.1
0.1
0.1
0.1
0.1
$10-\ldots . . . . . .$.

- 5.2
4.14
0.4

July 23, 1961.

| 0 m | $17.65{ }^{\circ} \mathrm{C}$ | pH 5.6 | 0.70 mg total $\mathrm{CO}_{2} \cdot \mathrm{I}^{-1}$ |  |  |  |  | $0.1 \mathrm{mg} \mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 - | $17.55^{\circ} \mathrm{C}$ | - 5.6 | 0.64 | - | - | - | - | 0.1 | - | - | - |
| 4 | $17.55^{\circ} \mathrm{C}$ | - 5.6 | 0.64 | - | - | - | - | 0.1 | - | - | - |
| 6 - | $17.55^{\circ} \mathrm{C}$ | - 5.6 | 0.64 | - | - | - | - | 0.1 | - | - | - |
| 8 - | $17.45{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.75 | - | - | - | - | 0.1 | - | - | - |
| $10-$ | $17.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.42 | - | - | - | - | 0.2 | - |  | - |
| 11 | $17.2{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.67 | - | - | - | - | 0.2 | - | - | - |

April 20, 1962.

| $0.05 \mathrm{~m} \ldots \ldots \ldots$ | $7.8^{\circ} \mathrm{C}$ | pH 5.6 | $1.02 \mathrm{mg} \operatorname{lotal} \mathrm{CO}_{2} \cdot 1^{-1}$ | $0.1 \mathrm{mg} \mathrm{HCO}_{3} \cdot \mathrm{l}^{-1}$ |  |  |  |
| :--- | :--- | ---: | :--- | :--- | :--- | :--- | :--- |
| $2.05-\ldots \ldots$ | $7.8^{\circ} \mathrm{C}$ | -5.6 | $0.98-$ | - | - | $0.1-$ | - |
| $4.05-\ldots \ldots$ | $7.0^{\circ} \mathrm{C}$ | -5.6 | $0.94-$ | - | - | - | $0.1-$ |
| $6.05-\ldots \ldots$ | $6.6^{\circ} \mathrm{C}$ | -5.6 | $0.92-$ | - | - | - | $0.1-$ |


| 8.05 m | $6.3{ }^{\circ} \mathrm{C}$ |  | pH 5.6 |  | 0.90 mg total $\mathrm{CO}_{2} \cdot \mathrm{l}^{-1}$ |  |  |  | $0.1 \mathrm{mg} \mathrm{HCO}-{ }_{3}^{-} \cdot \mathrm{l}^{-1}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 10.05 | $6.65{ }^{\circ} \mathrm{C}$ |  | 5.6 |  | 0.94 | - | - | - | 0.1 | - - | - |
| 11.05 | $6.25^{\circ} \mathrm{C}$ |  | 5.6 |  | 1.01 | - | - | - | 0.1 | - - | - |
| July 24, 1962. Transparency 11.40 m . |  |  |  |  |  |  |  |  |  |  |  |
| 0 m | $17.5{ }^{\circ} \mathrm{C}$ | pH 5.7 | 0.52 | mg total | $\mathrm{CO}_{2} \cdot{ }^{-1}$ | 0.1 |  | $\mathrm{HCO}_{3}^{-} \cdot \mathrm{l}^{-1}$ | $\mathrm{O}_{2}$-sat | ration | 103\% |
| 2 - | $17.3{ }^{\circ} \mathrm{C}$ | - 5.7 | 0.56 | - - | - - | 0.1 | - | - - |  | - | 103\% |
| 4 - | $17.1^{\circ} \mathrm{C}$ | - 5.7 | 0.46 | - - | - - | 0.1 | - | - - |  | - | 103\% |
| 6 | $17.1^{\circ} \mathrm{C}$ | - 5.7 | 0.51 | - - | - - | 0.1 | - | - - |  | - | 103\% |
| 8 | $16.65^{\circ} \mathrm{C}$ | - 5.7 | 0.56 | - - | - - | 0.1 | - | - - |  | - | 105\% |
| 10 - | $15.2{ }^{\circ} \mathrm{C}$ | - 5.6 | 0.69 | - - | - - | 0.1 | - | - - |  | - | $126 \%$ |
| 11 - | $14.9{ }^{\circ} \mathrm{C}$ | - 5.5 | 1.53 | - - | - - | 0.2 | - | - - |  | - | 107\% |
| $11^{1 / 4} \mathrm{~m}$ | $14.9{ }^{\circ} \mathrm{C}$ | - 5.3 | 3.66 | - - | - - | 0.3 | - | - - |  |  |  |
| 11.40 m |  |  |  |  |  |  |  |  |  |  |  |

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[^0]:    *) In 1962 the ice broke up about April 6th, and in 1964 about April 1st.

