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by Uwe Tessenow

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Investigations on the silica metabolism of inland waters[1]

by

Uwe TESSENOW

From the Institute of Hydrobiology,
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Ploen, Federal Republic of Germany

(With 3 Plates, 67 Figures and 35 Tables in the text)

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[1] Abridged version of the dissertation bearing the same title, prepared under the direction of Professor Dr. W. Ohle.

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Summary

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Summary

In the present study, concentrations of silica in the waters of the lakes investigated were determined photometrically using the molybdenum blue method following standardization with sodium silicofluoride (Na_2SiF_6). The dissolved silica was estimated directly. The silica suspended in the free water or settled in the leake sediments as diatomic silica was determined after heating for one hour in 0.25% sodium carbonate solution. The silica bound in minerals and, especially, in quartz was estimated after melting with sodium carbonate.

Only the true dissolved silica is determined using either the molybdate or the molybdenum blue method. Dissolved silica is stable in solution in concentrations up to 50 - 60 mg Si/1. Condensation may take place only above that saturation concentration. Almost all fresh waters, thus, are strongly undersaturated with silica. Inorganic precipitation of silica may occur only by adsorption, but not by flocculation of colloidal silica, which was found neither in running waters nor in the free water of the lakes.

The pore-waters of the soils and of the lake sediments—both of great importance for silica metabolism in bodies of water—exhibit saturation concentrations of dissolved silica often far below the level of the saturation concentration of amorphous silica depending on both the temperature and the pH (Figures 4 to 12; Tables 2 to 5). In these waters the dissolved silica is in equilibrium not with amorphous silica but with chemically bound or adsorbed silica. The latter equilibria determine both the concentrations of silica in running waters and the liberation of silica from the sediments. They are achieved also in the overlaying water of closed mud-water systems, but are stable only in the presence of the solid phase (Figures 10 to 12). The solution equilibria of silica in soils are surprisingly well buffered and show remarkable resistance to leaching (Figures 6 and 7). That situation leads to constant concentrations of silica in drainage and spring waters (Tables 10 & 11).

The concentrations of silica of lake inlets and running waters were—at least in the region of investigation—determined mainly by the mixing ratio of soil waters (4 - 6 mg Si/1.), of spring waters (11 - 16 mg Si/1.), and of the waters leaving the lakes (0 - 12 mg Si/1.). The varying mixing ratios of the originating waters largely lead to a dependence of the concentrations

of silica in running waters on the water masses (Figures 32 and 33). Concentrations of 5 to 10 mg Si/l. have generally been found in the running waters of both Sleswig-Holstein and Jutland (Denmark) (Tables 15 and 16).

During the spring the concentrations of silica may decrease to 0.2 to 0.3 mg Si/l. in ditches with small water masses due to the activities of diatoms (especially, Synedra ulna) (Figure 34; Tables 13 and 14).

The decrease in the concentrations of silica dissolved in lake waters is caused either by biogenic utilization or by dilution. Abiogenic precipitation in the free waters of lakes plays an unimportant role in the metabolism of silica. In most lakes of Sleswig-Holstein the amounts of silica incorporated by diatoms during the main depletion period are limited by both the actual concentrations of silica and the depth of silica uptake in the water bodies. The final concentrations generally amount to 0.02 to 0.05 mg Si/l., and they are entirely independent of the initial concentrations (Figures 14, 18, 20, 26, 28 and 30). Since the absorption of silica by diatoms is independent of light and, in fact, increases in darkness (Figure 13; Table 6), uptake of silica may occur also below the oxygen compensation point. In consequence, surprisingly great depths of silica depletion may be observed in lakes (Figures 17, 18, 20, 26, and 68).

The amorphous silica of the diatoms produced during spring bloom is almost completely embodied in the sediments, i.e. at the beginning of summer stratification, almost all silica is incorporated into the sediments (Figures 15, 21, and 22). The periods of Si uptake during the summer and fall vary largely from one year to the next one, and they reach the spring level of uptake only in shallow lakes (Figures 14 to 16, and 24 to 31).

The dissolution of suspended silica may be highly accelerated in lakes and, above all, in ponds by disruption of the diatom shells by species of Daphnia and other zooplankters (Figures 40 to 44).

Because of the inferiority of abiogenic hydrolysis of the amorphous silica of diatoms compared with the biochemical condensation of dissolved silica, there arise muds rich in diatom shells, since silica is continuously delivered autochthonously and either continuously or periodically precipitated by diatoms. The silica accumulated in the sediments represents the basis for autochthonous Si removal. In general, that amount is greater than the quantity of allochthonous silica introduced from the surroundings in the course of the annual cycle. Autochthonous removal increases with increasing accumulation of silica (Table 34).

The interstitial solutions of muds are enriched in dissolved silica at a level far above the concentrations of lake inlets (Table 4, 15, and 16). As the silical removal from the mud is based on the exchange between the free overlaying water poorer in silica and the interstitial solutions, we may occasionally find in relative shallow lakes that the Si concentrations increase above the level at the lake inlets. Therefore, short periods of leaching of silica from the lake may occur.

The exchange between mud and water leads to a decrease of the concentration of dissolved silica in the sediments (Figures 45, 47, and 52) and on to more pronounced redissolution (Figure 48). Finally, an equilibrium is reached between redissolution and release at a relatively constant level of undersaturation. A steady-state prevails, which is continually tending toward a chemical equilibrium (maximum of entropy) but never reaches it because of the activities of the organisms (diatoms).

The rate of Si release from muds depends on both temperature (Figures 49 to 51; Table 21) and the difference of Si concentrations between mud and overlaying water. This difference is influenced by the renewal of the overlaying water by currents, by movements produced by benthic organisms (for instance, larvae of chironomids; Figures 46 to 48, and 60), and by gas bubbles escaping from the sediments. A correlation to the redox conditions of muds has been observed only in experiments using thin layers of mud.

The release of silica from the sediments varies largely depending on the temperature and on the conditions of exchange at different depth levels in the lakes. These aspects as well as both the morphometric constitution of the lake and the horizontal transport by currents may lead to heterograde stratification of silica (Figures 20, 24, 54, 55, 56, 58, 61, 68, and 70).

The varying release of silica is reflected in the sediments in both their silica content and their microscopical pattern (Figures 62 to 67). In profundal sediments of stratified lakes, diatomic silica is strongly accumulated and, thus, prevented from participating in the Si metabolism. However, the silica settled at shallower parts of these lakes is returned rather rapidly into the autochthonous metabolism. Profundal sediments—in particular, if they involve only relatively small areas—are not representative for the Si metabolism of a given lake.

The rate of Si removal computed for the entire lake volume (and related to the entire area) is surprisingly constant in contrast to the shorter periods of Si uptake and removal (Figures 16, 27, and 29). This stability depends on the afore-described exchange equilibria between mud and water.

The Si metabolism in lakes is predominantly autochthonous in character, but it is controlled to a large extent by allochthonous factors.

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Introduction and statement of the problem

.3.

The silica concentrations observed in lakes depend on both the autochthonous metabolism and a more or less pronounced allochthonous supply of dissolved silica.

The autochthonous silica metabolism of lakes is characterized, on the one hand, by the biogenic condensation [or conjugation] of dissolved silica to polysilicic acid (amorphous silica) and, on the other one, by the re-dissolution of these products of condensation. Numerous authors have been occupied with the utilization of silica in relation to diatom growth, while the regeneration of dissolved silica in the lakes hitherto has not yet been investigated in quantitative terms Thus, certain aspects have remained largely unclear, i.e. the extent to which the increases in silica concentration observed outside of the periods of depletion may be ascribed to the occurrence of hydrolysis in the free water; the extent to which these increases may be based on a release from the sediments; and the extent to which allochthonous inflow interfers directly in the silica metabolism. Likewise, it appears that the factors influencing the dissolution of silica in the free water and, above all, in the sediments (i.e. temperature, pH, exchange reactions; redox potential) hitherto have been investigated to a small degree only. The Si liberation or Si removal from the mud, in fact, has occasionally been recognized as representing an important source for the autochthonous silica metabolism (Einsele and Vetter, 1938; Elster and Einsele, 1938; and Yoshimura, 1939), but, with the exception of Mortimer's (1941-1942) studies, has not been investigated by experimental means. It was, thus, of some importance to carry out an investigation of the liberation or removal of silica from the mud using mud-water systems under controllable experimental conditions and to compare the degrees of Si release from muds from different lakes both with each other and with the results obtained in the in-situ investigations. Particular attention was to be paid to the experimental work.

The fact that the silica concentration in lake waters, in part, depends on the geochemistry of the area surrounding the waters has been stressed repeatedly. However, the processes underlying these relationships are large unclear. In this connection there also arises the question regarding the extent to which the silica concentrations of the lake inlets are influenced by both the solubility conditions prevailing at their sites of origin and the water masses introduced at a given time as well as the question regarding the influence the latter factors may exert on the silica metabolism of stagnant waters. The continuous investigations carried out in the different lakes, thus, had first to be extended to both the lake inflows and their originating waters and, secondly, to be supplemented with comparative investigations of lakes located within different physical environments.

I. Methods

1. Analysis of the waters

(a) Sampling - The water samples were withdrawn with the aid of a Ruttner sampler. Only in the Danish lakes, water samples were taken with the aid of polyethyelen bottles, which worked in accordance with the principle of Meyer's sampling bottle.

Water samples from close to the bottom were taken, in the investigations in the Ploen Lake Region, with the aid of an automatic sampler after Ohle (1931).

Both transportation and storage of the water samples, in principle, were carried out in polyethylene bottles with exclusion of light.

(b) Determination of dissolved silica - The concentrations of dissolved silica were determined photometrically using the molybdenum blue method as described by Mullin and Riley (1955). That method is based on the reduction of silicomolybdic acid to silicomolybdenum blue(II) with Metol® (or Photo-Rex®, i.e. methyl-p-aminophenol) and sodium sulfite in strongly acidic solution. The procedure worked out by Mullin and Riley was modified only a little for our purposes. .4.

According to the investigations carried out by Weitz et al. (1950) and by Alexander et al. (1954), only mono-silicic acid will react directly with molybdate, while the oligo acids and the poly acids must first be degraded to mono acid involving a loss of time corresponding to the degree of conjugation. Since the rate of degradation of amorphous silica is very low, and since, as a rule, no silica showing low degree of conjunction is present in the waters under consideration (cf. Section III), the present method determined only the ortho-silicic acid.

The molybdenum blue method was preferred over the molybdate method, i.e. the photometric and colorimetric determination of the yellow silicomolybdic acid, since the former, first, possesses a sensitivity almost twice that of the latter one; secondly, is disturbed hardly at all by impurities like humus, iron, phosphate or small amounts of hydrogen sulfide; and, thirdly, involves dealing with reduced silicomolybdenum blue(II), which is considerably more stable than the unreduced silicomolybdic acid.

All Si values reported in the present paper are related to standard solutions, which were prepared with sodium silicofluoride (Na_2SiF_6) after King (1939). The latter substance is hydrolysed completely, but very gradually, to ortho-silicic acid, so that the standard solution must be prepared several days before use and must be shaken repeatedly. Compared to all the other calibration (or standard) substances frequently used in laboratories—like quartz, amorphous silica and alkali silicates—sodium silicofluoride possesses the advantage that it has a stoichiometrically defined composition, is water-soluble and is not hygroscopic.

A comparison of the sodium silicofluoride standard with a quartz preparation (melting with sodium carbonate) yielded good agreement of values. The deviations found using these two methods were below 1%.

Picric acid showed no merit as calibration substance. The calibration factors reported in the literature in connection with this acid are very different. These differences probably are due to both the presence of impurities and the varying water contents of the preparations. Each batch prepared must be calibrated against a valid standard. Only then can that batch be used. We have employed picric acid solution only in orientating, excursive investigations. In the latter we have determined, by means of making comparisons against the sodium silicofluoride standard, a calibration value of 109 mg picric acid ≙ 100 mg Si. That value agrees with those reported by Wattenberg (1931) and by King and Lucas (1928).

(c) Determination of suspended diatomic silica in water - Since counting of diatom cells and cell fragments is not suited as a method in serial determinations of the silica suspended in the water, we have dissolved our material in hot, diluted sodium carbonate solution, and neutralized the alkaline silicate solution with hydrochloric acid.

Comparative investigations using silicic shells of different diatom species as well as other forms of amorphous silica (precipitated and dried silica, kieselguhr [diatomite], and diatom gyttja) and employing different sodium carbonate concentrations and different reaction times have shown that a sodium carbonate solution of 0.25% will dissolve all amorphous silica .5.
present within one hour of boiling in a water-bath. Dissolution of fresh planktonic diatoms, in fact, is completed already after boiling for 30 minutes and occasionally even after boiling for 15 minutes.

We then have used the following procedure:

(1) Mixed 50 ml. of the water sample (well shaken and withdrawn with the aid of a wide-mouthed pipette) with 25 ml. of a 0.75% sodium carbonate solution.

(2) Heated for one hour in a boiling water-bath in a sealed nickel cup (replacing a platinum cup).

(3) Cooled under running tap water and neutralized with 0.4 ml. of concentrated hydrochloric acid (if necessary, against phenolphthalein as indicator).

(4) Determined silica using the molybdenum blue method. Following addition of the molybdate-sulfuric acid, the sample must be shaken repeatedly in order to, first, expel the carbon dioxide completely and, secondly, redissolve the calcium carbonate precipitated from calcium carbonate-rich water in the course of sodium carbonate treatment (in strongly alkaline solutions calcium carbonate is able to absorb some dissolved silica).

Determination of the suspended silica is made by substracting the dissolved silica from the total silica.

The sources of error associated with this particular method are found, above all, in the Si content of sodium carbonate and the salt content of the neutralized water sample. These errors bring about that the Si concentrations determined in the range of low concentration (< 1 mg Si/l.) are too high, and these determined in the range of high concentration are too low. The negative deviation due to the salt error lies below 1% at Si concentrations of up to 3 mg Si/l.; however, the positive deviation due to the Si content of sodium carbonate is relatively large, above all, at concentrations below 0.3 mg Si/l. For that reason it is useful to plot a calibration curve using standard solutions containing equal quantities of sodium carbonate and acid.

The method described above will yield reliable results in cases where the total Si concentration is not less than 0.1 mg Si/l. and where the concentration of suspended silica in relation to that of dissolved silica is not too low.

2. Analysis of the sediments

(a) Sampling - Mud samples destined only for chemical examination were taken with the aid of a drive sampler of the type described by Ungemach (1960). Mud samples destined for exchange experiments were taken with the aid of a sediment sampler after Lenz (1931).

(b) Determinations made apart from the silica determinations - In order to estimate their dry substance, mud samples were dried at 105°C. The residue from glowing was determined after Ungemach (1960) by ashing for two hours in a muffle furnace at 550°C. The pH of wet mud samples was determined by electrometric means without either dilution or addition of KCl. The microscopic examinations were carried out with the aid of a plankton microscope following sedimentation of a suspension of wet mud in a plankton chamber.

(c) Determination of silica dissolved in the pore water of mud (in mg Si/l. of mud water [SW]) - The determination of silica dissolved in mud water must, if possible, be carried out immediately after sample taking, and this, above all, in cases where the quantity of substance is small. Admission of air occasionally leads to rapid fixation of the dissolved silica. .6.

In cases where adequate quantities were available, the wet mud was centrifuged at a number of revolutions as high as possible, and the supernatant mud water was then siphoned off; next the sample was diluted in correspondence with the [expected] Si content, and the Si concentration was then determined in the usual manner with the aid of the molybdenum blue method. In cases where it was either strongly colored or turbid, the mud water obtained on centrifugation was either filtered through a membrane filter or re-centrifuged following acidification to pH 2 to 3. Acidification results in the almost complete flocculation of the colloidal or finely disperse components, without any change in the concentration of dissolved silica being observable.

In cases where the quantities of substance were only small, the wet mud was suspended in a certain quantity of water and the suspension was then immediately filtered. That method has the disadvantage that rapid re-dissolution takes place in some suspended muds, so that, following slow filtration, the Si values obtained may be too high under certain circumstances by 10 percent.

The Si concentrations determined in the diluted filtrates were converted to liters of mud water (mg Si/l. mud water) in correspondence with the gravimetric dilution of the water contained in the wet mud.

Occasionally we have treated the mud suspensions and the wet muds described above with hydrogen sulfide in a Kipp apparatus (for 5 to 10 minutes) in order to determine in a semi-quantitative manner, in particular, the quantity of silica present in the oxidized upper layer of the mud of mud-water systems. The hydrogen sulfide was removed from the samples with the aid of cadmium sulfate in weakly acidic solution following filtration or centrifugation of the suspensions or wet muds, respectively.

(d) Determination of suspended or bound silica in mud - (α) "Free silica" after Zuellig (1956) - The method reported by Zuellig (1956) for the determination of so-called "free silica" in normal sodium carbonate solution at room temperature does not yield real values, as is demonstrated in Figure 1. The diatomic silica is attacked so strongly during the course of this treatment with cold sodium carbonate that the Si value obtained after treatment for one hour represents only a momentary value for the silicate concentration gradually increasing in the solution. That method, at best, will yield relative values for the rate of dissolution. A small fraction of the "free silica" is present in the mud water in true solution, but the greater part is present as finely disperse, amorphous silica.

(β) Determination of amorphous (diatomic) silica (in % Si_a) - The amorphous silica of sediments consists, above all, of the silica of the diatom shells and the shell remains. As will be demonstrated in Section VI, continuous dissolution of silica takes place in the upper layer of the mud—

a layer measuring several centimeters in thickness. It then follows that the Si weights of the individual cells determined in living cells cannot be applied to the shells present in the mud or, at best, can be applied only .7. with strong reservations. Furthermore, counts include only the identifiable remains, but not the small fragments and the fragments contained in the detritus, since their origins usually can no longer be discerned. These fragments frequently are so small that they will pass through normal filter paper and will sediment out in the centrifuge only with difficulty; however, they will be retained quantitatively on membrane filters (mesh size 0.5 µ). Furthermore, attention has repeatedly been drawn (Einsele and Grim, 1938; Joergensen, 1955b) to the variability in the Si contents of the individual cells of the same diatom species. We then realize that the method of counting under the microscope is not suited for ous purposes, i.e. the determination of the content of amorphous silica in the sediment, due to both the reasons outlined further above and the expenditure of time involved.

For all these reasons, we have used a chemical method suited for serial examinations; that method involves bringing the amorphous (diatomic) silica of the sediments into an alkaline medium, i.e. it is the same one already described further above in connection with the determination of the diatomic silica suspended in the water. We therefore mention here only the modifications associated with sediment examination:

Ten to 20 mg of dry substance are weighed, transferred into a nickel or platinum cup, and suspended in 50 ml. of 0.25% sodium carbonate solution. The suspensions are heated for 60 minutes in a boiling water-bath, neutralized, permitted to cool, filtered, and made up to a volume of 100 ml. In cases of pronounced brown coloration, the pH is adjusted to 2 to 3 with the aid of hydrochloric acid, and the precipitated colloids are then removed by centrifugation. Dilution is frequently required prior to actual Si determination.

This particular method permits rapid and reproducible determination of sodium carbonate-soluble silica. The sources of error mentioned in Section 1.c. (i.e. errors due to sodium carbonate impurities and salt) can be largely eliminated by appropriate selection of substance quantities and dilutions.

The disadvantage of the afore-mentioned method is found in the co-determination of a part of the silica bound in silicate minerals. That error is particularly large in mineral sediments containing small amounts of amorphous silica. Since exact separation of amorphous silica from silica bound in minerals could not be attained with the aid of the methods available, we were forced to accept that error. The quartz contained in the sediments, however, does not go into solution under the conditions outlined above.

This method can be employed, above all, in the case of autochthonous sediments rich in amorphous silica. In mineral sediments, this method yields only maximal values.

(γ) Determination of the total silica (termed Si_{tot}) - The determination of the total silica present in mud (i.e. amorphous, crystalline and silicate-bound) was carried out in the following manner: 10 mg of dry substance were weighed and put into a platinum cup, ashed, mixed with 1 g of anhydrous sodium carbonate, and melted for five minutes; after cooling, the molten mass was dissolved in distilled water and filled to a certain volume with water with simultaneous neutralization. In the course of these manipulations, great attention must be paid to avoid that the solution—as in the case of all procedures involving alkaline solutions—comes into contact with glass. As in all disintegration procedures, neutralization must be carried out only following appropriate dilution, since condensation to polysilicic acid will take place in neutral or weakly alkaline media above the saturation concentration of 50 - 60 mg Si/l., and that acid is not determined using the molybdate reaction.

II. Characters of the lakes investigated .8.

(1) The Large Ploen Lake (Gross Plöner See) - The Large Ploen Lake—well known on the basis of numerous scientific papers published by the Ploen Institute of Hydrobiology—exhibits a maximal depth of about 60 meters, and a surface measuring 30 square kilometers; it is the largest one of the lakes investigated in the present study with respect to the Si metabolism[1].

The short-term stratification studies were carried out only in the north-western part of the north basin (Ploen Basin), which maximally measures 44 meters in depth at Sampling Site F shown in Figure 2. The line separating that basin from the rest of the lake (broken line in the Figure) was laid down in a manner excluding the SW part of the basin because of its deviating stratification conditions. The hypolimnion of the basin demarcated in that manner is well separated from the rest of the Lake by a submarine barrier. The epilimnic connection to the central part of the Lake interfered with the

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[1] The bathymetric map of the Large Ploen Lake recently prepared by Dr. Utermoehl unfortunately was not yet available to me, so that I was forced to use in my calculations the data reported by Thienemann (1928) and a preliminary bathymetric map prepared around 1940 (cf. Figure 2).

separate consideration of the basin to the extent that a continuous, small inflow of Si takes place into the north basin, due to the Si concentration in the central basin higher by about 0.2 mg Si/l. than that of the north basin.

With the exception of the Tensfelder Au (600 - 700 l./sec) flowing into the Lake in the south, all of the larger inflowing waters reaching the Large Ploen Lake are desilicified already in the lakes located in the front of this Lake (i.e. the Behler Lake, Vierer Lake, and the Kembser Lake), so that Si inflow into the north basin is relatively small. The Si concentrations of the Lake varied between 0.02 and 3.4 mg Si/l. during the years 1960 to 1963. A characteristic diatomic gyttja is deposited in the deep basin. The Large Ploen Lake is euproductive (cf. Ohle, 1955b; 1958a; and 1959) and rich in calcium carbonate (with an acid-binding capacity of about 2.4 mEq./l.).

(2) The Vierer Lake (Vierersee) - The Vierer Lake (Figure 3), which is located along the eastern rim of the Large Ploen Lake, consists of two basins exhibiting different morphometric aspects. The large north basin (measuring 86 hectares) represents a wide, shallow trough exhibiting a maximal depth of 11 meters and a mean depth of about 6 meters. A hypolimnion does not exist; however, during calm weather in the course of the summer, we may frequently observe Si accumulations and oxygen depletion above the sediment and, occasionally, also sulfate reduction.

The southern basin (measuring 55 hectares) exhibits a maximal depth of 17 to 18 meters and a mean depth of about 8.5 meters; during the course of the summer that basin shows stable stratification with a H_2S-containing hypolimnion. The surface values reported above were determined with the aid of planimetry using the ordnance-survey map No. 1828, Ploen. The surface values reported by Ule (1891) and by Wegemann (1922) for the entire lake, viz. 222.8 and 206 hectares, respectively, are wrong.

.9. The Vierer Lake is euproductive (cf. Ohle, 1959) and calcium-carbonate-rich (with an acid-binding capacity of 2.0 to 2.7 mEq./l.); it receives inflows from field drainages and from numerous springs located in the immediate area surrounding the lake; furthermore, there is one inlet from the Heiden Lake. With the exception of the latter inlet, all inflows are very rich in Si. The Si concentrations in the Vierer Lake varied between 0.02 and 8 mg Si/l. during the years 1961 to 1963.

(3) The Heiden Lake (Heidensee) - The Heiden Lake is a natural, pond-like body of water with a mean depth of about two meters; its location is shown in Figure 3. According to Wegemann (1922), its surface measures 16 hectares. This Lake possesses one relatively strong inflow (20 to 40 l./sec), which inflow is made up of field drainages and receives a large addition of spring water just before opening into the Heiden Lake.

Due to the marked importation of nutrients and the continuous mobilization, production in this Lake is extraordinarily large (cf. Ohle, 1959). Despite its little depth, the macroflora is restricted to the shore zone due to the strong absorption of light by the turbid lake water. Apart from a narrow shore belt, the deposited sediment is very uniform in character. Even in the reduced state, the sediment is represented by a yellowish-brown gyttja, which is rich in diatoms in an advanced state of degradation. The color of the sediment may be attributed to clayey minerals transported into the Lake following floodings.

The silica concentration values varied between 0.02 and 12 mg Si/l. during the years 1960 to 1963. The acid-binding capacity, as a rule, lies around 3 to 4 mEq./l.

(4) The Pluss Lake (Plußsee) - The Pluss Lake is located in a basin-shaped valley, the slopes of which are covered with high beech woods. It, thus, receives large quantities of leaves, which greatly affect the Lake's metabolism. According to Ohle (1962) the Pluss Lake is characterized by extraordinarily great production and intensive metabolism. At the time of complete fall circulation, the acid-binding capacity of the lake water amounted to between 1.6 and 1.7 mEq./l.

Due to the low degree of wind activity, the summer epilimnion measures only five meters in thickness, and the state of stratification is highly stable. As a rule, anaerobic conditions prevail in the hypolimnion, so that higher bottom animals do not exist there.

The surface of this Lake measures 13.5 hectares; the mean depth amounts to nine meters, and the maximal depth, to 29 meters. The Pluss Lake receives hardly any inflow at all; only during the winter months, some water flows into the Lake from the surrounding meadows and fields as drainage (approximately 2 l./sec). The outflow into the Schluen Lake, too, carries small quantities of water only during the winter months (maximally 5 l./sec).

Due to the practical absence of allochthonous inflow of dissolved silica, the Pluss Lake is deficient in Si. The average concentration of the entire lake volume varied between 0.05 and 0.45 mg Si/l, during the years 1960 to 1963.

(5) The Schoeh Lake (Schöhsee) - The Schoeh Lake—the Ploen Institute .10.
of Hydrobiology is situated along its southern shore—is a body of clear water exhibiting a production that is low in comparison to the afore-mentioned lakes (Ohle, 1952; 1959; and 1962). However, during the late summer we find

H_2S formation also in the hypolimnion of this Lake. The Lake deposits an iron-rich mineral sediment (Ungemach, 1960). During the periods of complete fall and spring circulation, the acid-binding capacity amounts to 1.9 to 2.0 mEq./l. Apart from small meadow-drainage ditches, the Schoeh Lake receives no inflow. Its surface measures 79 hectares; its maximal depth is 30 meters, and its mean depth amounts to 13 meters (Wegemann, 1922).

The Si content estimated for the entire lake volume varied between 0.02 and 0.4 mg Si/l. during the years 1961 to 1963.

(6) The Ihl Lake (Ihlsee) - The Ihl Lake is a small, calcium carbonate-deficient sand lake without any inlets; it is located north of Segeberg along the eastern edge of the central Holstein sand region. The soils surrounding this Lake are podzolized sands covered with pine woods or the remains of a former heath vegetation. The Ihl Lake is populated by a Lobelia-Isoetes association.

The acid-binding capacity amounts to 0.28 mEq./l.; the maximal Si concentration calculated for the entire lake volume amounted to 0.08 mg Si/l. during the winter of 1962-1963. As a sand lake without inflow, this Lake is extremely poor in silica.

According to Wegemann (1915) the surface measures 42.5 hectares, and the maximal depth is 22.5 meters. Recent re-measurements and re-calculations of both the surface area and the respective layer volumes have been based on the corrected mean depth of 6.6 meters (formerly given as 7.6 meters). The volume, thus, amounts to 3.23×10^6 cubic meters, instead of 2.83×10^6 cubic meters.

III. Equilibrium concentrations of dissolved silica

1. The solution equilibrium of amorphous silica and quartz

Already certain earlier investigations (Struckmann, 1955; Lenher and Merrill, 1917; and Jander and Heukeshoven, 1931), but, in particular, the studies published since 1050 by Alexander et al. (1954), Baumann (1955), Krauskopf (1956), Okamoto et al. (1957), and Kautsky et al. (1962) have demonstrated that there exists in waters a temperature-dependent solution equilibrium between the mono-molecularly dissolved silica and the different forms of polymeric silica. According to both Iler (1955) and Alexander (1957), that solution equilibrium is determined by both the size and the structure of the surface area of the silica particles, i.e. by the number of hydrolytically active surface groups." It then follows that aged, subcrystalline and crys- .11.
talline SiO_2 compounds, due to their lower surface energy, exhibit a lower solution equilbrium than does a freshly prepared silica sol. In the case of the young and, thus, highly active amorphous silica—which according to both Rogall (1939, and 1959) and Helmcke (1954) is employed in the construction of diatom shells—this solution equilibrium amounts to 50 to 65 mg Si/l. (= 100-140 mg SiO_2/l.) in the neutral and weakly alkaline region at 20 to 25°C. Solubility increases greatly above pH 9 due to the more pronounced dissociation taking place at that pH[2].

According to Krauskopf (l.c.) and Greenberg and Price (1959), the solution equilibrium of amorphous silica is influenced hardly at all by the ions dissolved in fresh waters or seawaters. The influence of the temperature, likewise, is small within the range of temperatures normally occurring

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[2] The solubility curve after Correns (1940) may be regarded as being dated.

on the surface of the Earth. Krauskopf (l.c.) has given 60 to 80 mg SiO_2/l. for 0°C, and 100 to 140 mg SiO_2/l. for 25°C. In our own experiments, we have obtained a constant final value of 85 to 96 mg SiO_2 for 5°C and pH 6 to 8, and one of 116 mg SiO_2 for 15°C and pH 7.5 on dissolution of a silica sol added in low excess.

Apart from a few exceptions the surface waters, thus, are highly undersaturated solutions with regard to amorphous silica, and in these waters condensation of dissolved silica to polysilicic acid cannot take place. Since the Si dissolved in the water is present to the greatest part by far in the form of undissociated silicic acid (silica), it is improper to speak of silicate dissolved in water.

The conclusions drawn regarding the saturation concentrations of dissolved silica in natural waters also are not impaired by the fact that quartz, due to its low surface energy, exhibits only a solubility of 3 to 5 mg Si/l. (Gardner, 1938; Van Lier et al., 1960; Morey et al., 1962), so that many waters are oversaturated with regard to quartz. Since the rate of dissolution of quartz as well as the rate of quartz precipitation from the water are extremely low under the conditions normally prevailing on the surface of the Earth, and crystallization of quartz takes place only under certain, as yet unknown, conditions; since, furthermore, there develops an amorphous weathered layer on the surface of the quartz crystalls (O'Connor and Greenberg, 1958; and Van Lier et al., l.c.); and since silicate minerals, as a rule, participate in the solution equilibria in the pore-waters, we must assume with Morey et al. (l.c.) that the solution equilibrium of quartz is only rarely realized in nature under normal conditions of temperature and pressure. .12.

The high silica concentrations found by various authors (Schmidt and Lüchtrath, 1955; and Morey et al., l.c.) must be attributed to the disturbed surface layer of quartz particles (O'Connor and Greenberg, l.c.). The hypothesis proposed by Baumann (l.c.) and Stoeber (1956), viz. that the different SiO_2 forms differ only with respect to their rates of dissolution, but not with regard to their solubilities, and that the dissolution of aged gels to the crystalline modifications is irreversible, must be regarded as having been refuted on the basis of the experimental results reported by the authors already mentioned a number of times.

Recent realizations regarding the solubility of silica permit us to conclude that the different forms of amorphous silica—whatever their state of conjugation may be—represent metastable compounds in the free water of inland waters and of the sea, which can come into being only by biogenic means. The "colloidal" silica found by Laaksonen (1956) in springs and ponds, and by Wawrik (1960a) in Lunz running waters; and by Jaernefelt (1963) in Finnish lakes (which authors have presented no description of their methods!), probably, represented only finely disperse, detritus-contained amorphous, absorbed or mineral-bound silica, which can be separated already with the aid of a bacterial filter. In the examination of silica suspended in water, we must absolutely distinguish between the finely disperse and the colloid-disperse fractions.

2. Equilibrium concentrations of silica dissolved in pore-waters of the soil and of the water-body sediments

(a) Introductory remarks - The saturation concentrations described further above for amorphous silica are attained only rarely in natural waters.

In the case of the surface waters that undersaturation is not surprising, because the Si concentrations are kept at a relatively low level due to the continuous biogenic fixation of Si. However, we find also in the case of the pore-waters of the soil, of the mineral sub-soil, and of the water-body sediments that the concentrations, in most instances, are below the saturation values of 50 to 60 mg Si/l. determined in the experiment using pure solutions.

(b) Silica concentrations in the pore-waters of the soil and of the mineral sub-soil - Only very recently workers have turned their attention to the problem regarding the factors determining the silica concentrations in the soil waters. This problem is of significance to the limnologist to the extent that it touches on the relationships existing between the geological -13- and edaphic features of the catchment area, on the one hand, and the silica metabolism of the inland lake, on the other one. The silica concentrations of the waters flowing into a given lake and that of the running waters are determined to a large extent by the solubility conditions existing at their respective sites of origin.

In the drainage waters, which feed the inlet opening into the Heiden Lake (cf. Figure 3), we have been able to demonstrate relatively uniform Si concentrations, which were strikingly constant during the entire course of the year. The Si concentrations in the latter waters were always between 4 and 6 mg Si/l. Even following instances of unussually strong precipitation, which led to inflow of large masses of water, we were unable to observe any decreases in the Si concentration. On the other hand, we found that the spring waters (ground waters) in the Ploen region exhibited a relatively uniform and constant concentration in the region between 12 and 15 mg Si/l. (cf. Tables 10 and 11, and pages 40 and 41). The difference in the concentrations between drainage and spring waters can hardly be explained alone by the different contact times of the respective waters with the silicate minerals in the soil or the mineral sub-soil, respectively, since, in that case, we would expect to observe large variations in the Si concentrations of the drainage waters in the course of the year. The situation rather suggests that we are dealing here with equilibria, which are well buffered against different degrees of loading (represented by the rate of percolation of the rain water).

We have carried out a number of different percolation experiments using soils, which we shall first describe and then discuss. The experimental design was as follows (cf. Figure 5, left part): The moist (preliminary experiment) or air-dried soil samples (remaining experiments) were put into 2000-ml polyethylene bottles after large stones and plant rests had been removed and large soil clumps had been crushed; the bottom of these bottles had first been cut off, and they were set up upside down filled to the rim. The percolating water was dripped onto the soil surface and, once the water holding capacity had been reached, collected at the lower end of the bottles. Experiments of this type were carried out in closed systems as well as in open systems. In the former case, the percolate was continuously returned within the closed system, i.e. dripped again onto the soil surface; in the latter case, water was dripped on in a continuous manner and collected, but not returned for additional runs. All experiments were carried out in the dark at room temperature.

First experiment (preliminary experiment using garden soil): Leaching (A) and regeneration (R) of dissolved silica in the soil (Figure 4).

Using moist, sandy garden soil from the Institute grounds, the dissolved and, in part, absorbed silica was first leached out by application of a high percolation rate (up to 300 ml./hour) and then again regenerated in the closed system.

(α) Leaching: With 11 mg Si/l., the maximal Si concentration was almost reached already in the first percolate (100 ml.). The concentration then increased to 11.8 mg Si/l. and subsequently decreased only to 10.6 mg Si/l. .14.
in the sixth 100-ml percolate, which had run through at Hour 12 after the start of the experiment. On the other hand, we found that the electrolytic conductivity decreased in the first six percolates from 1100 to 400 μS_{20}. Following a pronounced increase of the percolating rate and percolation of an additional eight liters of distilled water, we finally observed marked leaching from the soil sample. The final values of leaching and, thus, the initial values of regeneration were the following ones:

Si concentration:	0.62 mg Si/l.
Electrolytic conductivity:	38 μS_{20}
pH:	6.6.

(β) Regeneration: The regeneration experiment using the closed system was started with one liter of the percolating water collected last in the leaching experiment. Due to the continuous withdrawal of samples, that volume of one liter decreased within the experimental period of five months to a few milliliters. This continuous decrease of the percolating water accelerated the increase of the Si concentration. On average, one percolation was carried out each day. After three months, we found that the initial concentration of 11.8 mg Si/l. had been reached; however, there occurred a further increase to 12.7 mg Si/l. during subsequent percolation. The latter concentration level was not exceeded during the following two months. Even vigorous mixing of the percolating water with the soil sample or drying of the soil sample and subsequent re-saturation with water did not bring about a change in that level of concentration: The soil-water system had become saturated with regard to silica. The difference with respect to the initial value is small and may have been due to an increase in the experimental temperature: The experiment was started a few hours after obtaining the partly frozen soil sample (on December 4, 1962), but carried out at room temperature.

Second experiment: Equilibrium concentrations of silica dissolved in the upper soil and the sub-soil of the Heiden Lake catchment area (Figures 5 to 7).

(α) Description of the soil: The soils within the main catchment area of the waters flowing into the Heiden Lake are para-brown earths on top of boulder clay. The A horizon is greyish-brown, extensively scoured and, at some points, already strongly acidic. The B horizon shows evidence of clay and calcium-magnesium carbonate accumulation. This shifting of the calcium-magnesium carbonate has led to the formation of a calcium-magnesium carbonate horizont between the B and C horizons at a depth of 1.2 to 1.5 meters. In the sub-soil, numerous rust spots indicate dislocation of iron. Due to the density of the sub-soil, the soils tend, above all at level sites, to show wetness due to impounding, and, for that reason, must be drained. The soil samples employed in our experiments were obtained at a natural section along the road to Eutin close to the county border. That section had been laid bare recently in a field during the digging of a drainage ditch (A, in Figure 3).

(β) Description of the experiment: In the first part of the experiment (Vessels A_1 and B_1, in Figure 5), we have treated soil samples from the A and B horizons separately: Using the open system, 100 ml. of distilled water were percolated each day up to Day 20 of the experiment. That quantity of water corresponds to a "height of precipitation" of 10 mm in 24 hours. The solution equilibrium in the soil-water system, thus, was exposed to unnaturally high loading, and this, in particular, since the height of the soil column was only 20 centimeters. After Day 20 of the experiment, percolation was continued in the closed system using the 200 ml. of percolate collected last. The Si concentrations and the electrolytic conductivities measured in the individual percolates are shown in Figure 6. The remaining data have been summarized in Table 1.

Table 1 Tabelle 1 .15.

1. Perkolat	3. PA_1			5. PB_1		
Nr.	2. SBV	pH	4. Hufa[3]	SBV	pH	4. Hufa[3]
1	1,2	6,6	60	1,4	7,5	20
2	1,6	7,5	—	2,1	7,4	—
3	1,3	7,6	45	2,6	8,1	10
4	0,9	7,5	—	2,9	7,8	—
6	0,6	7,4	35	3,1	8,1	6
8	0,6	7,4	40	2,9	8,1	—
10	0,6	7,3	50	2,7	8,2	6
16	0,7	7,3	50	2,4	8,2	5
20	0,7	7,1	40	2,3	8,0	5

Table 1 - Key: 1, percolat No.; 2, acid-binding capacity; 3, percolate from soil A; 4, humus color given in color units after Ohle (1934), in 0.01 mg methyl orange/l., 5, percolate from soil B.

The electrolytic conductivity, at first, decreased greatly in the percolate of the A horizon sample as well as in that of the B horizon sample (PA_1 and PB_1), i.e. during the first ten days it decreased from 1800 and 1400, respectively, to about 300 μS_{20}. The silica concentrations, on the other hand, remained at the same level right from the start, apart from a few minor variations. The humus color and the pH values also were rather constant. The acid-binding capacity (SBV) initially increased slightly in order to decrease gradually.

The percolates of A_1 and of B_1 differed, apart from their silica contents, also in the three parameters acid-binding capacity, pH, and humus color. These different properties would have to be attributed to the translocation processes within the soil profile.

In the course of percolation in the closed system (Days 20 to 37 of the experiment) we observed no noteworthy changes. Only the electrolytic conductivity increased again gradually (Table 2).

Table 2

Tabelle 2

Versuchs-	2. PA_1			3. PB_1		
1. tag	mg Si/l	μS_{20}	pH	mg Si/l	μS_{20}	pH
23.	6,85	168	7,1	2,80	227	8,1
26.	6,90	211	6,9	2,80	232	7,8
31.	6,90	261	7,1	2,78	242	8,0
37.	6,90	326	6,9	2,80	251	7,9

Table 2 - Key: 1, Day of experiment; 2, percolate from soil A; 3, percolate from soil B.

In the second part of the experiment (Vessels A_2 and B_2, in Figure 5), we treated the soil samples from the A and B horizons up to Day 22 as an integrated system in correspondence with the natural situation: As is shown in Figure 5, the percolate of the upper soil sample (following withdrawal of a small quantity for Si determination) was subsequently passed through the sub-soil sample. After Day 22 of the experiment we—as already done during the first part of the experiment—percolated each vessel in a closed system. The Si concentrations found in Percolates PA_2 and PB_2 are shown in Figure 7 together with those obtained in PB_1 of the first part of the experiment.

Third experiment: Behavior of the silica solution equilibrium in the soil on artificial modification of the reaction conditions. .16.

(α) Continuous addition of hydrochloric acid or sodium hydoxide solution to the soil-water system: Following conclusion of the afore-described experiments, the soil samples from the A horizon (Vessels A_1 and A_2) were first percolated in a closed system without addition of either hydrochloric acid or sodium hydroxide solution until a certain steady state had been attained. Next—with continuation of the closed percolating system—we added a few milliliters of n hydrochloric acid or n sodium hydroxide solution to the percolating water at intervals of several days. Including the water held in the soil samples, a total ot 700 to 800 ml. of water was in circulation per Experimental Vessel. The afore-reported quantities of hydrochloric acid and sodium hydroxide solution, respectively, thus were diluted in correspondence with that quantity of circulating water. The pH values and the Si concentrations measured as well as the quantities of hydrochloric acid and sodium hydroxide solution added in the course of the experiment have been summarized in Table 3.

Table 3 Tabelle 3

1. Versuchstag	pH	A$_1$ mg Si/l	+ ml n HCl	pH	A$_2$ mg Si/l	+ ml n NaOH
1	6,92	7,00	2	6,90	7,40	2
3	—	7,05	2	—	6,95	2
6	6,86	—	5	7,05	—	5
11	6,70	7,10	5	7,04	5,85	5
21	6,50	9,10	3	7,20	4,50	3
31	6,65	9,90	5	7,38	4,45	5
38	6,68	11,40	10	7,63	4,25	10
50	6,50	13,80	—	7,80	4,00	—
1—50	—0,4	+ 6,8	32	+ 0,9	—3,4	32

Table 3 - Key: 1, Day of experiment.

(β) Decrease of acidity on addition of calcium carbonate and sodium hydrogen carbonate (Figure 8): In accordance with the experimental design outlined further above, we dripped [distilled] water onto air-dried soil taken from plough-land (approximately 2 kg) until an adequate excess (200 ml.) had been collected in the collecting vessel after the water holding capacity had been reached. Using that excess of percolating water, which decreased gradually in volume due to the withdrawing of samples, we then continued percolation in the closed system to the end of the experiment. The Si concentrations in the water dripped onto the soil samples amounted either to zero (distilled water) or to 20 mg Si/l. (silica solutions prepared by heating a greatly diluted, dialyzed silica sol), respectively.

The initial concentrations in the respective percolates, which had passed through the samples a few hours after the start of dripping, amounted to 10.5 and 17.4 mg Si/l., respectively. As is demonstrated by Figure 8, an equilibrium had been attained already in the first percolate by means of dissolution. However, the equilibrium was attained in a very delayed manner when binding of excess silica was involved. The rather high Si concentrations of 10.5 mg Si/l. (i.e. high compared to the results obtained in the second experiment, Vessels A_1 and A_2) and the distinctly delayed Si binding must be attributed to the relatively greater acidity of these soil samples: The pH value of the percolating water was 5.3 at the start of the experiment and then gradually decreased to 4.7.

On Day 21 of the experiment, 10 g of powdered calcium carbonate were washed into the loose soil with the percolating water. At first, we observed rapid fixation of the dissolved silica, which then gradually decreased, although the pH values in the percolating water continued to drop. Addition of calcium carbonate to isolated percolating water did not result in a change of the Si concentration. The latter finding then indicates that the binding of silica was not done directly by the calcium carbonate added; rather, treatment of the soil with calcium carbonate had created the preconditions required for a shift of the silica equilibrium in favor of fixation onto substances in the soil capable of absorption. .17.

Finally we found that the acidity of the soil-water system was completely neutralized following addition of 10 g of sodium hydrogen carbonate: The pH value of the soil water rose to 8.5, and the Si concentration dropped to a new level (1.5 mg Si/l.). In addition we found at that high pH value that a marked translocation of humic acids took place. The percolates were coffee-brown colored.

Summary and discussion of the experimental results

(1) Equilibrium concentrations of dissolved silica prevail in soil-water systems; the equilibria are attained immediately after the penetration of water into air-dried soil. In extraction experiments using soil samples, McKeague and Cline (1963), too, have made the observation that the Si concentration increased very greatly in the extracting agent already during the first minutes, and they have assumed that the soil particles are surrounded by an envelope of absorbed mono-silicic acid, which acid can be liberated very rapidly.

(2) The solution equilibrium of silica in soil water, in contrast to both the acid-binding capacity and the electrolytic conductivity, is surprisingly well buffered. That equilibrium shows great resistance to prolonged, unnaturally high loading produced by high percolation rates. These experimental results agree with the constancy of the Si concentrations found in both drainage and spring waters. McKeague and Cline, on the other hand, have observed a decrease in the Si concentration in extracts obtained in the course of continuous extraction by means of repeated soaking of soil samples with distilled water and subsequent removal of the pore-water by centrifugation after the moist soil samples had been stored for a certain period of time. That deviating result may have been caused by treatment of the soil samples not corresponding to the natural conditions (i.e. pronounced discontinuous change of water), but may also indicate that different soils exhibit different buffering capacities with respect to the Si equilibrium. As is demonstrated in Figure 4, the solution equilibrium is regained only gradually following severe disturbance due to intensive leaching. It appears probable that

the silica bound either in an absorptive manner or to exchanger substances, which silica is in equilibrium with the dissolved silica, must first be regenerated by means of silicate hydrolysis.

(3) The level of the equilibrium of dissolved silica in the soil .18. water depends to a large degree on the acidity of the soil. The percolate obtained from the strongly acidic soil sample used in Experiment 3.β. exhibited a significantly higher Si concentration (cf. Figure 8) then that of the neutral upper soil layer used in Experiment 2 (cf. PA_1 and PA_2, in Tables 1 and 2, and in Figures 6 and 7), although both samples had been obtained from the upper soil layer of plough-lands, which are located not far apart (several 100 meters). Increases in acidity (i.e. addition of hydrochloric acid) brings about a rise of the silica solution equilibrium of soil-water systems, while decreases of acidity (addition of NaOH, $CaCO_3$ or $NaHCO_3$, respectively) brings about a depression of that equilibrium (Table 3, and Figure 8).

Investigations carried out by McKeague and Cline (l.c.) and by Jones and Handreck (1963), using suspensions of the hydrated oxides of iron and aluminum (cf. also Ohle, 1964) as well as iron- and aluminum-containing soils and minerals, have shown that silica is particularly strongly absorbed in neutral to weakly alkaline media, while absorption above pH 10 decreases very rapidly, and in the acidic region, gradually. In a soil sample from the experimental grounds of the School of Agriculture of Melbourne University, which soil was available in different pH phases (pH 5.5 to 7.2), Jones and Handreck (l.c.) found that the silica concentrations in the soil water decreased with increasing pH from 60 to 23 mg SiO_2/l.

The transportability of silica in the soils, thus, is maximal under acidic conditions, and not—as has been generally believed hitherto—under neutral or weakly alkaline conditions (cf. Scheffer and Schachtschabel, 1960, page 20; and Hutchinson, 1957, page 790).

(4) Upper soils and sub-soils endow their percolates with different properties, among which properties we must stress in particular the pronounced difference in silica contents: In the present experiments, the Si concentrations in the percolates of the upper soil were more than twice as high than those of the percolates of the sub-soil. The silica concentrations in the percolates of the sub-soil exhibited identical levels when percolation was started with distilled water and when percolation was started with the percolate from the upper soil. In the former case, Si dissolution (liberation) takes place; in the latter one, Si fixation (depletion) takes place. In both cases, however, the final result was the same (Figure 7). Transportation of silica into the sub-soil may occur on the basis of the different equilibrium concentrations prevailing in the upper soil and the sub-soil, respectively. That transportation takes place in the dissolved form of silica, and not in the colloidal one. The results obtained in our second experiment (Figure 7) do not support the contention suggested by McKeague and Cline, *viz.* that the decrease in the Si concentration observed on increase of the pH value in soil-water systems represents an event due to pure absorption, which follows Freundlich's absorption therms, because we have found in our .19.
experiments that the final concentration was independent of the initial concentration despite high percolation rates. Attainment of the equilbrium takes place from above as well as from below.

The silica concentrations observed in the pore-waters may be regarded as complex acid-base equilibria, with the ions involved being either dissolved in the pore-water or bound as fixed ions to an exchanger substance.

Since silicic acid (silica) is a very weak acid, it follows that the equilibrium will be shifted toward increased silica fixation with increasing basicity, with the maximum of fixation and, thus, the minimum of free, dissolved silica, being shifted very far into the alkaline region (cf. Figures 8 and 9; McKeague and Cline, l.c., page 89; and Ohle, 1964).

The Si concentrations in the seepage waters of the soil are determined by the respective solution equilibria prevailing at the site of origin. These solution equilibria depend, above all, on the base saturation. We must count on an increasing liberation of silica with increasing acidification of the upper soil, which liberation, however, may be compensated by a corresponding fixation in the sub-soil, so that the silica does not get into the running waters. The uniform and strikingly constant Si concentrations found in the drainage waters of the ground moraine area of eastern Holstein must be regarded as being due to the uniform origin of these waters in the impounded waters of the calcium carbonate-rich B horizon.

(c) Silica concentrations in the pore-waters of [fresh-] water body sediments

With the exception of a very recent publication by Ohle (1964), the pertinent literature does not contain data on the Si concentration in fresh-water body sediments. Several investigations in that direction have been made in the case of sea-water sediments by Bruevich (1953) and by Emery and Rittenberg (1952).

The Si concentrations found in the mud waters of the lakes in Sleswig-Holstein and Jutland (Denmark) differ very greatly (i.e. between 3 and 50 mg Si/l.). Even within a given lake we may find deviating concentrations in the different depth regions. As a rule, Si concentrations increase with increasing water depth. The numerical values arranged in Table 4 demonstrate that the silica concentrations of the mud waters do not depend on the centent of the muds of amorphous (sodium carbonate-soluble) silica. As in the case of the soils, these concentrations are co-determined to a large extent by the sorptive properties of the sediments. The lowest values were found in the sand lakes without inflow (No. 1 to No. 5). However, these concentrations are strikingly high in the mud of the Little Uklei Lake (No. 6), which contains .20. only 0.05 to 0.09 % Si_a/dry substance. In that case we found that 20 to 40 per cent of the sodium carbonate-soluble silica of the dry substance had earlier been dissolved in the mud water!

The muds of the different depth regions of the Large Ploen Lake differed very greatly with respect to their contents of diatomic silica, but only a little with regard to their concentrayions of dissolved silica. As we .21. shall demonstrate in Section VI, the latter aspect is of decisive importance for the liberation of dissolved silica from the sediment.

The muds exhibiting high contents of amorphous silica (> 5% Si_a/dry substance) without exception also contained high Si concentrations in their pore-waters. These concentrations are particularly high in the Jutland sand lakes exhiting low to moderately high calcium carbonate contents and receiving dissolved silica through inflowing waters (No. 15 to No. 19). Following prolonged storage there appear in these mud samples equilibrium

Table 4 - Si concentrations in the pore-waters of different mud samples (mg Si/l. mud water), arranged in accordance with the Si contents of their dry substance (% Si_a/dry substance). Key: See = Lake; Lake No. 8 = Forest humus lake near . . .

Nr.	See Lake	Seetiefe Depth	% Si_a/Tr.S. dry substance				
		m	a	b	c	d	e
			0,1—1	1—2	2—5	5—10	10—16
			mg Si/l SW Mud water				
1	Ihlsee	5—21		2,5—5			
2	Bültsee	3—4			7—9		
		11		1—3			
3	Eggesö	4		5			
4	Mörkesö	7,5		6			
5	Gr. Langsö	11,5		6			
6	Kl. Ukleisee	8	8—11				
7	Kolksee	3	3				
		4	4				
		4,5		9,5			
		5,5			20—25		
8	Waldhumussee bei Silkeborg/Jütl.	1,5		13			
9	Plußsee	10—13		10—15			
		23—28			15—22		
10	Schöhsee	13—28		9—15			
11	Heidensee	2—3			20—25		
12	Grebiner See	5—10		10—11			
		15			11—13		
		23				27—28	
13	Vierersee	11				40—45	
		17					39—44
14	Gr. Plöner See	15—20		25—26			
		20—23			22—26		
		23—30				25—28	
		30—40					27—30
15	Söbysö	5,5					37
16	Sundsö	2,5				50	
17	Almindsö	15					50
18	Slaansö	11					48
19	Torsö	5					49

concentrations of between 52 and 56 mg Si/l. mud water at 5°C, and of between 71 and 77 mg Si/l. mud water at 20°C. With regard to amorphous silica, these mud waters, thus, must be described as saturated to weakly oversaturated solutions. About three weeks after mud-sample taking, the pH value of the centrifuged solutions amounted to 6.7 to 7.1; after prolonged storage at 20°C, it amounted to 5.5 to 5.8. These sediments are only weakly buffered by calcium carbonate.

In order to investigate the dependence of the equilibria of dissolved silica in the interstitial waters on various factors, we have carried out a number of experiments using muds and mud-water systems:

(α) Experiments with wet muds: The influence exerted by the temperature on the solution equilbrium of silica in mud water is demonstrated by the results obtained in the following experiment: Mud samples taken from the Heiden Lake on January 18, 1963, were first stored at either 5°C or 15 to 20°C. Once constant Si concentrations had appeared, the conditions under which these mud samples were stored were reversed on August 5, 1963, i.e. the "5°C-sample" was stored at 20°C, and the "20°C-sample" was stored at 5°C. As is demonstrated in the following compilation of data (Table 5), new equilibria appeared after a certain time in the respective samples in correspondence with the changes in temperature:

Table 5

Tabelle 5.

	18. 1	28. 1.	8. 2.	20. 2.		27. 7.	5. 8.
5°	22	21	22	22	5°	21	22
15°	22	29 .	30	31	20°	34	34

5. 8.	5. 8.	6. 8.	13. 8.	27. 8.	14. 11.
5° → 20°	22	25	28	30	33
20° → 5°	34	30	28	26	25

These data then indicate that temperature-dependent equilibrium concentrations of dissolved silica prevail in mud waters, which may be attained as a consequence of Si liberation as well as of Si fixation.

As in the case of the soil waters, we find also in that of the mud .22. waters that the solution equilibrium of silica is influenced by the pH value (or by the base saturation, respectively): Preliminary experiments on mud-water exchanges had shown that addition of calcium carbonate to the mud taken from calcium carbonate-deficient lakes resulted in a pronounced decrease of the liberation of Si from the mud into the water. We were in a position to assume that this increase of basicity led to increased binding of dissolved silica to the mud substances having adsorptive capacity. That assumption was confirmed by the results obtained in an experiment using Kolk Lake mud. The Kolk Lake—a small, calcium carbonate-deficient (acid-binding capacity: 0.40 mEq./l.), shallow forest lake—deposits a leaf-humus mud, which, according to Ungemach (1960) has a calcium content of 3% Ca/dry substance.

We have prepared different pH phases of mud by adding either hydrochloric acid or sodium hydroxide solution to mud samples, after a constant Si concentration of 24 mg Si/l. of mud water had been attained at 20°C. As a consequence of these pH changes (cf. Figure 9) we observed a pronounced tilting of the concentration curve at the initial pH value: Acidification had brought about a shift of the equilibrium in favor of dissolution, while increase in basicity had led to a depression of the level—a depression due to increased absorption. The decrease in fixation of dissolved silica observed in the region above pH 8.5 probably must be attributed to an increase in the solubility of amorphous silica due to both increased dissociation and a transformation of the absorbents or exchangers, respectively, into the hydroxide form.

(β) *Experiments using mud-water systems:* In his mud-water exchange experiments, Mortimer (1941-1942) found that the Si concentration in the overlaying water did not rise any further once a ceryain value had been reached. He stated: "The source of silica, whatever it may have been, appears to have become exhausted." As we have demonstrated further above, there exist true equilibration concentrations of dissolved silica in mud. The increase of the Si concentration in the overlaying water of mud-water systems, however, is the result of an exchange between the Si-rich interstial water and the less Si-rich overlaying water (cf. Section VI). This then would indicate that this exchange, in the course of time, must lead to equalization of concentration or, at least, must come close to it, and that, in consequence, no further increase of Si can take place in the overlaying water. A number of different experiments have demonstrated that the equalization of concentration between mud and water is not based on a simple mixing of bodies of water, but exchange and re-dissolution in the mud proceed in an integrated manner, and this until the equilibrium concentration characteristic for the mud in question has been attained in the mud as well as in the overlaying water. From that point on, .23.
water exchange takes still place across the mud-water interface, but no Si dissolution.

However, it is out of the question to speak in this connection of exhaustion: If the overlaying water is repeatedly removed [in the experiment] and replaced by fresh water having a lower Si content, we will find—at least in diatom gyttjas and other silica-rich muds—continuous dissolution and Si liberation into the water.

In one exchange experiment, which had been started during February of 1961 using a diatom gyttja from the Large Ploen Lake, we found that equalization of concentration had been practically completed after half a year at room temperature. The overlaying water of the aerobic experiment exhibited a concentration of 33 mg Si/l., and that of the anaerobic experiment, one of 34 mg Si/l. The situation had practically not changed at all by November of 1963 (!): In the overlaying water from these two experiments we measured 34 and 36 mg Si/l., respectively. After discontinuation of the experiment in November 1963, the Si concentrations of the centrifuged mud water amounted to 35 mg Si/l in the aerobic experiment, and to 38 mg Si/l. in the anaerobic experiment. The mud of the aerobic experiment was oxidized right through to the lower surface of the mud layer measuring 4 cm in thickness; the surface was covered with a rusty-brown oxide coating. The anaerobic mud was black and strongly smelled of hydrogen sulfide. The pronounced difference between the redox potentials of these two water-mud systems exerted only a minor influence on the respective solution equilibria.

The situation found in the case of experiments using Schoeh Lake mud was an entirely different one. In that case, we again found that the Si values increased in the water overlaying the layer of mud measuring 4 cm in thickness, i.e. they increased until a constant saturation value had been reached. That value amounted to 4 to 6 mg Si/l. in the aerobic systems, but to 15 to 18 mg Si/l. in the anaerobic systems; the latter high Si values were associated with pronounced formation of hydrogen sulfide.

This varying influence of the redox conditions on the silica equilibrium in the mud-water system of the Large Ploen Lake, on the one hand, and that of the Schoeh Lake, on the other one, must be attributed to the entirely different characters of these sediments, and this, above all, with regard to iron contents. The diatom gyttja of the Large Ploen Lake, according to Ungemach (l.c.), contains 1 to 2% Fe/dry substance, but the clayey mineral sediment of the Schoeh Lake contains 4.7% Fe/dry substance. The percentage values of sodium carbonate-soluble silica (% Si_a/dry substance) give a ratio of 16.0:1.5.

Equilibrium can be brought about in a mud-water system by either one of the two processes involved, i.e. by means of dissolution and by means of absorption (fixation). That fact has been demonstrated by the results obtained in the following experiment: Several 5-liter plastic containers were filled with a 4-cm layer of Schoeh Lake mud obtained at a depth of 26 meters; the mud layer was then covered with Schoeh Lake water. Once the equilibrium had been attained under aerobic conditions (4 to 5 mg Si/l.), the overlaying .24.
water was replaced by two liters of fresh lake water; a portion of that water had been enriched with silica. The initial concentrations in the overlaying water now amounted to 0.3 (a) and 9.8 mg Si/l. (b), respectively. As is demonstrated in Figure 10, a concentration of 5 mg Si/l. had again been attained in the (a) experiment after two months due to release of Si from the mud particles. In the (b) experiment, the concentration in the overlaying water had decreased to 6 mg Si/l. due to absorption (fixation). Simple equalization of concentration without dissolution (release) or fixation, respectively, could have led only to a change in concentration in the overlaying water of ± 1.0 mg Si/l. The course of the curve clearly indicates that we are dealing here with the appearance of an equilibrium of the type already described in our soil-water systems. The quantity of the overlaying water influences solely the time required until equilibrium is attained, but does

not influence the Si level. That level is determined solely by the mud.

Once the overlaying water of a given mud-water system has been isolated from its mud phase and silica is added in a different form, we find that the equilibrium conditions are different in that water. In an exchange experiment using Schoeh Lake mud—an experiment, in which the conditions corresponded to those described in connection with the other experiments—we added a small quantity of dialyzed silica sol (concentration: 1000 mg Si/l.) to the overlaying water, which had attained a constant concentration of 3.9 mg Si/l. Following addition of the sol, the overlaying water contained 5 mg Si/l. in the dissolved form and 13 mg Si/l. in the colloidal form. A portion of the overlaying water was removed with the aid of a feed scoop and stored in the same room in a sealed polyethylene bottle. Figure 11 shows the courses of the Si concentration in these two water samples: In the isolated parallel sample, the colloidal silica had dissolved almost completely after ten days and the concentration of dissolved silica had risen to the potential value of 18 mg Si/l. The situation in the water of the main sample, however, was an entirely different one due to the relationship existing between that water and the mud. The colloidal silica had been absorbed very rapidly by the mud, so that, alone for that reason, any increase in the concentration of dissolved silica in the overlaying water was possible only to a limited extent. However, apart from that, we found that dissolved silica was also bound by the mud, until the original equilibrium had again been attained one month later.

Corresponding experiments using Schoeh Lake mud under anaerobic conditions as well as Large Ploen Lake mud under both aerobic and anaerobic conditions have yielded similar results. Figure 12 illustrates the results obtained in the aerobic experiment using a diatom gyttja from the Large Ploen Lake. However, in this instance, we added such a large quantity of silica that the total Si concentration was at a level above the saturation .25. concentration valid for amorphous silica. That saturation concentration (54 mg Si/l.) was attained only in the water isolated from its mud, but not in the overlaying water of the mud-water system.

The solution conditions in the interstitial waters are completely different from those in the free water, and the results obtained in experiments using pure or electrolyte-containing, but suspension-free water cannot be applied to the situation existing in muds.

In the pore solutions of water-body sediments—as in those of the soils—there exist temperature- and pH-dependent saturation concentrations. These, however, are located at a very different level, and they are determined by the silica content, by the species of silica present, and by the sorptive properties of the mud in question. The saturation concentration for amorphous silica is reached only in muds with high contents of diatomic silica. The concentrations are strikingly high in the sediments of the calcium-carbonate-poor, but silica-rich sand lakes of Jutland. The low equilibrium concentrations found in other diatom gyttjas could be caused by a certain absorption of metal ions or metal oxides on the surface of the diatom shell and the consequent decrease in surface energy[4]. Absorption of that type is greatly promoted by calcium carbonate. The mobility (transportability) of silica is maximal also in the sediments at low pH values. We find that the concentrations

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[4] In addition we must, in the case of older sediments, take into consideration the decrease in surface energy brought about by aging of the amorphous silica.

of dissolved silica increase only above pH 9 to 10 (values rarely occurring under natural conditions). The antagonism assumed by Correns (1950; and 1951) to exist in the solubilities of calcium carbonate and silica in sediments (i.e. marked dissolution of calcium carbonate at low pH values, and marked dissolution of silica at high pH values) would, for that reason, hardly ever be realized as far as silica is concerned, and probably is valid only in the case of pure calcium carbonate-silica mixtures.

The view suggested by Emery and Rittenberg (1952)—viz. that the silica getting into the upper sediment layers with the interstitial water during sediment diagenesis is precipitated there because of the lower pH, among other factors—is no longer tenable for the same reason. The lower Si concentrations found in the upper sediment layers must be attributed in the first instance to the exchange with the water close to the bottom (cf. Section VI.3.).

IV. Biogenic determination of silica concentrations in lakes[5]

Both the marked variations in the silica content of lake waters during the course of the year and the fact that the Si concentrations in a given lake are almost always and frequently to a considerable extent at a level below that of the inflowing waters must be attributed to the utilization of silica by various groups of organisms, among which the diatoms occupy a predominant position. Birge and Juday (1911) and Broensted and Wesenberg-Lund (1911 - 1912) were the first authors to draw attention to that particular aspect.

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[5] Inorganic adsorptive precipitation of dissolved silica was not observed in our investigations of lakes, since the adsorptive agents are present in the free water of the latter bodies in quantities too low for observation.

The investigations carried out in the Eastern Holstein Lake Region did not yield any indications suggesting that there exists any marked Si consumption by other groups of organisms. The decreases in Si concentration observed, which decreases are very pronounced, above all, during the spring, must be attributed solely to diatom development and, above all, to the development of plankton. Other Si-uptaking organisms (Porifera and Chrysophyceae, among other ones) would be of importance for the Si metabolism of inland lakes only in a local and sporadic manner. On the basis of the mass occurrences of Porifera in Lake Baikal, Wotinzew [Votintzev] (1948) has concluded that these organisms exert a relatively pronounced influence on the Si metabolism of that lake, but he has been unable to present any direct evidence pointing in that direction.

1. Silica uptake: Process and limiting factors

Despite the fact that the silicic nature of the diatom shells has been known approximately since the middle of the last century, we at the present time know almost nothing about the biochemical processes involved in Si uptake and Si incorporation.

Since silicic acid (silica) is dissolved in the water in a mono-molecular form, but is present in the skeletal elements in the form of a more or less dehydrated silica gel, we must regard the process of incorporation as a form of biochemical condensation.

According to Lewin (1954; and 1955), silica uptake by diatoms represents an aerobic, respiration-coupled process, which takes place also in the absence of light. Diatoms (Navicula pelliculosa) kept in a silica-deficient nutrient solution took up silica upon transfer into a more silica-rich medium, and they did that also in darkness. Silica-starved cells reportedly add a second coat of silica onto the shell already present [when exposed to a silica-rich environment].

In our experiments using a planktonic biocoenosis—which had been obtained during May of 1961 from the Heiden Lake at the time of Asterionella mass development—we have, in fact, been able to determine an increased .27. uptake of Si during the dark period of 12 hours. In that planktonic biocoenosis, Asterionella formosa, representing the main phytoplantonic form, was present with 3 x 10^7 cells/l. and Fragillaria crotonensis, with 10^6 cells/l. In addition that biocoenosis contained Chlorococcales (Scenedesmus and Pediastrum) and, among its zooplankton, Bosmina and various Copepoda. The cultures, which were kept in polyethylene bottles, were continuously aerated, and illuminated in a 12-hour rhythm paralleling the day-and-night change; the light source was a 100-Watt bulb set up at a distance of 50 cm. Heiden Lake water was used as culture medium, to which no nutrients were added. The experiments were carried out at room temperature.

The courses of Si concentrations observed in two parallel experiments are shown in Figure 13. Already after six days, the initial Si content of 1.5 mg Si/l. had decreased to 0.06 and 0.18 mg Si/l., respectively. The concentrations remained below 0.1 mg Si/l. up to Day 50 of the experiment; following short-term concentration increases due to the addition of fresh, filtered Heiden Lake water, the concentrations dropped again rapidly to between 0.04 and 0.10 mg Si/l. Starting on Day 50, we determined the Si concentrations at the beginning and at the end of each light period (or each dark period, respectively), i.e. at 9 a.m. and at 9 p.m. Figure 13 and Table 6 show that Si uptake took place preferentially during the night,

Table 6

Tabelle 6

	Day Tag	± μg Si/l	Night Nacht
a	+ 132 — 30 = + 102		+ 28 — 54 = — 26
b	+ 137 — 21 = + 116		+ 4 — 92 = — 88
a + b	+ 269 — 51 = + 218		+ 32 — 146 = — 114

Table 6 - Key: Increase (+) or decrease (-) of the Si concentration, determined in each case over 12 hours and totalled for nine days.

while we usually observed increases in Si concentration during the day. The latter increases probably were due to the lysis of dead diatoms. This diurnal rhythm is particularly clearly evident in the course of the Si concentration observed in the case of our (b) experiment (continuous line, in Figure 13).

Dr. Stange-Bursche has informed me that she was able to observe vigorous multiplication in Asterionella formosa, in particular, during the night (in sedimentation chambers), while the cell number remained almost constant during the course of the day.

The ability of diatoms to carry out Si uptake in the absence of light or, in fact, to carry out that activity in a more vigorous manner under that condition, no doubt, is of some significance in connection with the biogenic silica utilization in lakes. Due to that ability, Si uptake can be continued .28. also in water layers located below the compensation point, into which layers living diatoms may be transported by convection currents, seiches or the force of gravity. This uptake of Si does not have to be connected with multiplication, since Si may be taken up later on and laid down onto the shell already present (Lewin, 1954). On the basis of the observation made in Lake Constance (Lower Lake) that the oxygen-depleting zone reaches up higher than the Si-depleting zone reaches down, Elster and Einsele (1938) arrived at the conclusion that it is possible "that the 'oxygen compensation point' is located at a level higher than the 'Si compensation point', i.e. that the predominance of Si utilization and consumption reaches below the level of positive oxygen balance."

The biogenic determination of Si concentration in lake waters is limited by the concentration of Si present at the onset of the period of depletion and the quantity of dissolved silica added during the course of that period. As a rule, silica can be taken up only once in the sourse of a period of depletion, since a "shortcircuited system" ("kurzgeschlossener Kreislauf") (Ohle, 1952) is practically absent due to the non-occurrence of Si release by the living cells, on the one hand, and the low rate of dissolution of Si present in the shells of dead diatoms. If the other growth factors permit, all silica present in the water may be fixed by biogenic means apart from a residual quantity of 10 to 20 mg Si/cubic meter—a concentration close to the limit of detection. Only the modern ion exchangers possess a similar desilicifying action!

In the lakes of eastern Holstein, total consumption and utilization of the dissolved silica during the spring represents the rule. Whether that total consumption is only a consequence of the more recent "rapid lake eutrophication" (Ohle, 1953b; and 1955a) cannot be determined with certainty, since no comparable investigations are available from the past. Similarly low residual quantities of Si have been reported repeatedly in the pertinent literature; these publications have been reviewed by Joergensen (1953).

However, a complete disappearance of Si from silica-rich waters can take place only on the basis of extensive storage or on that of intensive replenishing of nutrients. Nutrient-deficient waters exhibit a relatively narrow range of variation of Si concentrations, as has been demonstrated by the results obtained in numerous investigations carried out by Elster in Black Forest lakes and Lake Constance.

Hughes and Lund (1962) were able to demonstrate in laboratory experiments that Si depletion in Lake Windermere is arrested during the spring by phosphate deficiency. Addition of phosphorus (phosphate) to Lake Windermere water resulted in a greatly increased uptake of Si. In the nutrient-rich lakes of eastern Holstein, we find, on the other hand, that Si uptake is not limited by any minimal concentrations of other nutrients, and multiplication of diatoms is arrested only by Si deficiency.

In cases where the dissolved silica has practically been completely .29. consumed, we find that the depth of depletion ultimately determines the extent to which the total supply of dissolved silica available in the entire lake volume will be fixed (or precipitated) by biogenic means. The term "depth of depletion" indicates the depth level in a given lake, down to which the Si concentration is decreased on the basis of biogenic consumption and utilization. The depth to which the Si concentration in the lake water decreases to the same extent as in the mixed upper layer will be termed the "relative depth of depletion," and the depth to which any biogenic Si decrease at all occurs will be termed the "absolute depth of depletion." The "Si hypolimnion" (Elster, 1939) begins below the level of the absolute depth of depletion.

The exchange processes possibly taking place following discontinuation of depletion are not covered by these concepts, since they represent only processes of concentration equalization: The silica transported upward with the circulating water from the lower layers is not fixed by biogenic means, but increases the concentration of the surface water layer. The relative depth of depletion, as is demonstrated by Figures 17, 18, 20 and 26, can be readily discerned in the course of the Si isopleths. That depth does not represent a fixed parameter, and it may either rise or fall during the course of the period of depletion. The absolute depth of depletion cannot always be determined in an unequivocal manner.

It is advantageous to limit the use of the terms defined above to those cases, in which the main zone of diatom multiplication is located in the mixed upper layer, i.e. in which depletion, thus, can spread by means of the vertical water exchange from the upper layer to the lower body of water. The depth of depletion, thus, also indicates the thickness of the depletion layer. In the present investigations of the Holstein Lake Region, we did not observe any depleted layers isolated from the surface layer of the type reported by Birge and Juday (1911) from Beasley Lake, and assumed to exist by Stangenberg (1961) on the basis of his Si stratification curves.

The depth of Si depletion in a given lake, thus, is determined by the following factors:

(1) The position of the compensation point (maximal depth of positive assimilatory balance);
(2) The depletion intensity; and
(3) The extent of vertical water exchange.

In cases where the vertical water exchange reaches beyond the level of the point of compensation, we will find that biogenic decrease of Si concentration takes place also below that level: With the rising water fresh silicic acid is constantly transported into the zone of diatom multiplication, where it is rapidly consumed (i.e. utilized). However, the diatoms either sinking or transported to lower layers by the descending water masses hardly .30. ever release the silicic acid they have once incorporated; on the contrary, despite the negative balance of energy, these diatoms continue for a certain time to take up more silicic acid. The Si concentrations, thus, decrease continuously also below the compensation point, until the multiplication of these diatoms is arrested or exchange is discontinued.

The quantity of Si taken up either in a certain partial lake volume or in the entire lake volume cannot be determined exactly, since sedimentation of the formed suspensoids (diatomic silica) as well as continuous replenishment of dissolved silica take place during the period of depletion. Furthermore, it is not possible to determine in quantitative terms the amounts of Si fixed by littoral offspring growth. The quantity taken up, thus, corresponds neither to the decrease in dissolved silica nor to the increase in suspended silica. The decrease in concentration corresponds most exactly to the actual depletion when the interval of time between the two samplings is as short as possible; the value obtained for decrease in concentration, however, will never be equal to depletion because of the continuous autochthonous liberation of Si.

The total quantity of Si taken up during a certain interval of time corresponds to the difference between the change in concentration actually measured and the change expected on the basis of theoretical considerations, with that difference then being multiplied with the lake water volume. The measured change in concentration may be positive, zero, or negative.

The increase in concentration expected on the basis of inflow is, by all means, amenable to calculation; that increase has been taken into consideration by Elster (1939; and 1959) in his calculation of the Si depletion in Lake Constance and the Black Forest lakes. However, the highly unknown factor is found in the autochthonous liberation of Si, which is based, above all, on the release of Si from the sediment. As we shall demonstrate further below, it is possible in some lakes—at least for the summer and fall months—to make certain predictions regarding the increase of average Si concentration calculated for the entire lake volume, with that increase in concentration being almost exclusively of autochthonous origin. However, during the period of diatom development during the spring, we find that the depletion (uptake) processes in the deeper lakes predominate to such a large extent that we are permitted to neglect the authochthonous liberation, which, in any case, is greatly reduced at that time due to the low temperatures prevailing at that time.

2. Course and extent of depletion of silica in Holstein lakes

(a) The Large Ploen Lake - The course of the average Si concentration, calculated for the entire water volume of the north basin of the Large Ploen Lake (as plotted in Figure 14) shows a strikingly distinct periodicity. That periodicity is due to the gradual, relatively constant increase in the Si concentration in evidence well into the winter, and the subsequent drop in .31.
Si concentration during the months of March and April due to biogenic utilization, reversing the situation almost entirely. The periods of depletion occurring during the summer and the fall are relatively unimportant (cf.

Figures 16, 17, 24 and 25). Instances of minor depletion were observed in 1961 during July, and in 1962 around the end of May and the beginning of June and again during September-October.

In 1961 as well as in 1962, diatom development was arrested during the spring due to the complete consumption of Si by April. The minimal concentrations amounted to 0.01 to 0.02 mg Si/l. Only the depths of depletion differed in these two years, which depths were determined by the climatic conditions prevailing during the months of March and April. As is illustrated by the data presented in Figures 17 and 24, respectively, the courses of of depletion were identical in these two years up to early in April: From the surface down to the maximal depth (40 m), the Si concentration decreased in the course of one month from 3.0 to 1.2 mg Si/l.

In 1961, the vertical exchange of water was so greatly reduced beginning around April 15th due to a rapid warming of the surface water that subsequent depletion up to complete consumption was limited to the upper water layers. The relative depth of depletion decreased that year to 18 meters (from 40 m). In Figure 18, the conclusion of complete circulation is indicated by the 6° isotherm, and the end of Si depletion in the entire column of water is indicated by the 1.0-mg isopleth. These two lines show almost identical courses. In 1962, on the other hand, complete circulation took 14 days longer due to a very cold spring, and depletion was completed already ten days earlier than in 1961. The relative depth of depletion was identical with the lake depth up to the end of the period of depletion, i.e. complete consumption of Si occurred within the entire lake water volume. Even one meter above the mud, we were able at a depth of 40 meters to measure the minimal concentration of 0.02 mg Si/l. (Figures 19, 20 and 24). The different situations existing during 1961 and 1962, respectively, are summarized in Table 7.

Table 7

Tabelle 7

1. Jahr	2. Ende der Vollzirk.	3. Ende der Zehrung	4. Zehrungstiefe		5. Minimalkonzentr.	
			absol. m	relative m	über d. Schlamm	in 0-15 m
1961	ca. 5. April	ca. 20. April	40	40 → 18	1,20	0,02
1962	ca. 20. April	ca. 10. April	40	40	0,02	0,01

Table 7 - Key: 1, Year; 2, completion of full circulation; 3, end of depletion; 4, depth of depletion; 5, minimal concentration above the mud, and in the 0-15 m layer, respectively.

During the spring of 1962 we were able also in the other parts of the Large Ploen Lake to determine almost complete consumption of Si. On May 4th, we measured in the entire water mass of the remaining lake parts a concentration between 0.09 and 0.13 mg Si/l., while the concentrations prior to diatom development had amounted to 3.2 to 3.4 mg Si/l. We then realize that, within one month, almost the entire dissolved silica of this lake was fixed .32. by biogenic means. Calculations based on the lake volume (412 x 10^6 cubic meters) showed that that fixation corresponds to a quantity of about 1400 tons of Si (= 3000 tons of SiO_2)!

During the spring of 1963, we found that depletion was again restricted to the upper water layers, since rapid warming of the surface waters occurred after an unusually long period of ice coverage.

It then appears in the case of the Large Ploen Lake that the extent of biogenic fixation of the lake's silica supply is ultimately determined by the climatic conditions, which determine the onset and the end of complete spring circulation. The morphometric features of this particular lake, however, bring about that, even in years associated with depletion depth not reaching far down, more than 90 per cent of the Si supply present is consumed, as is demonstrated in Figures 14 and 17. However, the different depths of depletion are associated with very large differences in Si stratification, which differences remain intact until the onset of fall circulation (cf. Figures 54 and 55).

The surprisingly great depths of Si depletion—as observed, in particular, during the spring of 1962—occurred at a visibility depth of only three to four meters. The fact that the Si concentrations dropped within one month down to a depth of 40 meters from 3.2 to 0.2 mg Si/l., and down to a depth of 55 meters to 0.1 mg Si/l., thus, can only be explained by suggesting that Si uptake is not bound to the presence of light, but can also be continued at depth levels below the level of the compensation point. This is all the more possible, since the 0-to-5-m water layer makes up about one quarter of the total lake volume, and the 0-to-10-m water layer makes about one half of that volume. The average illumination conditions for the plankters apparently do not deteriorate to an extent during extensive circulation as might appear on first approach considering the depth levels mentioned above.

Numerous indications exist suggesting that diatoms gradually sinking toward the bottom in calm waters continue to take up silica for a certain period of time also in the dark depth, and this, in particular, in cases where these diatoms had earlier been Si-starved ("Si-undernourished") but otherwise were well nourished. Following onset of stagnation, we find toward the end of April a great accumulation of living diatoms (Stephanodiscus astraea) in the depth of the Large Ploen Lake, while the upper layers are rapidly evacuated. That process is illustrated in Figure 21 on the basis of the concentrations of diatomic silica measured. At the end of April, the upper layer had been evacuated apart from 0.6 to 0.8 mg of suspended Si/l., while the concentrations —in particular, at a depth below 25 meters—increased greatly and reached 4 mg of suspended Si/l. at a depth of 40 meters.

When comparing Figure 20 and Figure 21, we are struck by the finding that the increase in the concentration of dissolved silica commenced in the hypolimnion only at a time when the diatoms had almost completely sedimented. Earlier in the season, the limit of 0.05 mg Si/l. had not been exceeded for .33. more than one month. As will be demonstrated in Section VI on the basis of the results obtained in mud-water exchange ex/eriments, there occurs a continuous release of Si from the mud. That release takes place also prior to the sedimentation of the spring diatom population. That fact is demonstrated by the data presented in Figures 24, 55 and 58. We thus are forced to assume that living diatoms (Stephanodiscus astraea) accumulated in the depth during the spring of 1962 prevented the expected rise in Si concentration for more than one month by means of their Si uptake.

The periods of depletion occurring between the spring periods of depletion are relatively unimportant. They cause, at best, short-term and local decreases in Si concentration. With regard to the total lake water volume, these intermediate periods of depletion result only in slight decreases in the overall increase of Si concentration. The Si quantity taken up during the summer and fall amounted in both 1961 and 1962 to only ten per cent of the total annual uptake. The concentrations of suspended diatomic silica did not exceed 0.3 mg Si/l. (Figures 15 and 25). The species composition was an entirely different one compared to the spring plankton; above all, that population was not that greatly dominated by one single species. Only Stephanodiscus hantzschii occurred in relatively large numbers of individuals, and this, in fact, in both years immediately after the disappearance of the spring population. As is demonstrated in Figures 20 and 21, the pronounced multiplication of St. hantzschii took place around the end of May 1962 on the basis of an initial Si concentration of 0.04 to 0.06 mg Si/l. and continuous replenishment from the depth. A number of very different species were involved in the depletions occurring during the summer and the fall: Asterionella formosa, Fragillaria crotonensis, Synedra acus, Stephanodiscus astraea, St. hantzschii, St. binderana, Attheya zachariasia and Cyclotella.

No exact data can be provided on the role played by the littoral offspring diatoms in the Si metabolism of the Large Ploen Lake, since these organisms cannot be determined in quantitative terms. A part of the depletions reflected in the decreases in the concentrations of dissolved silica, however, must have been caused by the sessile diatoms of the littoral. According to Kann (1940, page 204), the main period of development of littoral diatoms falls also into the months of March and April, and ends once the water temperature exceeds 10°C (cf. Figures 18 and 19).

Joergensen (1957) has reported from Furesoe and Lyngbysoe that the maxima of development of planktonic and littoral diatoms, respectively, never coincide there. The littoral diatoms exhibited their main period of development following the disappearance of the planktonic diatoms during the spring, although the Si concentration had dropped also there to 0.02 - 0.04 mg Si/l.

(b) The Pluss Lake - The Pluss Lake exhibits a similar periodic course .34. of average Si concentration as the Large Ploen Lake; however, the level is significantly lower (cf. Figure 26). The short-interval examinations covered only the year 1961, but random samples taken during the years 1962 and 1963 revealed no really significant deviations. The Pluss Lake exhibited only one period of depletion, which was concentrated on the month of March (Figures 26 and 27). The silica present was almost completely consumed down to the relative depth of depletion of 20 meters (residual concentration: 0.02 mg Si/l.), although visibility depth was only three meters. The absolute depth of depletion was located at the 25-m depth level, where the Si concentration amounted to 0.8 mg Si/l. Complete consumption of Si down to maximal depth—as observed in 1961 in the Large Ploen Lake—was prevented by the sluggish vertical water exchange, which did not reach the lower water layers. Stephanodiscus hantzschii and Synedra acus represented the predominating diatom species. Diatoms in quantities worth mentioning were observed only during the spring. Cyanophyceae predominated during the rest of the year. The diatoms play a subordinate role in the Pluss lake since the Si quantity available in the lake (0.4 to 0.5 mg Si/l.) is relatively small, and liberation (recycling) proceeds at a very low rate (1 to 2 mg Si/cubic meter/24 hours). At least 80 per cent of the diatomic silica formed is eventually subjected to sedimentation.

(c) The Vierer Lake - Almost complete biogenic fixation of dissolved silica occurs during the spring also in the Vierer Lake (Figure 28); the Si concentrations in that lake are considerably greater than the ones found in the Large Ploen Lake. The main diatom species involved in this fixation of Si is Stephanodiscus astraea; however, numerous additional species are involved (including Synedra acus, Asterionella formosa, Melosira granulata, and Fragillaria crotonensis).

The consumption of Si by diatoms during the summer of 1961 and that during the summer of 1962 differed greatly, as is demonstrated in Figures 28 and 29. The difference in summer depletion is made evident in particular when we compare the September values for dissolved silica, which are shown in Figure 70 in the stratification curves 4 and 4a. During the entire summer, the concentration of suspended diatomic silica amounted in 1962 to about 0.3 mg Si/l.; during the summer of 1961, on the other hand, diatoms could hardly be found even under the microscope. During the summer we found that the main diatom species were the ones, which had played only a secondary role during the spring.

The greater part of the diatomic silica of the spring plankton goes into the sediment (during the spring of 1962, the total Si content dropped from 7.8 to 0.5 mg Si/l.); during the summer, however, we must count on more pronounced dissolution in the water. .35.

(d) The Heiden Lake - Due to both the greater inflow of nutrients from the surrounding area and the continuous mobilization of the nutrients due to the low depth of the water, we may in the case of the Heiden Lake—in contrast to that of the Large Ploen Lake—see mass diatom development during any season of the year and, thus, also pronounced consumption of silica, in which consumption, as is demonstrated by Figure 30, a number of greatly different species may be involved. The extraordinarily rapid changes in the concentration of dissolved silica (Figures 30 and 31) are characteristic for the Heiden Lake—changes of a type not observed in the deeper lakes exhibiting stratification during the summer.

As already mentioned in connection with the Vierer Lake, we found also in the case of the Heiden Lake that the depletion of Si was significantly more pronounced during the summer of 1962 than during [the summer of] 1961. These differences again are particularly evident when we compare the September values, giving a ratio of 1:10.

Wawrik (1960b) has carried out several Si determinations in Austrian ponds, describing the situation as relatively undefined. She, too, found maximal and minimal concentrations between 0.5 and 10.5 mg Si/l. [sic! 10.5 and 0.5 mg Si/l.] during any season of the year.

Despite the usually very intensive consumption, the great turbulence of the lake water, and the continuous replenishment of Si from the mud as well as from the environment, we found that the increase of suspended silica in the lake water corresponded only in a few cases to the decreases in the concentrations of dissolved silica. The maximal concentration of diatomic silica amounted to 2.8 mg Si/l.; however, that of the dissolved silica determined prior to the latter determination amounted to more than 6 mg Si/l. We then find that relatively rapid sedimentation of diatoms took place also in the Heiden Lake. A part of this deficit could also be due to the Si uptake by littoral offspring growth.

The amplitudes of the Si concentrations corresponded also in the case of the Heiden Lake to the maximal concentrations, as is indicated by Figure 30 and Table 8. Due to the vigorous metabolism involving mud and water, the total annual depletion (or consumption) amounts to a multiple of the maximal concentrations. Without taking autochthonous liberation into consideration, we already obtain an annual value for consumed Si amounting to 20 mg Si/l. The quantity of Si actually consumed would, at least, be twice as high.

Table 8 - Variation of Si concentration in the Heiden Lake. .36.

Jahr Year	Si concentration in water Si-Konzentration im Seewasser	
	Maximum	Minimum
1961	7,2	0,04
1962	8,7	0,02
1962/63	12,0	0,02

(e) The remaining Slesvig-Holstein lakes investigated - The extent of the Si depletion in the remaining lakes—usually investigated only in a random-type manner—will be characterized on the basis of their respective maximal and minimal concentrations determined in the course of a period covering well over two years; these concentrations have been compiled in Table 9. The values presented in that Table are related in most instances to surface-layer samples, and they may be regarded as being representative for the total water volume only cum grano salis (with due allowance for exaggeration). In instances where the values were calculated on the basis of results obtained in stratification studies, we have indicated that fact by adding a (S) behind the value.

In almost all eastern Holstein lakes, biogenic precipitation of Si during the spring leads to minimal concentrations of dissolved silica of between 0.01 and 0.03 mg Si/l. The latter concentrations may be found in the upper layers of water during any spring. We find variations in the depths of depletion, which depths depend on the climatic conditions. In cases where the onset of summer stagnation is delayed, we find that the entire supply of dissolved silica is depleted down to the maximal depth. The silica laid down during spring bloom in the diatom shells is almost completely sedimented.

Table 9

Tabelle 9

Lake Name des Sees	mean depth mittl. Tiefe m	dissolved silica / gelöste Kieselsäure Maximum Date	 mg Si/l	 Minimum Date	 mg Si/l	 Amplitude mg Si/l	 %		suspended silica / suspend. Kieselsäure Maximum Date	 mg Si/l
Behler See	10,6	10. 12. 60	3,5	5. 5. 62	0,07	3,43	98		2. 9. 62	0,45
Belauer See	9	10. 12. 61	4,2	23. 4. 61	0,06	4,14	99		23. 4. 61	1,0
Bornhöveder See	6,2	10. 12. 61	8,3	15. 4. 62	0,03	8,3	100		27. 5. 62	2,45
Dieksee	12,6	4. 3. 61	3,3	16. 4. 61	0,45	2,85	86		16. 4. 61	0,25
Edebergsee	6,9	21. 1. 62	1,1	30. 4. 61	0,10	1,0	91		26. 2. 61	0,6
Görnitzer See	1,8	19. 11. 61	9,7	7. 5. 61	1,0	8,7	90		27. 8. 61	0,3
Grebiner See	9,3	20. 10. 61	1,8 (S)	18. 4. 62	0,03	1,8	100	1.	mehrfach	0,1
Gr. Plöner See/Nb.	19,6	1/11. 62	3,2 (S)	7. 5. 62	0,02 (S)	3,2	100		17. 4. 62	1,9 (S)
~~gesamt~~ Total	14	21. 1. 62	3,4	4. 5. 62	0,10 (S)	3,3	97		19. 5. 61	0,5 (S)
Heidensee	2	23. 2. 63	12,0 (S)	1. 5. 62	0,02	12,0	100		16. 4. 62	2,8
Ihlsee/Segeberg	6,6	23. 1. 63	0,08 (S)	8. 6. 61	0,03 (S)	0,05	62		—	—
Kellersee	11,7	4. 3. 61	3,9	16. 4. 61	0,12	3,78	97		—	—
Kolksee/Eutin	4,5	21. 2. 62	0,9	24. 4. 62	0,15	0,75	83	1.	mehrfach	0,1
Krummensee	4	21. 2. 62	0,25	4. 3. 61	0,03	0,22	88		4. 3. 61	0,2
Plußsee	8,9	15. 2. 61	0,47 (S)	7. 4. 61	0,05 (S)	0,42	90		24. 3. 61	0,4 (S)
Schierensee/Bornh.	3,9	10. 12. 61	6,5	12. 7. 61	2,4	4,1	63		27. 5. 62	1,2
Schierensee/Grebin	6,1	28. 1. 62	2,2	7. 5. 61	0,14	2,1	94		19. 11. 61	0,2
Schmalensee	4,8	10. 12. 61	8,5	23. 4. 61	0,10	8,4	99		23. 4. 61	2,3
Schmarksee	4	27. 8. 61	3,9	7. 5. 61	0,10	3,8	98		19. 11. 61	0,9
Schöhsee	11	16. 1. 62	0,38	4. 4. 63	0,02	0,36	95		—	—
Vierersee	7	21. 1. 62	7,8	16. 4. 62	0,03 (S)	7,8	100		10. 6. 62	0,7

Key: 1, several times

In contrast to spring depletion, we find that the depletions occurring during the summer and fall, respectively, vary greatly from one year to the next one as well as from one lake to the next one: As a rule, we will find that the extent of the summer depletion processes increases with decreasing mean depth of the lakes. That increase probably must be ascribed to the increased mobilization of certain nutrients essential for both the growth and the multiplication of planktonic diatoms. The silica concentrations cannot represent the cause of these depletions, since they may, under certain circumstances, be relatively high also in the deeper lakes. That fact is demonstrated in a comparison of the summer Si values found in the Large Ploen Lake (Figures 17 and 24), in the Vierer Lake (Figure 28), and in the Heiden Lake (Figure 30), respectively. Furthermore, we know that marked diatom development may occur also on the basis of very low Si concentrations (cf. Figures 20, 21 and 26).

Figures 19 to 25 indicate the existence of a certain connexion between .38. the periods of depletion and the occurrence of relatively pronounced, wind-induced exchange processes.

The differences in the extent of Si depletion observed in the years 1961 and 1962, respectively, may have been caused by the different climatic conditions prevailing then, and this, in particular, by the temperatures prevailing during the summer of 1962, which were far below the mean values. Extensive depletions were observed during that cold summer also in the running waters (cf. Section V. 2b.).

V. Silica concentrations in running waters, and the allochthonous silica supply of lakes

1. Introductory remarks - The deficit in dissolved silica in a given lake—a deficit, which is due to the pronounced biogenic utilization, above all, during the spring—is completely made up during the course of the year, so that the diatoms appearing during the following year have available for their purposes the same Si quantities as those of the preceding year. In the investigation of the problem of the origin of these—frequently considerable—Si quantities, we must first consider the allochthonous supply of Si.

Comparative investigations, carried out in the lakes of Sleswig-Holstein and in those situated in Jutland, have shown that the Si concentrations observed in these lakes outside the periods of depeltion depend largely on the presence or absence, respectively, of waters flowing into the lake in question. The differences are particularly large in the sand lakes of Jutland: During September of 1962, we found in the lakes having no inflowing waters Si concentrations of less than 0.2 mg Si/1., while the lakes with inflowing waters exhibited concentrayions of up to 8 mg Si/1. The eastern-Holstein lakes having no inflows or almost without inflowing water—the Ihl Lake, the Buelt Lake, the Pluss Lake and the Schoeh Lake—showed during the years 1961 and 1962 average concentrayions not exceeding the limit of 0.5 mg Si/1. (these average concentrations have been calculated for the entire lake volume); the lakes with inflowing waters, i.e. running waters, exhibited values of up to 12 mg Si/1.

The question then arises: To which extent are these differences produced by a direct increase of Si concentrations; and, to which extent do the inflowing waters influence indirectly the Si balance of the lake, in that they, by way of biogenic silica precipitation in the lake, bring about the conditions for increased autochthonous Si release from the sediment.

2. Factors determining the silica metabolism of running waters

The concentrations of Si in streams and rivers are determined by the following factors:

(a) The mixing ratio of the different waters and the Si concentrations of these waters; and

(b) the changes in the concentrations along the course of the streams .39.
or rivers—changes that are due not to the mixing in of lateral inflows but, above all, to the biogenic consumption of dissolved silica.

(a) The Si concentrations determined at the openings of stremas or rivers —apart from the changes mentioned under (b)—represent the result of mixing of water bodies of different origins and, thus, usually also exhibiting different Si concentrations. The Si concentrations in the individual bodies of water depend on the patterns prevailing at the sites of origin; they may be largely constant or may be subject to large (seasonal) variations.

In the region investigated in the eastern Holstein hill country, the following originating waters may be distinguished with respect to their Si contents:

Waters of precipitation flowing off on the surface of the soil: These particular waters exhibit the greatest variations with regard to both their Si contents and their volume; they are characterized by their high contents of turbidity-producing substances and their low concentrayions of dissolved silica (and this, above all, during the period of snow melting).

The seepage waters originating in the interstitial system in the soil, which do not flow into the ground water, but leave the soil in the form of small rills or by means of artificial drainages after passing through one or several more or less thick soil layers. These waters usually originate in the waters impounded in the soil, either at low lying areas close to the groundwater or above compacted horizons in the soi, as, for instance, above zones of accumulated clay over boulder clay or hardpan layers in soils over glacial sand. The latter type of water was investigated in particular in the case of drainage waters in the Heiden Lake catchment area, which waters originate in the water impounded in para-brown earth over boulder clay. As is shown in Table 10 and as has been discussed already in Section III, these particular soil waters are distinguished by their strikingly constant and uniform Si contents, and this in the percolation experiment as well as in the field.

Table 10 - Silica concentrations in drainage waters (D). Key: 1, Catchment area; 2, . . inlet; 3, freshly dug field drainage ditch close to D_1; 4, östl. = east of; 5, am = at the; 6, range of variation; 7, date; 8, acid-binding capacity.

1. Einzugsgebiet	D	7. Datum	mg Si/l	8. SBV	μS_{20}
Kleinmühlenbach 2. (Heidensee-Zufluß)	D_1	27. 11. 60	5,3	—	—
		20. 3. 61	4,5	5,4	597
		5. 11. 61	4,8	3,4	835
	D_2	27. 11. 60	4,9	—	—
		20. 3. 61	5,4	6,2	710
		5. 11. 61	6,0	6,1	756
		28. 4. 62	5,5	—	704
		21. 5. 62	5,4	5,8	747
		5. 5. 63	6,8	6,2	—
	D_3	27. 11. 60	4,5	—	—
		20. 3. 61	4,1	4,1	538
		28. 4. 62	4,3	—	525
		5. 5. 63	4,0	4,5	—
	D_4	28. 4. 62	5,0	—	525
		5. 5. 63	5,3	4,5	—
	D_5	27. 11. 60	4,5	—	—
		20. 3. 61	5,7	3,3	522
3. frisch ausgehobener Ackerentwässerungsgraben nahe D_1		5. 5. 63	4,5	5,2	—
4. Schwartau östl. Kl. Meinsdorf	D_1	19. 3. 61	4,8	2,0	409
	D_2	19. 3. 61	4,5	4,2	530
Kossau	D_1	5. 2. 61	5,1	4,0	604
	D_2	5. 2. 61	5,2	—	—
Schluensee		5. 2. 61	5,2	2,9	512
5. Schwentine am Bungsberg		16. 4. 61	5,2	3,1	444
		6. 5. 62	4,3	2,9	440
6. Schwankungsbreite			4—6 (6,8)	3—6	400—800

The spring waters originating in the mineral subsoil and the ground water accumulating in wells exhibit a similar constancy with regard to their Si contents; however, we find that the range of concentration in their case lies between 11 and 16 mg Si/l. The individual values are presented in Table 11.

Table 11 - Silica concentrations in well and spring waters. Key: 1, Type of water, and location of the well or the spring, respectively; 2, Ploen tap water; 3, well water at . . .; 4, six springs along the Small Ploen Lake, north shore; 5, springs along the Dick Lake; 6, Luisen spring along the Keller Lake; 7, seven springs along the Vierer Lake, east shore; 8, spring inlet into the Vierer Lake (12 to 14 l./sec); 9, springs opening into the Heiden Lake inlet; 10, range of variation; 11, date; 12, acid-binding capacity.

1.	Art des Wassers Lage des Brunnens oder der Quelle	Datum 11.	mg Si/l	SBV 12.	μS_{20}
2.	Plöner Leitungswasser	1960—63	12—13	4,2	790(Cl⁻)
3.	Brunnenwasser bei Sevel, Jütland	Sept. 62	13	4,0	—
4.	6 Quellen am Kl. Plöner See, N-Ufer	11. 5. 63	15,2—16,3	5,6—6,0	570—600
		8. 12. 63	14,9—15,3	5,7—6,0	570—600
5.	Quellen am Dieksee, N-Ufer	23. 5. 63	14,3	5,5	—
	S-Ufer	4. 3. 61	11,9	—	—
6.	Luisenquelle am Kellersee	23. 5. 63	13,3	5,4	—
7.	7 Quellen am Vierersee, O-Ufer	1961—63	12,0—14,8	4,1—4,7	460—510
8.	Quellzufluß zum Vierersee (12—14 l/sec.)	3. 2. 61	11,9	4,1	508
		2. 6. 61	12,2	4,1	507
		23. 8. 61	12,4	4,2	510
		5. 11. 61	12,0	4,2	508
		31. 3. 62	11,5	4,2	506
		4. 5. 62	11,3	4,2	510
		15. 7. 62	11,8	4,2	513
		5. 5. 63	12,4	—	—
9.	Quellen zum Heidensee-Zufluß	1961—63	11—13	4,0—4,6	500—560
10.	Schwankungsbreite		11—15 (16)	4—6	460—600

The water flowing out from stagnant surface waters—ponds, pools and lakes—with regard to its character depends to a greater or lesser extent on the characteristic metabolic processes in the originating waters. All concentrations within the range between 0.02 and 12 mg Si/l. have been observed by us.

Apart from the running waters, which contain relatively large quantities of water from stagnant waters, and apart from the short periods following strong precipitation, during the course of which large quantities of rain water flow off on the surface, we find that the Si concentrations of the streams in the eastern Holstein hill country are determined by the mixing ratio of drainage water and spring water. On the basis of that finding, we obtain a range of concentration between 4 and 16 mg Si/l.: .40.

Drainage (seepage) waters:	4 - 6 mg Si/l.
Spring waters (groundwaters):	11 - 16 mg Si/l.
Mixed waters:	6 - 11 mg Si/l.

The respective mixing ratios determine the differences between the individual streams as well as the variations in the Si concentrations in dependence on the rate of flow (water-mass): .41.

The stream flowing into the Heiden Lake, which originates about 4.5 km east of that Lake in the form of drainages from fields, receives a relatively large inflow of spring water before opening into the Lake; the Si concentration (12 mg Si/l.) as well as the volume of that spring water are constant. Since the water masses of the stream vary very greatly at a relatively constant Si concentration (6 mg Si/l.), we find at the opening into the Heiden Lake very interesting relations between Si concentrations and rates of flow (water-masses). These relations are based on the combination of the three constant factors—

Si concentration of the water of the main stream; Si concentration of the spring water; and the spring water volume—and the one variable factor—rate of flow in the main stream.

If the stream dries up before reaching the point of junction with the .42. spring water inflow during periods deficient in precipitation, we find that the Lake receives only the small amount of spring water, which exhibits a Si concentration of 12 mg Si/1. On the other hand, the spring water becomes more and more diluted with increasing rate of flow (water-masses) in the stream above the point of spring water inflow, until finally, if the stream carries very great water masses, the water flowing into the Lake exhibits simply the Si concentration of the main stream. The situations described above are illustrated in Figures 23 and 33, and the corresponding data have been compiled in Table 12. The concentrations of the mixed water, calculated on the basis of a constant spring water inflow of 17 l./sec at a Si concentration of 12 mg Si/l. and increasing water masses flowing in the main stream at a concentration of 6 mg Si/l., are presented in Figure 32 as the thick continuous curve.

<u>Table 12</u> - Cf. Figures 32 and 33.

Tabelle 12. (Zu Abb. 32 und 33)

Nr. No.	Datum date	Nr. No.	Datum date
1	27. 11. 1960	12	21. 1. 1962
2	2. 6. 1961	13	31. 3.
3	22. 6.	14	16. 4.
4	23. 8.	15	28. 4.
5	17. 9.	16	19. 5.
6	29. 9.	17	9. 6.
7	14. 10.	18	24. 6.
8	19. 10.	19	15. 7.
9	4. 11.	20	2. 9.
10	20. 11.	21	20. 1. 1963
11	17. 12.	22	23. 2.

That curve corresponds with almost mathematical accuracy to the average of the values obtained by measurements actually carried out during the year 1961 (Nos. 2 to 11) and during the winter of 1963 (Nos. 22 and 23). On the other hand, the values obtained during 1962 (Nos. 15 to 20) are significantly lower. That finding must be attributed to the pronounced Si depeletion in the main stream water during the spring of 1962 (cf. Figure 34), which lasted into the summer of that year. As can be seen in Table 12, the values for the year 1961 were obtained during the summer, fall and winter months; those for the year 1962, however, were obtained during the spring, i.e. at a time when the Si concentrations in the main stream had dropped to 0.8 mg Si/l. due to the pronounced Si depletion.

We then realize that the Si concentration of the water flowing into the Heiden Lake is determined—apart from the depeletion processes taking place in the main stream—above all, by the varying mixing ratio of the two bodies of water exhibiting constant Si concentrations. A third body of water—the surface rain water exhibiting low Si concentrations—is involved only following extraordinarily heavy precipitation or during the period of snow melting.

Similar relations between water-masses and Si concentration have been .43. found to exist in a number of additional small streams. In each one of these instances we found that the waters originating either in the interstitial system of the soils or in the mineral subsoil and exhibiting relatively constant Si concentrations determine, in variouscombinations, the Si content of the running waters in eastern Holstein.

(b) Decrease in silica concentration due to biogenic consumption - The decrease in the Si concentrations in running waters due to biogenic consumption hitherto has been investigated only to a small extent. That decrease, however, must be taken into consideration in the comparison of the Si concentrations of different waters, since samples taken during the periods of marked diatom growth will yield an inaccurate picture of the average conditions for a given year.

In a comparison involving "open and closed running waters," Wawrik (1960a) found that the former waters exhibited a significantly wider Si concentration amplitude than the latter ones, and he attributed the Si minima observed during the fall and the winter to the increased occurrence of diatoms during these periods, in addition to a decrease in the water masses transported.

We have found that a considerable depletion of Si takes place in the running waters in the eastern Holstein hill country and this, in particular, during the months of April and May.

Inflow into the Heiden Lake - The constancy of the Si concentration described further above in the case of the stream flowing into the Heiden Lake--a constancy observed, in particular, above the point of influx of spring water in this stream--is not valid during the spring months. That fact is demonstrated by the data shown in Figure 34: During April and May of 1962, we found considerably lower values, which occasionally dropped down to 1 mg Si/l. (On May 5, 1963, we even found a value of only 0.18 mg Si/l.). The somewhat decreased January values could not with certainty be attributed to Si consumption by diatoms; however, the lowest Si values found during April and May were associated with mass development of Meridion circulare in the small drainage ditches and of Synedra ulna in the main ditch (stream). As is indicated by the data presented in Table 10, the waters emerging from closed drainage pipes exhibited Si concentrations that were unchanged compared to the annual average. These Si concentrations, however, frequently decreased already after the waters had flown in the open over a short distance only, i.e. once large quantities of diatoms (chiefly <u>Meridion circulare</u>, but also <u>Cocconeis</u>, <u>Navicula</u> and <u>Cymbella</u>, among other species) started to develop under the good illumination conditions.

On April 28, 1962, we took samples at different times from the main stream above the spring water inflow point; the analytical values obtained in these samples are presented in Table 13. .44.

<u>Table 13</u>

Tabelle 13

Uhrzeit Time	t° C Wasser water	mg Si/l dissolved	 suspended	μS_{20}
10.00	9,8	1,00	0,88	540
12.00	11,3	0,80	1,08	518
14.00	11,3	0,80	0,88	530
16.00	11,1	0,78	0,76	530
20.00	8,2	0,66	0,88	556

The water flow amounted to about 10 l./sec; the weather was bright to cloudy, and there was no precipitation.

The concentration of dissolved silica dropped within ten hours from 1.0 to 0.66 mg Si/l., i.e. it drooped by 34 per cent. The content of diatomic silica, in part, was greater than that of dissolved silica. Similar observations have been made by us in the waters flowing into the Schieren Lake.

<u>Upper course of the Schwentine River between Bungsberg and Kasseedorf</u> - The so-called Bungsberg Schwentine has its source at the foot of the Bungsberg, representing the highest elevation in Sleswig-Holstein (168 meters

above mean sea level), and, following a stretch having a rather steep slope, opens behind Kasseedorf into the chain of the Schwentine Lakes. The gradient of the slope along the stretch between Bungsberg and Kasseedorf measuring six kilometers in length amounts to 1 per cent.

On two different days in 1962, i.e. on May 6th and on September 9th, we took samples at different sites in the ditch (stream) in order to compare the variations in concentration of dissolved and suspended silica, respectively, within a certain section of the ditch (stream) during different seasons. The days of sample taking were selected to ensure that one day was located within the main period of depletion, and the other one, outside of that period.

We shall first characterize the sampling sites shown on the map (Figure 35):

No. 1: Two small subsurface water outlets at the foot of the Bungsberg. Due to impounding, these two outlets form a small, shallow pond, in which considerable Si depletion takes already place.

No. 2: Outlfow from the little pond.

No. 3 and No. 4: The two originating ditches above their junction.

No. 5: The Schwentine River above Bungsberghof. Below this sampling site, the ditch water is greatly polluted by a rill containing dung water.

No. 6: Road bridge near Bergfeld. .45.

No. 7: Schwentine River below the points of junction of two small lateral ditches.

No. 8: Above a relatively steep stretch through deciduous forest.

No. 9: Below the points of junction of three relatively large lateral ditches.

No. 10: Final sampling site; highway bridge near Kasseedorf above the Kasseedorf pond.

The data obtained on the two days of investigation are arranged for comparison in Table 14.

Investigation carried out on May 6th, 1962, at the time of the diatom maximum: As in the case of the Heiden Lake inflow, we were able also in that of the Schwentine River to observe pronounced Si depletion already in the small originating ditches. Shortly below the point of junction of the two spring-water ditches (Site 5), the concentration of dissolved silica had already dropped to 0.70 mg Si/l. That concentration then rapidly dropped to its minimal value of 0.25 mg Si/l. The Si concentration reached values of barely 2.0 mg Si/l. only between Sites 8 and 9, following the inflow of the forest ditches, in which Si depletion was less marked probably due to deficiencies in both light and nutrients. No Si depletion could be determined along the last stretch to Kasseedorf. The Si concentration continued to increase due to the inflow of small, short Si-rich meadow drainage ditches.

The concentration of suspended (diatomic) silica (almost exclusively represented by Synedra ulna) reached at some points almost 1 mg Si/l. (Table 14).

Table 14

Tabelle 14

Datum date	Station	l/sec.	SBV	μS_{20}	mg Si/l dissolved	suspended
6. 5. 62	1	—	2,2	418	4,06	0
		—	3,6	470	4,44	0
	2	1	3,04	397	0,99	0,09
	3	1	2,90	416	0,98	0,09
	4	3	3,68	460	0,66	0,29
	5	4	3,50	450	0,70	0,20
	6	5,4	3,70	487	0,26	0,66
	7	9,3	3,43	465	0,25	0,97
	8	10,6	3,46	470	0,27	0,58
	9	31	3,40	460	1,96	0,05
	10	32	3,56	468	2,32	0,06
9. 9. 62	5	22	3,30	406	3,96	0,04
	6	—	3,40	409	4,00	0,04
	8	—	3,56	434	4,40	0,02
	9	100	3,80	454	4,68	0,08
	10	100	3,90	460	4,88	0,16

Key: SBV, acid-binding capacity

Investigations carried out on September 9th, 1962: Following a cool and rainy summer, we found that the rate of flow was greatly increased compared to the investigation of May 6, 1962, so that a direct comparison of data is made difficult. Due to the very large difference in the Si concentrations of the Schwentine River water between May 6th and September 9th, 1962, (the ratio being 1:17), we find, however, that the comparison of the data is adequately instructive. On May 6th, we found a drop in Si concentration from 4 to 0.25 mg Si/l. between the origin of the ditch and Site 6; on September 9th, on the other hand, the original concentration of 4 mg Si/l. was in evidence along the entire stretch. .46.

3. Regional-limnological comparisons of concentrations of silica dissolved in running waters

In contrast to the standing or stagnant waters, brooks and small streams do not exhibit individual balances. In the interplay of Nature, running waters play the role of mediators between the surrounding area and the standing waters within that area. The waters carried by these brooks and streams have largely enjoyed intimate contact with the soils and the mineral subsoils, and, for that reason, reflect the properties of the catchment area better than the water in the standing bodies of water. For the purposes of regional comparison, we find that those ditches or streams are best suited, which contain no large shares of lake water and do not reflect too strongly the purely local conditions (as, for instance, due spring water ditches and seepage water ditches), but contain already waters of different origins. In the region investigated by us, ditches (streams) of that desirable type are available only to a limited extent, since, due to the abundance of lakes in eastern Holstein, all large ditches (streams) contain considerable shares of lake water. The more important chemical data and the flow rates of several ditches (streams) investigated by us during the years 1960 to 1963 are compiled in Table 15. Instead of the average values, we are presenting in that Table the main ranges of variation (i.e. extreme values occurring occasionally are not included in this Table).

Table 15

Tabelle 15

1. Graben	4. Zufluß-See	5. Wfg. l/sec.	mg Si/l	6. SBV	μS_{20}
Tensfelder Au	Gr. Plöner See	600—700	7—10	2,9—3,2	430—460
Schmarkau	Behler See	200—300	4— 6	3,0	450
Höllenau 2. bei Neumünster	(Stör, Nordsee)	100—200	5— 6	3,0	440
3. Wiesengraben (südl. Schierensee-Zufluß)	Schierensee b. Wankendorf	60—100	6—11	2,8—3,3	405—443
Kührener Au	Bornhöveder See	100—150	8—10	2,3—2,7	385—410
Kleinmühlenbach	Heidensee	20— 60	6—12	4,0—4,8	500—560

Key: 1, Ditch; 2, bei = near; 3, meadow ditch; -bach = brook or little stream; 4, flowing into; 5, rate of flow; 6, acid-binding capacity.

A value of 7 to 8 mg Si/l. may be given as a rough concentration average for the relatively large running waters not affected by lake waters within the predominantly calcium carbonate-rich eastern Holstein hill country. .47.

Similar Si values, associated with considerably lower acid-binding capacity and conductivity values, were obtained in the calcium carbonate-deficient sandy regions of central Jutland, in the course of an excursion made during September of 1962. The data obtained in Jutland have been compiled in Table 16.

The waters of the Jutland sand regions are derived largely from the waters impounded above thick hardpan layers. Due to their richness in iron, these waters usually show a rusty-brown tinge: The ditches in the region of

Table 16

Tabelle 16

1.	Gewässer und Probenentnahmestelle		l/sec.	mg Si/l	SBV	μS_{20}
2.	1. Seengebiet Skanderborg bis Silkeborg					
3.	Gudenaa vor Mossö		(5—10 m³)	7,0	2,2	307
	Saltenaa vor Salten Langsö		ca. 1000	7,4	1,2	—
4.	Zuflüsse zum Torsö	a	20	9,7	0,9	—
5.	bei Virklung	b	10	8,8	0,4	—
4.	Zuflüsse zum Almindsö	a	17	6,8	0,5	166
		b	10	9,7	1,1	266
4.	Zufluß zum Ornsö		500	8,3	0,8	—
6.	2. Heidelandschaften Mitteljütlands (Brande — Sunds)					
7.	Graben nördl. Brande		ca. 200	4,1	0,04	—
4.	Zufluß zum Söbysö		20	5,5	0,2	190
8.	Graben bei Kölker nördl. Söbysö		ca. 200	5,1	0,05	—
	Herningsholm Aa		—	7,4	0,8	—
	Storaa		500—600	4,4	0,8	300
8.	Graben bei Sunds		ca. 100	6,6	0,8	233
4.	Sundsö-Zuflüsse	a	400	6,1	0,4	230
		b	60	7,1	0,8	224
		c	40	7,0	0,9	240
9.	3. Stubbergdsö-Gebiet					
	Skive Aa	10 vor ihrem Zusammenfluß	ca. 1000	7,8	0,9	—
	Haderup Aa			7,8	0,8	—
11.	kleine Zuflüsse zum Hellesö	a	—	7,4	2,7	—
		b	—	5,5	0,7	—
		c	—	7,4	1,0	—

Key: 1, Waters and sampling points; 2, lake region between . . . and . . .; 3, vor = above; 4, inlet(s) into . . .; 5, bei = near; 6, heath region in central Jutland; 7, ditch north of . . .; 8, ditch near . . . north of . . .; 9, Gebiet = region; 10, above the site of their junction; 11, small inlets into the . . .

the Sund contained up to 4 mg Fe/l. in either dissolved or suspended form. The acid-binding capacity values, as a rule, were below 1, and the pH values varied between 6 and 7. We are thus dealing with a type of water entirely different from that found in the eastern Holstein ditches (streams), but the Si values, nevertheless, are of similar magnitudes. During September of 1962, the Si concentrations [in the Jutland lakes] varied between 4 and 10 mg Si/l., with a concentration of values around 7 to 8 mg Si/l.

A more detailed investigation of the originating waters, unfortunately, could not be carried out; however, it appears that the Si content of the waters from the impounded pore-water space above the hardpan layer is higher than that determined by us in the drainage waters of eastern Holstein. Furthermore, groundwater effluxes play hardly any role at all in Jutland, and this, above all, in the flat heath regions of central Jutland. In well water obtained at Sevel, we determined, as in the case of Holstein groundwater, a Si concentration of 13 mg Si/l.; however, the maximal Si concentration—and this also in small ditches—amounted only to 9.7 mg Si/l. On the basis of our—admittedly highly sporadic—investigations, it appears that the concentration range of 10 to 16 mg Si/l. is absent in the Jutland brooks and streams. .48.

In Central Europe, the lowest Si concentrations are found in mountain regions:

Elster (1955a) found in Black Forest brooks values in the range between 2 and 6 mg Si/l., with certain ranges being characteristic for individual brooks.

Wawrik (1960a) found in running Lunz waters Si concentrations between 0.5 and 1.5 mg Si/l.; and in the Danube (Wawrik, 1962), values between 1.5 and 3.5 mg Si/l. According to Elster and Insele (1937) and Elster (1939), the Rhine, at its opening into Lake Constance, exhibits Si concentrations between 1.1 and 1.9 mg Si/l.

However, higher concentrations have been found in other continents. Kobayashi (1960) found values of 3 to 25 mg Si/l. in 225 Japanese rivers, with the higher values having been obtained in volcanic regions, and the lower ones, in regions with sediment rock. The latter author has explained that difference on the basis of the very intensive silicate weathering taking place in volcanic soils.

Loeffler (1960) found very high values in springs (of the non-thermal type) in volcanic regions in Chile (around 25 mg Si/l.).

The extremely high Si values found in thermal springs are due to special solubility conditions (temperature, pressure) prevailing in the interior of the Earth, and these values cannot be considered within the framework of the present study. However, these high Si concentrations can, under certain circumstances, influence the Si metabolism of the surface waters to a decisive extent (Ruttner, 1951).

The values compiled by Clarke (1924) for different running waters of the world showed an accumulation in the range of concentration between 2 and 10 mg Si/l.; values exceeding 20 mg Si/l. were found only in a few exceptional instances. The relatively highest Si concentrations as well as the absolutely highest ones were found in the electrolyte-deficient river waters of North- and South-America (4 to 15 mg Si/l., corresponding to 10 to 50 % SiO_2 in the inorganic dry residues; cf. also Sioli, 1950).

Apart from this relative and, frequently also, absolute Si abundance in electrolyte-deficient waters, it is not possible to discern any correlations between Si content and either calcium content or total electrolyte concentration. Silica rather exhibits the tendency to occur in all waters within the same range of concentration. The Si concentrations found in the Alp rivers, admittedly, are strikingly low. .49.

4. Direct increase of concentration of dissolved silica in lakes due to inflowing waters

The change in the concentration Ks of a certain substance in a given lake volume Vs due to the inflow of a given volume Vz having the concentration Kz is given in the following equation:

$$\Delta \mathrm{Ks} = \frac{\mathrm{Vz} \cdot \mathrm{Kz} + \mathrm{Vs} \cdot \mathrm{Ks}}{\mathrm{Vz} + \mathrm{Vs}} - \mathrm{Ks}$$

Transformation gives Equation (1):

$$\Delta \mathrm{Ks} = \frac{\mathrm{Vz}}{\mathrm{Vz} + \mathrm{Vs}} (\mathrm{Kz} - \mathrm{Ks}) \qquad (1)$$

The change in concentration in a given lake, thus, depends on both the dilution factor introduced by the inflowing water, $\frac{Vz}{Vz + Vs}$, and the difference in concentration, $\underline{Kz} - \underline{Ks}$. Since we may regard only the lake volume as a constant parameter, and since all other parameters vary with the changing seasons to a greater ($\underline{Vz}$, $\underline{Ks}$) or lesser extent ($\underline{Kz}$), we find that $\Delta\underline{Ks}$ may vary very greatly.

Usually we will find that the Si concentrations in lake water, due to the biogenic precipitation of silica, are lower than those in the inflowing waters. This finding indicates that the Si concentrations in the lake water are increased by the inflowing water. In order to be able to estimate the extent to which a given inlet intervenes directly in the Si balance or metabolism of a given lake, we must compare the increase in concentration expected on the basis of inflow with the concentration actually measured. The increase in concentration brought about by inflowing waters over a relatively long period of time can be calculated with the aid of a negative exponential function. Equation (1) presented further above is not suited for calculations involving relatively long periods of time, since the inflowing water causes a continuous change of the concentration difference $\underline{Kz} - \underline{Ks}$. The theoretical course of Si concentration in lakes, thus, cannot be linear are in character.

In connection with the derivation of our function, we will proceed on the basis of the following theoretical considerations: Let the initial concentration of dissolved silica in the lake be zero; let the Si concentration be gradually increased by inflowing water having both a constant rate of flow and a constant concentration of Si; in the course of this rise in Si concentration, let there occur in the lake no autochthonous processes, like biogenic Si utilization or Si release from the sediment. Let the lake volume remain constant by means of an outflow of water identical to the rate of inflow. And, finally, let the lake be in a state of ideal mixing. The increase .50. in concentration of Si in the lake during a certain interval of time, t, is given by the following Equation

$$K_s = K_z \left(1 - e^{-\frac{V_z}{V_s} t}\right) \qquad (2),$$

which formally corresponds to Nernst's Law of Dissolution.

We will now go ahead and compare the calculated increases in concentration brought about in lake water by inflowing waters with the increases actually measured, using the Heiden Lake and the Vierer Lake as examples.

These two Lakes show hardly any stratification at all, so that the preconditions for complete mixing are given. The volumes were regarded as constant, neglecting the minor variations in the Lake levels.

(a) Heiden Lake - As has been demonstrated further above, there exist certain relations between the rate of flow (water-mass entering the lake) and Si concentration at the point where the inlet flows into the Heiden Lake. The Si concentration initially decreases with increasing rate of flow, and then tends towards a constant final value. Since the mass of inflowing water as well as the Si concentration of the inflowing water are of importance for the increase in Si concentration of the lake water, there arise interesting relations between the latter factors and the Si balance of the lake.

For the calculation of the increase of the Si concentration in the lake water, we have selected the following three examples from Figure 32 (Table 17).

Table 17

Tabelle 17

	Vz l/sec	Kz mg Si/l	1.theoretische Durchflußdauer (Tage)	Ks ($Ks_1 = 0$) mg Si/m³ · 24 h
a	17	12,0	220	55
b	30	9,5	125	76
c	50	8,0	75	107

Key: 1, Theoretical time of turnover (in days).

The increase in concentration initially increases more rapidly with the increasing rate of flow of the inflowing water, despite the associated low Si concentration in the inflowing water. However, once the Si concentration in the lake water has reached the limiting value of 7.5 to 8.0 mg Si/l., we find that the concentration of Si increases in the lake with increasing Si concentration of the inflowing water, despite the fact that the rate of inflow is then lower.

In cases where the Si concentrations are already high in the lake, we
find that only low rates of flow (water-masses) with correspondingly higher .51.
Si concentrations are able to bring about an increase in Si concentration in the lake water. In cases of marked inflow, we thus find occurrence of leaching in the upper range of concentration in the lake water.

An increase in Si concentration in the lake water up to 12 mg Si/l.—as we have observed during the winter of 1962-1963—cannot occur solely on the basis of influx, since the time required for such an extensive increase exceeds one year by far, and the depletion-free periods last only a few months.

The Si concentration in the lake water rises significantly more rapidly than one would expect on the basis of the daily 'importation excess.' That fact is demonstrated in Figure 37. In that Figure we have compared certain Si concentration increases determined during different seasons in the years 1961 to 1963 with the values possibly brought about by inflowing water. This particular representation is based on Curve a, since low rates of flow (water-masses) and high Si concentrations in the inflowing water are characteristic for the periods of Si feedback. The initial concentration of a given period was plotted on the Curve of the theoretical concentration, and the end concentration was plotted against time, so that the observed increase in concentration can be divided into two sectors: The lower sector of the vertical represents the increase in concentration attributable to the inflow, and the one located above it represents the autochthonous feedback based on the release of Si from the mud. The extent to which this autochthonous Si quantity is already reduced by biogenic Si utilization or consumption cannot be established. Conclusions regarding the actual Si consumption cannot be drawn—in the case of shallow bodies of water—on the basis of the numerical increase of the diatoms, since a large fraction of these organisms—a fraction, which varies very greatly, depending on the movement of the water masses—sediments rapidly, apart from the fact that it is not possible to determine the quantitative development of the sessile species in the littoral zone. However, the values presented have been obtained during periods associated with low development of diatoms in the plankton.

The Figure under consideration shows clearly that even the small and shallow Heiden Lake with its Si-rich inflow possesses pronounced autochthonous liberation of Si, which usually exceeds the allochthonous supply to a significant extent, but, at least, is as marked as the allochthonous supply. This autochthonous feedback is particularly evident in the higher range of concentration, since the concentration of the inflowing water is practically reached in that range. The concentration of the mud water, however, is reached only up to 30 to 50 per cent, so that exchange between mud and contact water still leads to liberation of Si from the mud (cf. Section VI).

(b) The Vierer Lake - Since only the northern basin of the Vierer Lake receives inflowing waters, we have carried out calculations only for that part of the Lake. The inflowing waters are: The outflow from the Heiden Lake, exhibiting a Si concentration, which, as a rule, deviates only a little from that .52. of the Vierer Lake and, for that reason, does not have to be taken into consideration; two relatively small ditches with spring water contributions; and numerous and, in part, vigorous springs located within the area immediately surrounding the Lake or along its shore.

The average rate of flow of all these inflows amounts to 60 l./sec, at an average Si concentration of 10.9 mg Si/l. The theoretical duration of turnover approximately amounts to 2.7 years.

Figure 38 illustrates that the relatively Si-rich inflow results only in a shift of the autochthonous Si balance somewhat in favor of feedback and release. The maximal concentrations of 7 to 8 mg Si/l. observed in this Lake, would be reached only after about three years, but these concentrations, in fact, are reached significantly more rapidly. In the year 1962, the Si concentration rose within five months from 0.2 to 7.3 mg Si/l.

(c) In the Large Ploen Lake, we find that the inflows are hardly noticeavle at all, if we disregard the water bodies located in the immediate proximity of the inflow mouth. The greater part of the inflowing water is desilicified already in the preceding lakes (viz. the Vierer Lake and the Behler Lake). Only the Tensfelder Au, exhibiting a rate of flow of 600 to 700 l./sec and a Si concentration of 7 to 10 mg Si/l., is able to participate in the direct feedback in the southern basin of this Lake. Between the late summer and the spring, we find that the Si concentrations of the inflowing water reaching the Vierer Lake are 2 to 3 mg Si/l. above those of the Large Ploen Lake; however, the rate of flow, being between 100 and 200 l./sec, is relatively low. At this small difference in concentration, it would appear that the water flowing out from the Vierer Lake is hardly able to play a role in the Lake presently under consideration. The highest rate of flow (which, however, cannot be determined accurately due to backwater control measures) is exhibited by the Schwentine River, which flows into this Lake directly from the Behler Lake. The Si concentrations of that water, however, differ hardly at all from those of the Large Ploen Lake. The Si concentration in the lake water would increase in the course of a year due to the Si supplied by the inflowing waters only from zero to 0.4 mg Si/l. The observed increases in Si concentration in the Large Ploen Lake, thus, are due to about 90 per cent to the autochthonous feedback of Si.

(d) The importance of the inflowing waters is similarly insignificant in the other lakes in eastern Holstein, i.e. in the Grebiner Lake, the Wielener Lake, the Pluss Lake, the Trammer Lake, the Little Ploen Lake, the Behler Lake, and the Schmalen Lake, among other ones. These Lakes receive either only small inflows of Si-rich water (i.e. the Grebiner Lake, the Wielener Lake, the Pluss Palke, and the Trammer Lake) or the inflowing water has already been desilicified in the preceding lakes, so that the respective concentrations are approximately equal.

In cases where the Si concentrations of the lake water and of the inflowing waters are equal (i.e. Ks = Kz), we realize that any change in the concentration in the lake water is solely of autochthonous origin. The autochthonous processes (Si depletion and Si feedback), of course, create on their part a concentration gradient, so that the allochthonous influence increases .53.
again. In chain lakes, which are interconnected by means of ditches or a stream, we find that the state of concentration equality may exist for long periods of time despite pronounced depletion or feedback of Si in these lakes, since the autochthonous metabolic events proceed in these lakes in a relatively synchronous manner. These relationships may be illustrated in the chain of lakes stretching between the Bornhoeveder Lake and the Stolper Lake (Table 18).

Table 18 Tabelle 18

Seenverbindung Lake connection	Datum Date	Kz — Ks
Bornhöveder See → Schmalensee	23. 4. 61	0,4 — 0,1 = + 0,3
	12. 7. 61	1,2 — 1,5 = — 0,3
Schmalensee → Belauer See	23. 4. 61	0,1 — 0,1 = ± 0,0
	12. 7. 61	1,5 — 1,7 = — 0,2
Belauer See → Stolper See	23. 4. 61	0,0 — 0,0 = ± 0,0
	12. 7. 61	1,7 — 1,3 = + 0,4

Depletion and release of dissolved silica proceed in a similarly synchronous manner in the chain of the Schwentine lakes and in the chain of lakes represented by the Heiden Lake → Vierer Lake → Large Ploen Lake → Little Ploen Lake (cf. also Lake Constance: Upper Lake → Lower Lake; Elster and Einsele, 1938).

However, we also find in the case of inflowing waters not carrying water from preceding lakes that their Si concentrations occasionally are only a little above the Si concentrations of the respective lake waters. That particular case may arise during the winter before the onset of diatom development, when the lake water has reached its maximal Si concentration, but also during the spring, when the Si concentration of the inflowing water is greatly reduced due to depletion-associated processes.

Direct increase in concentration in the lake water due to importation of dissolved silica, as a rule, is low--apart from local modifications of certain parts of the lakes or of bodies of water. Even in small lakes (like the Heiden Lake), exhibiting a theoretical turnover time of only 100 to 200 days and a maximal concentration difference between lake water and inflowing water of 12 mg Si/l., we find that autochthonous feedback predominates. Increases of concentration observed in lakes associated with inflows must not necessarily be of allochthonous origin!

The direct allochthonous influence is particularlysmall in chain lakes interconnected by a river, since in these cases depletion and feedback proceed in a relatively synchronous manner, so that large concentration differences between lake water and inflowing water arise hardly ever.

The parallelity between the quantity of inflowing water and the maximal Si concentration in the lake water mentioned further above, thus, cannot be attributed to a direct increase in the concentration by the inflowing water.

VI. Autochthonous liberation of silica .54.

1. Introductory remarks - The dissolution of amorphous or bound silica occurring in the lake (i.e. in the free water, in the littoral or in the sediments) is called the autochthonous liberation or release or feedback of silica. In this connection it is, initially, immaterial whether these Si-containing particles have been formed in the water body in question (as, for instance,

the silica of authochthonous diatomic plankton) or whether they have gotten into the water body by way of inflows or eolian transportation (as, for instance, diatomic silica washed into a given lake together with the water from running waters or preceding lakes, or leaves blown by the wind into forest lakes). As is indicated by the extreme Si deficiency of small sand lakes having no inflows, sublacustrine hydrolysis of silicate either in the littoral or in the sediments is of no real importance in the Si balance of lakes.

In the hypolimnion of Danish lakes, Broenstedt and Wesenberg-Lund (1911 - 1912) found a marked increase of Si concentrations with increasing depth; on the basis of that finding and the simultaneous presence of markedly corroded diatom shells, these authors concluded that diatom shells underwent dissolution during sinking. This type of dissolution is assumed at least in the case of the thin-walled asterionelles and fragillarians, since they are hardly ever found in the muds.

Loeffler (1960) believed that the dissolution of diatomic plankton in the water represented the main cause of the extraordinarily rapid increase in the Si concentration in Lake Vallarrica in Chile (from 8 to 24 mg SiO_2/l. at all depth levels within one month), and he wrote: "Perhaps, it should be stressed in the case of large lakes that the bottom sediment with certainty plays an insignificant role in the supply of silica."

Nauwerck (1963) has stressed that the decomposition of most diatoms takes place very rapidly: "Already before the algal cells have passed the hypolimnion, we find that only indistinct outlines indicate the former shape of the shell. Most cells never reach the bottom."

On the other hand, Einsele and Vetter (1938), Elster and Einsele (1938) as well as Yoshimura (1939) have drawn attention to the importance of diatomic silica for Si feedback.

2. Dissolution of suspended diatomic silica in free water

The extent to which the quantity of diatomic silica formed in a given body of water is sedimented, and the extent to which that silica is already dissolved during the course of sedimentation depend on the rate of dissolution, the settling rate, and the settling distance of the particles in question. Both the rate of dissolution and the rate of settling, in turn, depend on a variety of different factors (viz. temperature, pH, water movements, specific .55. surface properties of the diatoms, extent of disintegration by zooplankton), and we are unable to deal with the entire complex of problems within the framework of the present paper. We will draw attention here only to a few factors, which hitherto have been somewhat neglected.

(a) Settling rate - Only a few investigations are available in the literature on the rate of settling of diatom cells or colonies.

Broenstedt and Wesenberg-Lund (1911 - 1912) have assumed that the diatoms require about two to four weeks in order to sink from the surface layer to the bottom of the Fure Lake (38 meters deep), and that the greater part of the sinking diatoms is dissolved during the course of settling.

Investigating stratification and stratification sequences and calculating losses to the sediments, Grim (1939) has made an attempt to determine the rates of settling of different diatoms in Lake Constance. One Fragillaria population or its accumulation zone, respectively, settled in the upper water layers 1.2 to 1.5 meters per day; in the 30 to 50 meter space, 3 meters; in the 50 to 100 meter space, 5 meters; and in the space below 100 meters, 7 meters per day.

On the basis of observations made in Finnish lakes, Jaernefelt (1955) came to the following conclusions regarding settling rates:

Asterionella: 0.2 - 1.0 m/24 hrs.

Staurastrum pingue: 0.9 - 1.9 m/24 hrs.

Fragillaria crotonensis: 0.2 - 2.7 m/24 hrs.

In the case of the *Stephanodiscus astraea* population of the Large Ploen Lake, we have calculated during the spring of 1962 that the average velocity of settling amounted to 2 meters per 24 hours; that calculation was based on the course of the isopleths for suspended silica shown in Figure 21. The daily losses of total silica suspended in the northern basis of that Lake to the sediment amounted to 4 to 6 per cent during the course of the main sedimentation period (April 17th to May 16th 1962).

Attempts to determine the rate of settling of diatoms in the laboratory experiment have hitherto been undertaken hardly at all. Experiments of that type can be carried out only in tranquil water, and the results obtained in that manner actually would throw no light on the velocity of settling prevailing in the lake, since lake water, even at great depths, exhibits turbulence. However, laboratory experiments can provide relative values for different species and, furthermore, valuable indications regarding maximal velocities of settling.

Fritz (1935) has carried out several experiments in sedimentation chambers. That author filled a Kolkwitz chamber with experimental material and covered it with a slip of paper; he then turned that chamber upside down, .56.
placed it on top of an Utermoehl chamber (volume: 100 ml; height: 11 cm) containing filtered lake water, and pulled the slip of paper out from between the two chambers. However, we are forced to assume that turbulences were created by these manipulations in the zone of contact between the two bodies of water, which turbulences would have produced rather marked effects in such a small

chamber. The results obtained in these particular experiments will be discussed further below together with our own experimental results.

In our own experiments, we have observed sedimentation of diatoms in a plexi-glass "column" measuring one meter in height and having a square bottom of 15 by 15 cm. We poured a dense suspension of living diatoms onto the surface of the water in a manner ensuring that these diatoms were concentrated at the surface in a layer measuring about one to two centimeters in thickness. The diatoms had been cultured in a diluted nutrient solution (20% Chu No. 10), separated from the solution by means of centrifugation, and suspended in Schoeh Lake water. The experiments were carried out in a dark, closed room at a temperature of 15 to 16°C. The column-shaped container had been filled with filtered Schoeh Lake water several days prior to the start of the experiment. At intervals of one to two hours, we withdrew samples for microscopic counts from the middle of the water column eight centimeters above the bottom of the experimental vessel. The counts were carried out in a reversed microscope. We found that the individual diatom cells and colonies were uniformly distributed over the bottom of the chamber, i.e. no agglomeration of cells or colonies had taken place during centrifugation. The drop in the water level due to sample taking (25 ml. per sample) amounted only to one centimeter and could be neglected. The settling distance amounted to 90 cm. The results obtained in the experiments using _Synedra ulna_, _Asterionella formosa_ and _Stephanodiscus hantzschii_ are presented in Figure 39. In the case of all three species, the settling density maximum passed the sampling site in a surprisingly corresponding manner, i.e. nine to eleven hours after the start of the experiment. That velocity corresponds to a settling rate of 2.0 to 2.4 meters per 24 hours.

The correspondence of the settling velocities found in the three species investigated by us is in contradiction of the results reported by Utermoehl (1925), Grim (1939), and Fritz (l.c.), since these authors had found, in part, very different settling velocities in different diatom species. It would be desirable that future experiments dealing with this particular aspect be carried out using sedimentation columns as tall as possible (best suited are plexi-glass tubes having a minimal diameter of 20 cm) in order to elucidate the problems still unsolved.

The settling velocities of 2.0 and 2.4 m/24 hrs. found in our experiments are strikingly low compared to the values calculated by Grim (1939) for Lake Constance. The reason for this discrepancy would be found in the fact that our experiments were carried out using living cells undergoing exponential growth, while the diatoms observed by Grim in the hypolimnion of Lake Constance .57 were already dead. Grim, too, has observed significantly greater settling velocities in dead diatoms than in living ones, and he attributed that finding, above all, to the absence of a gelatine sheat, which in living cells greatly reduces the average specific gravity of the cell or the colony, respectively. Fritz (l.c.), too, has found significantly greater settling velocities in fixed diatoms than in living ones, and he assumed "that the buoyancy of phytoplankton is increased to an extraordinary degree during life due to physiological processes (assimilation, respiration), and that these effects are abolished by fixation."

It then appears that the settling velocity of a diatomic cell increases with increasing lake depth (1) due to the decrease in water movement, and (2) due to progressing decomposition of the cell. However, this increase in the settling velocity may be counterbalanced, in part, by the lower temperatures prevailing at the greater lake depths. In cases where the wind-induced water currents reach down to the bottom of the water body, we will find that the numbers of both dead and living cells decrease uniformly in all layers—a fact already stressed by Utermoehl (1925).

(b) The rate of dissolution - The pronounced dependence of the rate of dissolution of silica on the pH value—which has been established by both Joergensen (1955a) and Goltermann (1960) in diatom suspensions, and which is also made evident by the data presented in Figure 73—according to both Stoeber (1957) and Budd (1961) is due to the asymmetry of the Si-O-Si bonds, which leads to positive excess charges on the Si atom. These excess charges exhibit great affinity for anions and, in particular, for OH^- ions. Following the nucleophilic reaction of the OH^- ions with the Si atoms of the hydrolytically active boundary groups, there takes place the electrophilic reaction of the H^+ ions with the O atoms, leading to "complete hydrolysis of monosilicic acid" (Kautsky et al., 1962) No low- or high-molecular-weight intermediates are formed in the course of this process! According to Stoeber (l.c.) other anions —apart from the OH^- ions—and in particular those of the halogens bring about an increase of the rate of hydrolysis; this, at least, at low pH values. The corrosive action of fluoride ions on glass is well known. However, the Cl^- ions are also able to exert a catalytic effect on the rate of dissolution of silica, as has been demonstrated by Lewin (1961) in dissolution experiments using diatoms in freshwater, seawater, and NaCl solutions. Dissolution experiments using precipitated silica in Schoeh Lake water, to which we had added increasing amounts of NaCl, have confirmed the pronounced catalytic action of

Cl^- ions. At a pH value of 7.5 and a temperature of 20°C, we found that the rate of dissolution of silica was increased—on comparison with salt-free water—by 20 to 40 per cent on addition of 1.5% NaCl, and by 50 to 60 per cent on addition of 3.5% NaCl. That fact must absolutely be taken into consideration in comparisons of Si balances under limnic and marine conditions, respectively.

A factor hitherto hardly taken into consideration in connection with .58. pelagic Si feedback is found in the zooplankton; it was Lewin (1961), above all, who has drawn attention to this particular aspect.

According to the investigations carried out by Hart (1934; 1942) and by Marshall and Orr (1962), diatoms frequently represent the main food base for the zooplankton in the sea. That is the case, above all, in the antarctic waters, where the diatoms are the main primary producers and represent the basis of the entire food chain up to the fishes and the whales. Hart (1934) has described the redissolution of diatomic silica in seawater as a "steady process," and he indicated that the sediments, bird guano and the stomach contents of zooplankton always contain only the more strongly silicified diatoms, while the thin-walled diatoms—which represent the main share of the oceanic diatom plankton—are hardly found. Many fragments—in particular, of the bulky forms—have also been found in the stomachs of calanids, euphansiids and pteropods.

In the freshwater of moderate latitudes, we find that the diatoms play only a subordinate role in the nutrition of the zooplankton, since in that water the more strongly silicified forms are subject to more rapid sedimentation. Furthermore, the main development of the freshwater diatoms takes place during a period (i.e. March and April), during which the crustacean plankton is only sparsely developed. According to Apstein (1892) and to Zacharias (1911) diaptomids and cyclopids prefer to feed on diatoms, and "diatom fragments" have also been found in the intestinal tract of water fleas.

On the basis of examinations of intestinal contents of different crustaceans (*Daphnia*, *Diaptomus*, *Bosmina*, *Sida*, and *Alona*) inhabiting the Schlein Lake, Vetter (1937) has stated "that shell residues of various phytoplankters were found in the intestinal tract of all zooplanktonic forms investigated. These phytoplankters are represented chiefly by diatoms (i.e. *Cyclotella*, *Asterionella*) . . . . During January and February, the intestinal contents contained almost exclusively *Cyclotella* species and other diatoms."

In order to determine the extent of disintegration of diatomic frustules by zooplankton and the corresponding acceleration of the rate of dissolution of diatomic silica, we have carried out a number of different feeding experiments using diatoms.

Experiment No. 1: Asterionella formosa and *Daphnia magna* - *Methods*: The asterionelles grown in nutrient solution were centrifuged and then suspended in a certain quantity of Schoeh Lake water resulting in a concentration of suspended diatomic silica of 5 mg Si/l. (corresponding to 75 to 80 x 10^6 cells per liter). Two one-liter polyethylene bottles were filled with that suspension. One bottle served as control sample (A), and ten adult females of *Daphnia magna* were put into the other bottle (B). The suspensions were .59. continuously agitated with the aid of a rotatory mixer (number of revolutions: 6 per minute). An air bubble was permitted to be present in the bottles, which bubble increased continuously in size in the course of the experiment due to the withdrawing of samples. That bubble ensured an adequate supply of oxygen for the daphniae and promoted mixing of the bottle contents. The experiment was carried out at a temperature of 20 ± 2°C. In the course of the experiment, we determined dissolved silica, total silica and pH, and carried out microscopic examinations. For the microphotographs, we withdrew at certain intervals

10 ml of the suspension, diluted that sample to give 25 ml., and transferred the diluted suspension into a 25-ml. plankton chamber.

Observations: The daphniae multiplied very vigorously during the first two weeks of the experiment, and they exhibited good growth. Toward the end of the experiment, the population density, however, decreased to a marked extent, since the food reserves had finally been exhausted by that time.

Microscopic examinations: In captured daphniae we were able to observe that the filtered asterionelles were compressed into a food "sausage" located median in front of the oral appendages; the completely crushed particles were pushed into the foregut through the esophagus by means of the constantly working mandibles. The *Asterionella* colonies were ground to an amorphous mass by the mandibles. The microphotographs (Figures 40 and 41, on Plate 1) reveal a surprisingly rapid advance of mechanical disintegration. Already after eight days, we were unable to find any intact cells at all. In the control bottle, on the other hand, we were unable to observe any marked disintegration even after prolonged continuation of the experiment.

Chemical investigations: The initial concentration of dissolved silica amounted to 0.18 mg Si/l. As is demonstrated in Figure 42, the mechanical disintegration in Bottle B led to a significantly more rapid dissolution of the diatomic silica than in Control Bottle A. The acceleration of dissolution brought about by the activity of *Daphnia magna* is given by the proportionality factors + mg Si/l. B/ + mg Si/l. A; these factors are plotted in Figure 42. The question whether this two- to three-fold acceleration of the rate of dissolution is due only to the enlargement of the active surface, or whether chemical degradation or exposure of the membranous silica to substances in the intestinal tract of Daphnia plays a role in this connection must be elucidated with the aid of future experiments. According to Von Dehn (1931), the pH in the intestinal tract of Daphnia lies between 5.5 and 6. Pectin reportedly is not attacked.

The initial pH value of the suspension of 7.8 decreased in the course of the experiment to 7.0 and 6.8, respectively. During the entire course of the experiment, we found that the pH value of Suspension B—due to the increased rate of degration (respiration)—was about 0.2 lower than that of Suspension A. On Day 9 of the experiment, we filtered a portion of the suspensions through Blue Tape[1] ('Blauband') or membrane filter, in order to compare the behavior of the particles of the main (B) culture and of the control (A) culture. Following filtration using a Blue Tape filter, we found in the filtrate of Suspension A 0.3 mg Si/l., but in that of Suspension B 1.5 mg Si/l. of suspended silica. However, when the respective suspensions were filtered through membrane filters (mesh size: 0.5 µ), we found that complete separation of the suspended silica took place in both suspensions. No colloidal intermediates appeared during the process of dissolution despite the rapid mechanical and chemical degradation of the material. However, absorption of colloids possibly occurring by the detritus particles cannot be excluded. On the other hand, if the dissolution of suspended silica is to be regarded as complete hydrolysis of monosilicic acid (Kautsky et al., 1962), then we cannot expect appearance of low-molecular-weight intermediate products.

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[1] Translator's note: Despite an intensive search in various German handbooks on chemistry, biochemistry, and marine biology, I have been unable to establish what a "Blaubandfilter" is. It would seem to me that it is a special filter identified by a blue tape or ribbon.

The enlargement of the active surface of the diatom shells by means of disintegration is of importance for the pelagic feedback of Si not only because it increases the rate of dissolution, but also because it significantly reduces the settling velocity. The fecal balls produced by the zooplankton dissolve relatively rapidly into loose detritus flakes, so that the diatomic fragments are liberated or float in the form of detritus for a long period of time in the water. .60.

Experiment No. 2: Disintegration of a diatom gyttja from the Large Ploen Lake by *Daphnia magna* - In order to determine whether other, i.e. larger diatoms are also mechanically disintegrated by *Daphnia magna*, we have suspended, in Schoeh Lake water, a diatomic gyttja obtained in the Large Ploen Lake at a depth of 34 meters, which gyttja consisted chiefly of *Stephanodiscus astraea* and *Melosira islandica*; the suspensions again contained 5 mg/l. of suspended silica. The experiment was carried out in the same manner as Experiment No. 1.

As is demonstrated by Figures 43 and 44 (on Plate 2), rapid disintegration of the empty, relatively strong diatom shells took place. Many shells had been broken already after two days, and only small splinter-like fragments could be found after five days.

Since *Daphnia magna* does not occur as planktonic form in deep lakes, but plays a relatively large role only in nutrient-rich, shallow waters (as, for instance, in the Heiden Lake), it follows that our results cannot be generalized directly with regard to the conditions existing in other inland lakes. The results obtained in the experiments described above may be regarded only as an indication for the importance of the zooplankton for the dynamics of silica in bodies of water. Future work must deal with the extent to which the pelagic crustaceans of the larger lakes utilize the large supply of diatoms and, thus, may influence Si feedback. In this connection we would have to think in particular of the small cyclotelles and the stephanodisces.

(c) Observations in eastern Holsteinian lakes - The silica precipitated during the spring bloom of the various diatoms, which silica usually amounts to more than 90 per cent of the total Si supply present in the lake, is almost completely incorporated in the sediments, i.e. following sedimentation almost the entire silica present in the lake water is incorporated in the sediments.

In the northern basin of the Large Ploen Lake, the total Si content (i.e. the dissolved silica plus the suspended one) decreased during the spring of 1962 from 3.2 to 0.2 mg Si/l. (Figure 15). Since the sedimentation of diatomic silica and the release of dissolved silica from the sediment, respectively, overlap already to some extent toward the end of the period of sedimentation, it follows that the true share of sedimented silica that year was in fact somewhat greater than 3.0 mg Si/l. The course of sedimentation of suspended silica and the losses suffered by the individual water layers in total silica are shown in Figures 21 and 22. The concentration of dissolved silica, which had dropped during the period of depletion to 0.02 mg Si/l. in the entire lake water volume, remained at that low level during the period .61. of sedimentation lasting one month (Figure 20). Thus, we can by no means speak of any marked dissolution, although there occurred a transitory, pronounced accumulation of diatomic silica in the hypolimnion (Figure 21). Similar observations were made in both the Pluss Lake and the Vierer Lake.

In the case of the summer diatomic plankton, we must count on a relatively intensive dissolution in the water, first, since that plankton consists chiefly of thin-walled forms (*Stephanodiscus hantzschii*, *St. binderana*, *Asterionella formosa*, *Fragillaria crotonensis*, and *Synedra acus* among other ones); secondly, since the zooplankton is more strongly developed during that time; and, thirdly, since the water possesses a more marked power to dissolve amorphous silica due to both the higher temperature and the higher pH values prevailing. During the summer, we are frequently able to observe large quantities of fragments showing marked evidence of dissolution into hardly identifiable splinters, like diatomic chips. This is the case, in particular, in the more shallow lakes, *viz.* the Heiden Lake, the Vierer Lake and the Bornhoeveder Lake, in which mass development of diatoms (i.e. bloom) occurs also during the summer months. Counting of the identifiable diatomic shells and conversion to Si weight in these cases frequently led to determination of only a fraction of the silica actually suspended in the water. The rest was contained in the detritus, which, no doubt, represented in part the excretory products (fecal balls) of the zooplakton. As a rule, the values for suspended silica determined by chemical and mathematical means, respectively, coincide only during the peak of rapidly developing diatomic blooms.

In the case of the deeper lakes, we must assume that the dissolution of the diatomic residues—to the extent that dissolution takes place at all prior to sedimentation—takes place above all in the epilimnion, since the more favorable dissolution conditions prevail there.

With regard to the annual overall Si balance, it would appear that the Si dissolution in the free water—perhaps, with the exception of shallow, pond-like bodies of water—plays a subordinate role in the inland lakes under consideration, since the main period of diatom development occurs during the early spring, and the summer and fall populations attain only low densities.

3. Silica liberation from the sediments

(a) Experimental studies on mud-water exchanges

(α) Silica release from mud as an exchange process - The exchange experiments using mud-water systems discussed in Section III have already demonstrated that the final values of Si concentration in the overlaying water (above the mud) correspond to the equilibrium concentration prevailing in the mud, and that the influences exerted on the overlaying water by the mud are based on an exchange between the interstitial water and the overlaying water. .62.
Since frequently considerable quantities of silica are released by the mud into the water, while the diatomic silica in the mud, on the other hand, exhibits a relatively low rate of dissolution, we are forced to assume that dissolution is not restricted to the layer of contact (the interface) between mud and water, but takes place also in the mud. That, however, is possible only if the interstitial water in the upper mud layers is undersaturated with respect to silica, since, according to the Laws of Dissolution, the rate of dissolution is directly proportional to the degree of undersaturation:

$$\frac{dc_i}{dt} = kO\,(c_s - c_i) \tag{3}$$

where c_i is the concentration of monosilicic acid in the interstitial water; t is the time; O is the surface of the suspended silica; c_s is the saturation concentration; and k is the proportionality factor.

The degree of undersaturation in the interstitial water ($c_s - c_i$), thus, may be used as a measure of the relative rate of dissolution in the mud.

In order to determine the depth to which formation of dissolved silica takes place in the mud, we have carried out several exchange experiments using layers of mud of varying thickness. Four plastic containers were filled with different quantities of mud (taken from the Large Ploen Lake at a depth of 17 meters), with the individual layers measuring 1, 3, 5, and 8 cm in thickness. We then added certain quantities of lake water with the result being that 10 ml. of water were present per square centimeter of mud surface. That surface amounted to 200 square centimeters. In order to prevent development of micro-stratification, we lightly aerated the overlaying water in a continuous manner, and a part of the water was replaced once a day by fresh lake water in order to maintain a constant concentration level. The experimental temperature was between 18 and 20°C[7].

The Si concentration of the water portion withdrawn once a day initially was relatively high, but it then dropped rapidly to a constant level, which was different in the individual experimental containers. The average values of Si release determined in the course of two months and the Si concentrations measured right after the discontinuation of the experiment in the interstitial water of the mud columns measuring 1 and 8 cm, respectively, in thickness are presented in Figure 45. The experimental vessel containing the 5-cm layer of mud was left untouched at first following conclusion of the experiment, and this until the concentration in the overlaying water had increased .63.

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[7] All experiments dealing with mud-water exchanges undertaken within the framework of the present study were carried out with exclusion of light.

within fifty days to 18.5 mg Si/1. As in the muds of the 1-cm mud layer and the 8-cm mud layer experiments, we determined only the stratification of dissolved silica in the mud (Figure 45).

Results of the experiment: The exchange between mud and water led to a gradient of concentration of dissolved silica in the mud due to a partial leaching from the upper mud layers. However, the release of Si was based only to a small extent on this leaching, as is indicated by the date presented in Table 19.

Table 19 - Key: 1, mud layer thickness (in cm); 2, average Si concentration in the mud at the beginning; 3, average Si concentration in the mud at the end; 4, absolute Si concentration decrease in the mud; 5, absolute Si removal from the mud.

1. Schlammhöhe cm	2. Ø Si-Konz. im Schlamm Anfang mg Si/l	3. Ende mg Si/l	4. absolute Si-Abnahme im Schlamm mg Si	5. absolute Si-Abgabe aus dem Schlamm mg Si
1	26	6	4	60
8	26	22	7	110

In both the experimental containers under consideration, the Si quantities leached from the mud amounted, at the point in time where the experiment was discontinued, to only 6 to 7 per cent of the quantity of Si released. Since leaching of the upper layers of mud represents a non-recurring event due to the experimental design employed, it becomes apparent that the varying releases of Si—at adequate duration of the experiment—are based solely on varying degrees of re-dissolution of silica. In all the experiments carried out, we obtained in the end a constant rate of Si release after initially high values of Si release (cf. Figures 49, 50 and 51).

In the case of the mud layers *isolated* following discontinuation of the experiment using the 8-cm mud layer, we repeated after one month our determination of the silica dissolved in the mud water: In the mud of the upper-most layer measuring 1 cm in thickness, the concentration had increased from 12.7 to 24.5 mg Si/l., i.e. by 11.8 mg Si/l., while that concentration had increased by only 1.3 mg Si/l. in the samples representing the 3-to-4-cm layer and the 5-to-6-cm one, respectively. In correspondence with Equation (3), the rate of dissolution depends on the degree of undersaturation. The data on Si release at varying mud thicknesses—which data were presented in Figure 45—indicate that the more pronounced dissolution takes place in the uppermost (i.e. most strongly undersaturated) layer of the mud.

In cases where the concentration of Si increases in the overlaying water (as in the 5-cm mud layer experiment with no replacement of water), we find that the concentration in the mud also increases gradually, but this not to the same extent as in the water (decreases in dissolution due to approximation to the saturation value), so that the gradient of concentration between the .64. mud and the water becomes less and less steep (Figure 45: 5), and the release of Si from the mud decreases.

The dependence of Si liberation from the mud on the degree of undersaturation of silica dissolved in the mud water can be particularly well demonstrated on the basis of experiments using varying degrees of colonization of the mud with chironomide larvae. According to Tessenow (1964) the concentration of dissolved silica in the mud is kept at a steady low level by the respiratory and nutritive pumping movements of the chironomide larvae dwelling in the mud, so that the dissolution of Si in the mud takes place at an accelerated rate. Apart from the experiments described in the afore-mentioned paper, we have carried out a number of additional experiments with chironomide larvae, among which one experiment, supplementing the afore-described mud-layer experiment, is particularly illustrative in nature:

A sample of chironomide-free mud smelling strongly of hydrogen sulfide obtained in the Large Ploen Lake at a depth of 34 meters was distributed over six plastic containers (5-liter Hostalen[®, i.e. polyethylene; Transl.] pails), so that the thickness of the mud layer amounted in all containers to 10 cm, and the mud surface amounted to 260 square centimeters. Two liters of Schloeh Lake water were given into the containers, which were lightly aerated during the course of the experiment. The experimental temperature was 15 - 16°C. Twice a day at the same hour, i.e. in the morning and in the evening, one liter of the overlaying water was removed and replaced by fresh lake water having a low Si content (0.2 mg Si/l.). After about one week, we observed in all vessels a constant and well corresponding release of Si from the mud. In order to determine the range of error, the experiment was carried out first without chironomide larvae, but otherwise in the same manner as during the subsequent course. The deviations determined between the six experimental containers are shown in Figure 46 in the form of the heavy black line. In all containers the Si release amounted to 95 ± 5 Si/m^2/24 hours.

Following this preliminary study, we placed different numbers of adult <u>Chironomus plumosus</u> larvae (obtained in the Heiden Lake) into the containers, <u>viz.</u> 0, 0, 5, 15, and 20 individuals, respectively. In the Figures, we have converted the numbers of larvae to correspond to one square meter of surface in order to facilitate comparisons with known population densities.

Figure 46 shows that addition of the larvae was reflected in immediate increase of Si liberation. Following that rapid increase of the initial Si release values, we finally reached the dynamic equilibrium or the steady state in all our containers; the level of that equilibrium was determined by the different numbers of chironomide larvae present. Comparison of Figures 46 and 47 reveals the direct relationship between the release of Si from the mud and the degree of undersaturation in the mud water of dissolved silica, which degree is determined by the exchange intensity.

As already done in the case of the mud-layer experiments, we have calculated the quantities of Si released during the course of the experiment, .65. and have then compared these values with the individual deficits in the mud (Table 20) in order to determine the extent of Si dissolution. Our calculations of the deficits were based on the equilibrium concentration in the mud water (c_s) of 38 mg Si/1.

Table 20 - Key: 1, vessel; 2, larvae added; 3, quantity of Si liberated from the mud; 4, total; 5, from the deficit; 6, from the redissolution.

Gefäß 1.	Larvenzusatz 2.	3. aus dem Schlamm abgegebenes Si				
		gesamt 4.	aus dem 5. Defizit		aus der 6. Nachlösung	
		mg	mg	%	mg	%
1 + 2	0	55	12	23	43	77
3	5	73	18	25	55	75
4	10	90	23	26	67	74
5	15	115	27	23	88	77
6	20	120	29	24	91	76
1 — 6	—	—	—	24	—	76

These values confirm the direct proportionality between Si release and Si re-dissolution already found to exist in the mud-layer experiments: At the time when the experiment was discontinued, the share of re-dissolution of Si amounted in all experimental containers to 76 ± 1% of Si release.

Silica regeneration in the isolated mud layers proceeded in accordance with the same pattern detected in our mud-layer experiments (Figure 48). In correspondence with Equation (3), accelerated Si dissolution took place in the layers exhibiting pronounced undersaturation, so that the final state (c_s) was attained in all samples at about the same time.

Our experimental results (cf. also the additional experiments described on the following pages) lead to the following view of the liberation of Si from the mud:

The increase in the concentration of dissolved silica in the overlaying water of a given mud-water system (or in the water layer close to the bottom of a given lake, respectively) is based on an exchange between the Si-rich interstitial water of the mud and the mud-contacting water, which, under natural conditions, is always less rich in Si (perhaps, with the exception of bodies of water drying out in arid regions). This exchange leads first to a decrease of the concentration in the interstitial water, and, thus, in accordance with Equation (3) to a re-dissolution of silica in the mud, the source of which is found in the amorphous silica of the diatomic shells. In closed systems this re-dissolution is arrested once the saturation concentration of the mud (c_s) has been reached in the entire system. If the mud layers used are too thin, we will find that the mud-to-water volume relation .66. is of no importance for the equilibrium level of dissolved silica; that relation influences only the rate of attainment of equilibrium.

The waters, however, should be regarded as open systems, which systems tend in a continuous manner toward the chemical equilibrium (i.e. the maximum of entropy), but never attain it due to the activities of organisms (in our case represented by silicic organisms, i.e., above all, diatoms). Due to either continuous or periodical (seasonal) biogenic desilicification, we find that the initial conditions are constantly being re-established, so that the Si concentrations are continuously kept at a relatively low level, which concentration levels are different in individual bodies of waters. These conditions can be imitated in the experiment by replacing the overlaying water by fresh water in either a periodic or a continuous manner. Under such conditions—conditions corresponding to a "dynamic equilibrium" or a steady state (Von Bertalanffy, 1942, page 26)—we find in the mud a characteristic concentration gradient for dissolved silica, which corresponds to a dynamic equilibrium between Si release and Si re-dissolution (cf. Figures 47 and 52). The gradient of concentration of dissolved silica in the mud will—at equal exchange intensity in different muds—increase, first, with increasing saturation concentration of the mud; secondly, with decreasing concentration in the overlaying water; and, thirdly, with increasing rate of dissolution of silica in the mud. The latter, in turn, is determined—apart from the quantity of precipitated silica and the specific surface properties of that silica—by the degree of undersaturation of the mud, which, in turn again, is a function of the exchange intensity.

On the basis of the constancy of the concentration gradient in the mud under the conditions of a dynamic equilibrium or steady state (where supply equals removal), we then find that the Si release per unit time and per unit mud surface is equal to the rate of dissolution per unit mud surface. In the initial phase of an exchange experiment, when the gradient has as yet not reached the equilibrium state, there occurs a partial leaching from the upper sediment zones, so that the release of Si from the sediment is greater than the rate of dissolution. As is indicated by the high release values at the start of the respective experiments (cf. Figures 49, 50 and 51), this leaching initially is very marked, but then rapidly decreases in order to finally tend toward the value of zero. The time-independent dynamic equilibrium or steady state has been reached at that point. In calculations dealing with the absolute release value in the experiment, the deficit of dissolved silica arising initially in the mud is contained as a constant in the continuously increasing absolute quantity released (cf. Tables 19 and 20).

Since the formation of dissolved silica in the mud takes place not at a defined interface, which would simultaneously represent the starting point .67.
of the gradient, but in the layer of the gradient itself, we find that the Laws of Diffusion and Exchange, respectively, cannot be applied in this instance.

Undersaturation is most pronounced in the surface layer of the mud, so that there also takes place the most pronounced dissolution of silica. Down in the depth of the mud, where c_i is equal to c_s, dissolution equals zero. From the point of view of the Si metabolism, the permanent sediment begins right below that boundary layer. The depth of that boundary is greater with decreasing rates of dissolution of Si particles in the mud, and with the increasing exchange between mud and water. Chironomide larvae are able to shift that boundary layer toward considerably deeper levels in the mud due to the greatly promoted exchange due to their activities (cf. Figure 47).

(β) Effects of temperature on silica release from mud - The intensity of release of Si from the mud into the overlaying water depends to a large degree on the experimental temperature. That fact is illustrated in Table 21 as well as in Figures 49, 50, 51 and 52. The release data presented in Table 21 were obtained in various chironomide-free muds. The different temperatures reported for the higher temperature level used (i.e. 15 to 20°C) unfortunately could not be prevented, since a temperature-controlled room was not available to us. The values presented show that the influence of temperature on Si release differs to a rather large extent in the different muds; however, in all cases that influence was significantly greater than the temperature-induced modification of the equilibrium concentrations (c_s).

Table 21

Tabelle 21

1. Herkunft d. Schl. 2. See	3. Tiefe m	4. Versuchs-temperatur t° C	5. Si-Abgabe mg Si/m² · 24 h	6. Verhältnis der Si-Abg. 15—20°/5°	7. Verhältnis cs 20°/5°
Ihlsee	20	5	0,5—1	3—4	1,8
		20	1,5—2,5		
Schöhsee	13	5	10	4,5—5	1,5
		15—16	45—50		
	21	5	15	3,3—3,7	—
		20	50—55		
Plußsee	13	5	9	2,4	1,3
		20	22		
	23	5	14	2,4	1,2
		20	34		
Gr. Plöner See	34	5	40	2,5	1,3
		20	100		
Heidensee	2,5	5	25—60	3—4	1,5
		15	100—200		

Key: 1, Origin of mud; 2, lake; 3, depth; 4, experimental temp.; 5, Si release; 6, ratio of Si release; 7, ratio.

The extraordinarily rapid response of Si liberation to changes in the .68.
temperature represents a finding worthy of note. The new release values corresponding to the changed temperatures are attained in this case at the same rate observed on modification of the chironomide larval population density (cf. Figures 46, 49, 50 and 60). This rapid response as well as the—in relation to the equilibrium concentration (c_s)—significantly more markedly changed release of Si indicate that both the diffusion and exchange coefficients are greatly influenced apart from any decrease or increase, respectively, of the concentration gradient.

(γ) Effects of redox conditions prevailing at the mud-water interface - On the basis of the fact that the diatomic shells frequently represent a considerable component of the sediments, Gessner (1959, page 579) drew the conclusion, first, that these particular shells are dissolved only to a very minor extent and, secondly, that the pronounced accumulations of Si in the water layers close to the bottom of eutrophic lakes during the periods of stagnation could by no means be explained by a re-dissolution of the silica derived from the settled diatomic shells. The latter author saw the main cause of these accumulations of dissolved silica in the reductive disintegration of ferri-silicium-humate complexes of the type assumed by Mortimer (1941 - 1942) to exist on the basis of both his investigations in British lakes and his experimental studies using mud-water systems. However, Mortimer's exchange experiments were carried out in exactly the same manner as those described by us in Section III, page 23 f., *viz.* using rather thin mud layers measuring only 3 to 4 cm in thickness. As indicated by the results presented in Mortimer's Figure 18, there occurred, in aerobic experiments, a gradual oxidation of the mud down to the bottom of the experimental vessel —a finding also obtained in our own experiments. The gradients from the depth of the mud to the oxidized surface of the different properties of the mud observed under natural conditions—including, among others, the concentration of dissolved silica—were not present in that experiment; the dynamic equilibrium (steady state) between oxidation and reduction, which, in the case of relatively thick layers of mud, leads to the formation of an oxide layer, which is distinctly demarcated in the downward direction and, as a rule, rarely measures more than one centimeter in thickness, was also missing. The experimental findings obtained by Mortimer, in our view, cannot be applied to the conditions existing in nature (and this, in particular, since the experiments in question were carried out in the presence of light, so that there existed different conditions of depletion in aerobic and anaerobic vessels).

Our view is based on the following experimental results: We filled two plexi glass containers with about six liters of Schoeh Lake mud obtained at a depth of 21 meters; the respective layers of mud measured 20 centimeters in thickness. We used Schoeh Lake mud because the strongly absorptive properties of that mud were known to us on the basis of earlier experimental .69. results (cf. Section III, page 23 f.). In these particular experiments we used only the upper 10 cm of mud brought to the surface by the sampler. The mud in the containers was covered with Schoeh Lake water, and the water in one of the two containers (i.e., the one used in the anaerobic experiment), in turn, was covered with a layer of liquid paraffin. A continuous, but very weak stream of either air or nitrogen gas was bubbled through in order to prevent the development of stratification in the overlaying water, and the daily replacement of water using either oxygenated or oxygen-free Schoeh Lake water, respectively, ensured that the Si concentration of the water in the experimental containers was at a low level at all times (1.5 to 2.0 mg Si/l.). The aerobic experiment as well as the anaerobic one were initially carried out at a temperature of 20°C; later on, we lowered the temperature temporarily to 5°C.

In the aerobic experiment we found already after five days that the mud was covered with a rusty brown oxide layer, measuring 3 to 5 mm in thickness; after 15 days that layer had attained its final thickness of about 10 mm. This rapid oxidation was supported by the activities of tubificides; chironomide larvae were not present. In the anaerobic experiment, we found, on the other hand, that the surface of the mud remained black; that the water was free of oxygen; and that there appeared a smell of hydrogen sulfide, which increased with time.

As is demonstrated by the data presented in Figure 50, there existed no differences either at 20°C or at 5°C in the release of Si from the reduced mud and the surface-oxidized mud, i.e. the oxide layer measuring 1 cm in thickness is unable to block the continuous equalization of Si concentration. A continuous supply of dissolved silica takes place from the deep, reduced mud layers, which supply is greater than the absorptive capacity of the upper layer of oxidized mud.

Figure 52 shows the gradient of the concentration of dissolved silica in the mud determined upon discontinuation of the aerobic experiment using Schoeh Lake mud (obtained at a depth of 13 meters); the experiment itself is illustrate in Figure 51. The oxidized upper mud layer exhibits no pronounced decrease in concentration in comparison to the lower, reduced mud layers, although precipitation of silica has taken place. The latter aspect is illustrated in Figure 53. The separated mud layers used in the 5°C-experiment were treated with hydrogen sulfide in order to determine the quantity of silica that may be liberated by reducing the absorption complex (cf. page 6). The layers of reduced mud exhibited only a parallel shift (probably due to the liberation of Si from silicates or due to sorptive complexes present also in the reduced state), while the oxidized surface layer showed a strikingly pronounced liberation of silica. The amount of 28 mg Si/l. liberated in excess (compared to the reduced mud) must have been precipitated during the course of the experiment; that excess amount, however, would be adequate for increasing the Si concentration of a column of water measuring one meter in height by only 0.3 mg Si/1. But since the Si liberation from the mud takes place not only from the 1-cm thick upper layer, and since, furthermore, this liberation is based on a process involving dissolution (the intensity of .70. which is determined by the degree of undersaturation of the mud water), it follows that any reductive liberation of silica in the upper layer must lead to a decrease of the rate of dissolution of amorphous silica. The silica released into the overlaying water, then, is due either not at all or only in part to processes involving dissolution, but above all to the liberation of silica bound by absorptive means. For that reason we are hardly permitted to expect that the Si release from the mud will be significantly higher during the gradual (!) disintegration of the complexes than during the period preceding that disintegration. That fact is indicated already by the finding showing that that release is also not influenced by the formation of these complexes (cf. Figure 50). The continuous "flux" of dissolved silica—which follows the gradient of concentration between the reduced mud and the overlaying water—passes across any oxidized upper layers possibly present, once the latter have become saturated. This saturation probably takes place at the expenses of a more pronounced re-dissolution in the adjacent lower reduced mud layers.

Processes of absorption and desorption dependent upon the redox potential do take place in the upper layer of the mud, but they do not determine in any significant degree the Si release from the mud. The Si accumulations observed in the hypolimnion of lakes during the periods of stagnation represent not the consequence of the simultaneously increased reductive processes, but a parallel phenomenon of the latter: Due to the decreased exchange, we find that the silica released by the mud is not distributed over the entire lake water volume, so that there occurs a rapid increase of the Si concentration in the usually relatively small hypolimnion of eutrophic lakes. The quantity of silica rleased per unit surface and per unit time, thus, does not have to be greater during these particular periods than during the time of complete circulation (Figures 14, 16, 26 and 27).

(b) In-situ observations in the bodies of water under consideration

(α) The Large Ploen Lake - Since the short-term stratification investigations were carried out only in the northern basin (i.e. the Ploen Basin), we are able to present more detailed data on the intensity of Si liberation only in the case of that part of the Lake. In the Sub-Sections following further below we will then, for the purpose of comparison, present the corresperding data obtained in the other Lakes under consideration.

The autochthonous release of Si in the Large Ploen Lake is characterized by a distinct pattern: The Si present is almost completely utilized during the course of the spring, and that depletion is reversed by an increase in the concentration taking place during the entire year; in contrast to the intensities of depletion, that increase in concentration is subject only to minor seasonal variations (Figures 14 and 16).

During the periods of stagnation the increases in the concentrations .71. of dissolved silica proceed in the different depth regions at different intensities, so that there develop heterograde Si stratifications with a metalimnic maximum (Figures 54 and 55). During the year 1962, this stratification became evident already during the second half of May about ten days after the appearance of stable stratification conditions (Figure 20) and remained intact until the onset of fall circulation (Figure 24). Whether the partial fall circulation during November is associated with the 5a type or the 5b type of Si tratification depends—as demonstrated on comparison of Figures 54 and 55—on the hypolimnic residual concentrations, since these concentrations are intact during the entire summer stagnation period; they influence the relation between the epilimnic and the hypolimnic concentrations to a very large extent.

Following a period of complete circulation leading to homogeneous Si distribution, there exists the possibility that the stratification known from the summer months may appear again under a closed blanket of ice (cf. Figures 24 and 58).

In the Large Ploen Lake—with the exception of the Ascheberg region of that Lake—it appears that the metalimnic Si maximum represents an apparently annual, pattern-like phenomenon; similar maxima have been observed also in certain other lakes, like the Vierer Lake (Figure 70) and the Grebiner Lake, for instance.

Figures 20 to 25 and Figure 54 as well as the considerations outlined in Section IV.2. together indicate that dissolution of suspended silica in the free water must be excluded in connection with any explanation of the metalimnic Si maxima as well as in connection with the explanation of the Si stratification in the Large Ploen Lake in general. That dissolution may be involved to some degree in the development of stratification, but it does not represent the determining event. The dissolved silica of the pelagial is derived from the neighboring mud areas and is distributed from there over the pelagial by the horizontal currents. The fact that we are justified to assume the existence of a metabolic exchange of that type, i.e. one predominantly horizontal in character. in the metalimnion as well as in the hypolimnion is indicated by the results obtained, above all, by Alsterberg (1927), Hutchinson (1938) and Elster (1955b) in their numerous investigations. The section through the northern basin of the Large Ploen Lake shown in Figure 56 reveals this horizontal pattern within the same basin (!). That pattern was found also in the case of the Si stratification of the Pluss Lake, which is protected from the wind.

As is revealed by a comparison of Figures 55, 57 and 61, the silica stratification---in contrast to the hydrogen carbonate stratification (cf. Hutchinson 1938 and 1941)---does not reflect the current relation between mud area and layer volume ("bottom factor" after Elster and Schmolinsky, 1954).

The dissolution of silica in the sediment is subject to patterns, which differ from those to which the dissolution of carbonate is subject. That .72.
dissolution must take place at a significantly greater intensity in the sediments of the littoral to the upper profundal than in those of the lower profundal.

In the case of the summer stagnations of 1961 and 1962, we observed different time intervals, during which neither depletion nor pronounced vertical exchange processes were taking place; during these particular intervals we have calculated the increases of dissolved silica in the different layers and then related these values to the corresponding areas (Table 22).

Apart from the latter calculations we have carried out a separate calculation in the case of the 30-to-40-meter region, since that water volume appeared to be well isolated from the overlaying maximum by a layer of low

Table 22 - Si liberation in the Large Ploen Lake, north basin

Tabelle 22. Si-Rückführung Gr. Plöner See, Nordbecken

Zeitraum Interval	Tage Days	mg Si/m² · 24 h 0—15	15—25	0—25	25—40	0—40
17. 5.—29. 6. 61	43	410	280	350	100	270
29. 7.—24. 9. 61	57	530	160	360	64	260
11. 6.—27. 7. 62	46	430	370	400	85	300
27. 7.—19. 8. 62	23	530	105	340	124	270
⌀	169	470	240	370	87	275

Si concentration located at the 30-meter level. Since pronounced exchange processes reach only rarely down to these dapths, we are able to carry out a considerably greater number of calculations (Table 23).

Table 23 - Si liberation in the Large Ploen Lake, north basin, 30-40 m

Tabelle 23. Si-Rückführung Gr. Plöner See, Nordbecken, 30—40 m

Year Jahr	Period of observation Beobachtungszeitraum	Days Tage	mg Si/m² · 24 h
1961	17. 5.—29. 6.	43	84
	29. 6.—29. 7.	30	84
	29. 7.—24. 9.	57	62
1962	7. 5.—25. 5.	18	64
	25. 5.—11. 6.	17	56
	11. 6.—27. 7.	46	67
	27. 7.—19. 8.	23	72
	19. 8.—11. 9.	23	31 Austausch! (Exchange!)
	11. 9.—17. 10.	36	58
	17. 10.— 8. 11.	22	65
1961/62		315	(31) 56—84
Average for Durchschnitt für 315 Tage 315 days:			66

The Si release from the low level sediments amounted to between 60 and 80 mg $Si/m^2/24$ hours below the 30-meter level, and to between 80 and 120 mg $Si/m^2/24$ hours below the 25-meter level; that release is considerably greater from the sediments of the sublittoral and of the upper profundal. The values for the 0-to-15-meter and the 15-to-25-meter layers cannot be given separate consideration, since relatively extensive exchange processes take place in these layers, so that—due to the fact that the bottom factor decreases with decreasing depth—the values calculated for the lower region are too low, and those calculated for the upper region are too high. The release of Si from the intermediate sediment zones probably amounts to about 400 mg Si/m^2/24 hours; in this instance we must count also on a more pronounced return of Si from the littoral. It is probable that both the littoral off-spring diatoms, which show very marked development during the spring, and the macrophyte residues undergo rapid dissolution in the littoral due to the relatively high temperature, the high pH value, and the continuous movement of the water masses. Einsele and Vetter (1938), too, have attributed the marked epilimnic increase of Si in the Schlein Lake to the release of Si from both the littoral and the sublittoral. On the basis of the Si values reported by Meloche et al. (1938) for Lake Mendota, Hutchinson (1957) arrived at a similar conclusion.

Taking into consideration experimental results, we find that the varying release of Si from the sediments of different depth regions must be attributed to the following causes: .73.

1. Currents and the exchanges brought about by these currents in the water close to the lake bottom;

2. The temperature prevailing at the mud-water interface and the temperature in the mud; and

3. The extent of chironomide colonization of the mud.

<u>Re. 1</u> - The dissolution of diatomic silica in the mud is greatly promoted by low Si concentrations in the water in contact with the mud. These favorable conditions of low Si concentration at that interface, however, are

present only at sites, where strong currents and vigorous exchange processes prevent the formation of micro-stratifications, which are found, in particular, in the sublittoral and in the upper profundal. Turbulent water movements predominate in the epilimnion, bringing about a uniform distribution of the silica present over a water volume, which is very large in relations to the corresponding bottom area; in the metalimnion, on the other hand, there takes place only a horizontal shifting of the water in contact with the mud, due to the predominance of the horizontal current component. In both these cases we find, however, that the concentrations in the water close to the bottom are kept at a constant, low level. Despite the presence of stable stratification, we find that the Si concentrations over the mud surface are hardly higher than in the center part of the pelagial at the same depth level (cf. Figure 56). The same is valid also in the case of the upper hypolimnion (cf. Asterberg, 1927; Elster, 1955b). In the deeper lake regions, we find that partial circulations in the hypolimnion (Einsele and Vetter, 1939), "eddy currents" (vortices) induced by internal seiches (Olszewski, 1963) or gass bubbles escaping from the sediments ("methane convection" after Ohle, 1958b) bring about equalization of concentration, which, however, is not as pronounced as that taking place in the upper regions.

While the increase in the concentration of dissolved silica is reversed every year in the hypolimnion of holomictic lakes, we find in the monimolimnion of meromictic lakes, according to Findenberg (1935), that an extensive saturation takes place. The latter author observed that the Si concentrations in the monimolimnic layers of meromictic lakes were hardly higher than those in the hypolimnion of holomictic lakes, and he attributed that finding to .74.

precipitation of gels or an arrest of dissolution in the former. We must assume that the Si concentrations in this instance approximate the saturation value of the mud water already so closely that only weak dissolution is taking place. We probably must assume in this instance that there exists an equilibrium state between that weak dissolution and the exchange with the upper water layers (an exchange present also in lakes of that type, so that the concentrations remain constant. In the case of lakes of that type, it is probable that the dissolution of silica deposited in the deepest lake regions is particularly low.

In connection with the concentration conditions in the water layer close to the bottom, we must also take into consideration the thermal and chemical equalization currents (density currents) assumed to exist by Brönsted and Wesenberg-Lund (1911 - 1912) and described by both Alsterberg (1928 and 1929) and Hutchinson (1941). The latter currents are effective in particular during the period of winter stagnation, and they lead to marked accumulations of silica in the water layer close to the lake bottom at the maximal depths or in isolated basins, while they prevent accumulation along slopes. In this manner these currents promote the release of Si from the sediments of the more shallow lake regions, and inhibits that release from the sediments of the deeper lake regions. We must assume that the silica, which accumulated during the period of winter stagnation of 1963 between January 10th and March 10th in the basins of the Large Ploen Lake (cf. Figures 58 and 59), to a large extent were not derived from the corresponding depths, but had "flowed down" from the sediment regions located at higher levels. The development of the Si maximum at the 25-meter level must be attributed either to the after-effects of wind-induced currents following formation of the ice blanket (on January 5th) or to the development of stratification due to chemical and thermal density currents.

Re. 2 - The experimental investigations using mud-water systems have demonstrated that the hydrolysis of amorphous silica in the mud follows Van t'Hoff's (reation rate/temperature) law. The Si release at 5°C amounted at best to 40 per cent of the release observed at 15°C (Table 21; Figures 49 to 51).

During the year 1962, the temperature jump layer (metalimnion) was located at first at the end of June between 12 and 20 m; at the end of July, between 18 and 22 m; and between early August and the middle of October, between 20 and 23 m (cf. Figure 23). The exchange processes extended down to the lower water layers only during the second half of October and the
first half of November; in consequence, there occurred in these layers .75.
a transitory warming of the lake water, which lasted until the middle of December. During the periods of summer stagnation of 1961 and 1962, respectively, we measured temperatures > 10°C only above the depth level of 20 to 22 meters. Below the 25-meter level, we found that the summer temperatures amounted to 5 and 6°C. In addition to the other factors already mentioned, that particular temperature gradient must lead to a more pronounced release of silica from the sediments at the lower lake depths. The metalimnic maximum of dissolved silica must be attributed, above all, to the fact that there still prevail horizontal currents despite the higher temperatures in the metalimnion. The decrease in temperature during the winter exerts effects, above all, on the release of Si from the sediments of the more shallow lake

regions, since the temperatures in these regions are 15 to 20°C lower than during the summer, while those in the hypolimnion are only 2 to 3°C lower. During the winter of 1962-1963, we were able to follow the gradual decrease in Si release (calculated for the entire water volume of the northern basin) in a particularly distinct manner, since utilization of Si by diatoms started only toward the end of March following break-up of the ice (Table 24).

Table 24 Tabelle 24

Zeitraum Interval	Si-Rückführung Si liberation mg Si/m² · 24 h		
8. 11.—24. 11. 62	250		
24. 11.—10. 12. 62	190		
10. 12.—10. 1. 63	80		
10. 1.— 2. 2. 63	70	46	(Eisdecke!) (Ice cover!)
2. 2.— 9. 3. 63	30		

Re. 3 - Both Lundbeck (1926) and Berg (1938) have demonstrated that chironomide larvae exist in nutrient-rich lakes, above all, in the upper profundal and in the lower sublittoral, since favorable nutritive conditions and tolerable oxygen conditions coincide in these zones. In the Large Ploen Lake, the main area of distribution, according to Lundbeck, is located in the mud regions at depths between 15 and 25 meters. Since Lundbeck carried out his investigations, this distribution pattern probably has shifted slightly in the upward direction, due to the increasing oxygen utilization in the summer hypolimnion (Ohle, 1953a; 1953b); however, even at the present time, extensive population densities—above all, represented by Chironomus anthracinus—are present down to the lower edge of the metalimnion. This statement is applicable in particular during the spring and the early summer. During the summer of 1962 the oxygen content of the water layer close to the bottom had dropped by August 19th to 0.6 - 0.7 mg O_2/l. at the 20-meter level, and to 0.2 mg O_2/l. at the 25-meter level, so that the chironomide larvae in the metalimnion probably had not yet died. Hydrogen sulfide could be detected only below the 35-meter level.

In a mud-water exchange experiment—the results of which are presented in Figure 60—we have compared the release of Si from a chironomide-free .76. mud sample obtained at a lake depth of 34 meters kept at 5°C under anaerobic conditions with the release of Si from a chironomide-populated mud sample obtained at a lake depth of 21 meters kept at 15°C under aerobic conditions. In this way we tried to imitate the conditions prevailing in the lake during the period of summer stagnation. The experiments were carried out in plexiglass containers measuring 50 cm in height and 20 cm in diameter; the water in these containers was continuously bubbled at a low rate using either air or nitrogen gas. The water was replaced once a day in a manner ensuring that the Si concentration of the overlaying water amounted, on average, to 1.5 mg Si/l. In the anaerobic experiment, the atmospheric air was excluded with the aid of a layer of liquid paraffin. The mud layers measured 20 cm in thickness. The chironomide larvae present in the mud obtained at a depth of 21 meters were first removed; however, about ten individuals remained in the mud sample. At intervals of about one week, we added ten juvenile Chironomus larvae (corresponding to 350 larvae/square meter), which had been obtained during February at the same lake depth level. Due to this continuous increase of the population density, we found that the release of Si, at 15°C, from the mud sample obtained at the 21-meter depth level and populated by larvae amounted finally to the ten-fold value determined in the deep mud (i.e. the sample obtained at the 34-meter level, and kept at 5°C), although the respective Si contents of these mud samples yielded an approximate ratio of 1 to 5 (i.e. at the 21-meter level the content was 3% Si_a/dry substance, and at the 34-meter level, 15% Si_a/dry substance; cf. Figure 62). Since the numbers of larvae used in the experiment were not abnormally high, we must count on finding similar values in this Lake under natural conditions.

On Day 46 of the experiment, we added a small amount of potassium cyanide to the overlaying water, so that the KCN concentration in that water amounted to 50 mg/l. A part of the larvae (20 individuals) were driven out of the mud by the poison and could then be removed from the surface of the mud with the aid of suction; the rest of the animals probably died inside the mud. As is illustrated in Figure 60, the consequence of the addition of cyanide was a sudden decrease of the rate of Si release from 440 to 100 mg $Si/m^2/24$ hours. The KCN treatment probably had also resulted in the death of a part of the other animal and plant life normally present in the upper layer of mud, so that the rate of release of Si from the chironomide-free, but otherwise undisturbed mud sample probably would be somewhat above 100 mg $Si/m^2/24$ hours. The tubificides, however, were injured hardly at all on addition of potassium cyanide, and this even after relatively high KCN concentrations had been applied for several days.

Figure 61 shows the temperature and Si stratifications prevailing on July 27, 1962, the mud-water relations ("bottom factor") prevailing in the northern basin, and the Chironomus bathophilus (= anthracinus) population densities reported by Lundbeck (l.c.) for July 31, 1924. We are unable to go as far as to state that there exists a direct correlation between the depth distribution of chironomide larvae and Si stratification, since these two phenomena, in part, are parallel in character. However, taking into consideration our experimental results, we must assume that the chironomide larvae .77. participate to a significant extent in the pronounced release of Si from the sediments at lake depths between 10 and 25 meters. The marked accumulation of Si in the epilimnion during the summer as well as the development of the metalimnic maximum must be attributed—apart from the higher temperatures and the prevailing current conditions—also to the exchange-promoting pumping movements carried out by the numerous chironomide larvae present.

The varying release of Si from the sediments of different depth regions is reflected in the contents of diatomic silica in the sediments:

During August and September of 1963 we, using a mud sampler, obtained a total of 40 sediment samples at different sites in the northern basin of the Large Ploen Lake; the upper 10-cm portion of these samples was examined with respect to its content of soda-soluble silica (i.e. amorphous silica, "Si_a"). We determined the average values for the mud columns measuring 10 cm in length as well as the Si contents of the different sediment layers, and, furthermore, the residues obtained on ignition.

The results obtained in these particular investigations are presented in Figures 62 to 64. The sampling sites are shown on the bathymetric map of the northern basin (Figure 2). The large differences in the average Si contents of the 12-to-24-meter sediments, on the one hand, and the 28-to-41-meter sediments, on the other one, can in no way be explained solely by differences in the sedimentation of diatomic plankton. The plots shown in Figure 62 (% Si_a/dry substance) can be readily fitted to give a curve, which, in general, represents the mirror image of the temperature and oxygen curves, respectively, of summer stagnation, while the data obtained on examination of the ignition residues show pronounced scattering in Figure 63. The distribution curve shown in Figure 62 reflects—at least, in part—the varying release of Si from the different sediments. The relative distribution of the Si contents in the sediment columns (Figure 64) also leads to the same conclusion. In the deep sediments we initially find even a relative accumulation of amorphous silica amounting to up to 120 per cent; however, the relative Si content decreases with increasing sediment depth at decreasing water depth. The lower sediment layers (8-10 cm) of the samples obtained at a lake depth between 15 and 22 meters finally exhibited only 40 per cent of the surface layer (o-1 cm) content. It must be kept in mind that corresponding sediment layers obtained at different water depths cannot be compared directly, since they are of different ages and, thus, reflect different developmental phases of the lake in question (and, perhaps, also of the silica metabolism of that lake). However, the differences found, which are apparent in particular in the upper six centimeters, are too large to be explained solely on the basis of age factors.

The varying release of diatomic silica from sediments of different lake depths is reflected also in the microscopic findings obtained by us (Figures 65 to 67, on Plate 3). The diatom shells present in the deep sediments appear to be entirely intact; the sediment samples obtained at relatively low lake depths, on the other hand, exhibited predominance of diatomic fragments and strongly corroded residues. At the latter depths we must count also on a more marked mechanical disintegration of the diatom shells by the mud-dwelling fauna. .78.

In summary, we are then in a position to state that the autochthonous Si metabolism of the Large Ploen Lake is based, above all, on the pronounced release of silica from the sediment zones above the 25-meter level. The diatomic residues sedimented above the latter depth level are returned relatively rapidly into the metabolic cycle, while the water depths below the 25-meter level represent storage basins. The fact that diatom shells belong to the most important guide fossils does not exclude marked re-dissolution of these shells in the sediments, since the extent of dissolution differs very greatly in the different regions of a given body of water. In addition, we must take into consideration the fact that diatom gyttjas are formed only in cases where a continuous allochthonous supply of dissolved silica is present (cf. Section VII).

The extensive degradation of diatomic silica in the sediments of both the sublittoral and the upper profundal is made possible, above all, because the equilibrium concentrations of dissolved silica in the interstitial water are influenced only to a minor extent by the decrease of the Si content of the mud (cf. Table 4, page 20), and because these equilibrium concentrations are not reached by far in the upper sediment layers due to the intensive exchange processes taking place in the mud as well as in the water layer close to the bottom. Because of that situation we find that more dissolved silica is released from the silica-poor muds of the more shallow regions of lakes than from the deep muds very rich in silica (cf. Figure 60).

As is demonstrated by Figure 68, the stratification situations prevailing in the southern part of the Large Ploen Lake were rather similar to those found in the northern basin. The concentrayions found in these two parts during the same seasons also deviated only to a small extent. In the central basin, which measures 56 meters in depth and is located east of the Lange Warder, we were also able to determine on September 11, 1962, the existence of a metalimnic Si maximum, which, however, was located there at a depth of 30 meters. The deviating stratification situation observed in the south-western part of the northern basin (cf. Figures 2 and 56) must be attributed to the connection existing between that part and the central basin. That fact is indicated also by the temperature stratification observed.

On the other hand, we have observed an entirely different situation in the Ascheberg part of the Lake, due to the entirely different morphometry of that part (Figure 69): The Ascheberg part of the Lake represents a wide, relatively shallow basin, in which stratifications appear only during the midsummer under calm weather conditions or during the winter under a blanket of ice. In this part, we find that favorable dissolution conditions prevail at the mud interface at all depth levels—conditions which in the rest of the Lake are given only down to the lower edge of the metalimnion. On September 11, 1962, we carried out measurements directly above the mud at a .79.
depth of 25 meters and a temperature of 15°C. Due to the intensive release of Si, we found that the Si values frequently were considerably higher than those determined in the northern basin (cf. July 27th, September 11th, and November 8th, 1962, in Figures 55 and 69). However, since relatively intensive processes of depletion take place there also during both the summer and the fall due to the continuous supply of nutrients by the mud, we find that the quantities of Si available to the diatoms during the spring differ hardly at all from those available in the northern basin. Due to the low mean depth, we then find that the Si metabolism in that part is significantly more intensive than in the deeper basin.

On the basis of both the increases in concentrations in the different parts of the Large Ploen Lake and the morphometric data presented by Thienemann (1928), we have computed the release values for the entire Lake for the interval between May 4, 1962, and March 10, 1963 (= 310 days), and compared them in Table 25 with the values determined in the northern basin.

Table 25

Tabelle 25

Zeitraum Interval	Tage Days	North basin mg Si/m² · 24 h Nordbecken	Whole lake ges. See	
4. 5.—27. 7. 62	83	210	140	Zehrung! Depletion!
27. 7.—11. 9. 62	46	240	300	(0—30 m = 310)
11. 9.—10. 3. 63	181	140	80	
4. 5.—11. 9. 62	130	220	200	
4. 5. 62—10. 3. 63	310	170	130	

The release values for the northern basin related to unit area, on average, were silghtly higher than the values computed for the entire lake. That difference is due to the fact that the Si concentrations in the epilimnion of the central basin usually are slightly higher than those of the northern basin (approximately 0.2 mg Si/l.); due to that situation, there takes place—and this, in particular, when south-westerly winds prevail—a transportation of Si into the northern basin. The low Si concentrations in the northern basin must be attributed to both the greater mean depth of that basin and the lower allochthonous supply. The epilimnic release values presented in Table 25 for the northern basin, thus, would be a little too high.

(β) Vierer Lake - As is demonstrated by Figures 28 and 29, the release processes taking place in the Vierer Lake correspond with regard to the fundamental aspects to those observed in the Large Ploen Lake. For that reason, it will be sufficient to present only a summary of our more significant findings: In the case of the Vierer Lake we also found that almost the entire silica of the lake was present following completion of diatom development (bloom) in the spring in the form of amorphous silica in the diatom shells settled in the sediment. During the spring of 1962, the total Si content of the lake water (i.e. dissolved plus suspended silica) dropped from 7.7 - 7.8 mg Si/l. to 0.4 - 0.6 mg Si/l.

During the depletion-free intervals of the summer season (May to September of 1961, and September to October of 1962), the mean Si release amounted to 300 - 330 mg Si/m^2/24 hours or 45 mg Si/m^3/24 hours, respectively. During the winter months, that release decreased to 100 to 200 mg Si/m^2/24 hours, and finally changed into the spring depletion. .80.

Since the mean depth of this Lake amounts to only approximately 7 meters, we find on comparison with the Large Ploen Lake that significantly higher Si concentrations are attained at liberation (release) values that are only a little higher.

In the southern part of this Lake, exhibiting a maximal depth of 17 meters, we observed similar stratifications as in the north-south part of the Large Ploen Lake. In the case of this Lake, too, we found that a distinct Si maximum develops in the intermediate depths, which maximum gradually disappears with the increasingly more profound circulation (Figure 70). This particular Si stratification appearing during the course of the summer must be attributed to the same causes established already in the case of the Large Ploen Lake.

The Si stratifications in the northern part of this Lake (Figure 71) correspond to those observed in the Ascheberg part of the Large Ploen Lake, with these two parts exhibiting similar morphometric properties (shallow, wide basins). In this northern part there occur marked accumulations of Si above the mud at a depth of 10 meters during the periods of stagnation, which periods, however, are only short with the exception of winter stagnation. (During the midsummer, we may in that part of the Lake occasionally observe also occurrence of oxygen depletion as well as of sulfate reduction.)

(γ) Heiden Lake - In the Heiden Lake we have determined release values of between 160 and 220 mg $Si/m^2/24$ hours (Figure 31). Taking into consideration the quantity of Si transported into the Lake by the Muehlen Brook, we obtain values between 80 and 140 mg $Si/m^2/24$ hours for the autochthonous component of the Si release.. These values are surprisingly low, and the following reasons suggest that these values are already greatly lowered due to the occurrence of depletion processes:

During December and January, we determined an autochthonous release value of 130 mg $Si/m^2/24$ hours under the ice blanket at a water temperature of 2 to 3°C and a Si concentration of 9 to 11 mg Si/l. We must deduct about ten per cent from that value, which percentage must be attributed to the formation of the ice cover. Biogenic utilization was impossible during that period due to the presence of the thick ice and snow blanket. Even during the summer at water temperatures above 20°C and significantly lower Si concentrations in the water, we found that that winter release was exceeded only once with a value of 140 mg Si/l. However, in experiments using Heiden Lake mud, a Q_{10} value of 3 to 4 was determined for the release of Si (Tessenow, 1964, and Table 21). The actual release during the summer, thus, must be considerably higher than the value of 130 - 140 mg $Si/m^2/24$ hours.

Examination of sediment samples, obtained at sites distributed over .81. the entire lake bottom, has shown that—with the exception of a narrow shore belt measuring a few meters in width—similar Si concentrations prevailed in the interstitial water at all sites sampled. At the end of December of 1962, we determined in the upper 5-cm of the mud a content of 20 to 25 mg Si/l. at a Si concentration of 11 mg Si/l. in the lake water. The sediments of the shallow lake basin measuring, on average, two meters in depth are very uniform also with respect to the Si content of their dry substance (2 to 3% Si_a/dry substance), so that the release values found in the experiment may be generalized to a large extent.

The periods of depletion, with one following right after the first one (cf. Figures 30 and 31), permit us to conclude that the increases in concentration determined between the main depletion periods represent only the excess of release over utilization, i.e. that a continuous biogenic utilization is taking place, which is reflected in a decrease of Si concentration only during periods where utilization intensity is great. On the basis of both our observations made during the winter months and the results obtained in our experimental investigations using Heiden Lake mud, we must count on a release of Si from the sediment during the summer amounting to a minimum of 300 mg Si/m^2/24 hours.

The determination of the actual autochthonous release of Si taking place in a shallow, pond-like body of water, like the Heiden Lake, is not possible solely on the basis of data on the Si concentrations in the lake water and consideration of Si transported into the body by inflowing waters. The increase in concentration corresponds to the actual release only under extreme conditions of the type encountered during the cold winter of 1962-1963.

(δ) Schoeh Lake - The Schoeh Lake is relatively deficient in silica. During the years 1961 to 1963, the average Si concentration of the entire water volume amounted maximally to 0.4 mg Si/l. The maximal Si concentration determined above the mud at the maximal Lake depth of 29 meters amounted to 1.2 mg Si/l.

The increases of the Si concentrations in the different layers of the Lake during the summer of 1962 are presented in Figure 72 with the aid of stratification curves. The increases in concentration related to the corresponding .82. area surface—which increases may, with certain restrictions, be regarded as representing the actual release from the sediment—are given in Table 26.

Table 26 - Si liberation in the Schoeh Lake, Summer 1962
Key: A = exchange; Z = depletion.

Tabelle 26. Si-Rückführung im Schöhsee, Sommer 1962
(A! = Austausch, Z! = Zehrung)

Zeitraum Interval	Tage Days	mg Si/m² · 24 h 0—10 m	 10—20 m	 0—20 m	 20—28 m	 0—28 m
20. 4.—25. 7.	96	13	27	20	13	19
25. 7.— 1. 9.	37	30	8 A!	20	12	19
1. 9.—15. 10.	45	3 Z!	2 Z!	2,5 Z!	14	4 Z!

In order to enable us to make a better comparison between the release data determined in the Lake and our experimental results, we are presenting the corresponding temperatures in Table 27. These particular data, furthermore, enable us to assess the exchange processes.

Figure 72 and Table 27 indicate that a good separation of the individual layers was given during the first interval of observation; however,

Table 27 - Temperature stratification in the Schoeh Lake
Tabelle 27. Temperaturschichtung im Schöhsee, Sommer 1962 Summer 1962

m	20. 4.	25. 7.	1. 9.	15. 10.
1	1.Voll-zirkulation 5—6°	18,1	15,6	13,6
5		—	15,3	13,6
10		13,9	15,2	13,4
15		7,6	7,8	12,9
20		6,6	6,7	7,1
25		6,4	6,7	6,8
28		6,3	6,5	6,6

Key: 1, Full circulation

during the period of time between July 25th and October 15th, we were able to observe separately only the 0-to-20-m and the 20-to-28-m layers.

The release values determined by experimental means for Schoeh Lake mud from lake depths of 13 and 21 meters, respectively, at 5°C and 15 to 20°C are presented in Figures 50 and 51 and in Table 21.

The following conclusions may be drawn with regard to the Si release taking place in the Schoeh Lake.

1. A strikingly uniform release of silica takes place from the sediments of the hypolimnion, which release with 12 to 14 mg Si/m^2/24 hours corresponds to the release values obtained at 5°C using experimental means.

2. The release of Si from the sediment is not influenced by the redox conditions prevailing at the mud-water interface—conditions which differ during the summer and the winter (in the hypolimnion, there prevail aerobic conditions up to the middle of August, but after that point in time, anaerobic conditions). That observations corresponds to the results obtained in our experimental investigations (cf. page 68).

3. As is indicated by the release values obtained during the first interval of observation, we must also in the case of the Schoeh Lake count on a

more intensive release of Si from the sediments of intermediate water depth. The actual extent of that release cannot be determined because of the continuous occurrence of exchange processes.

The low release of Si in the Schoeh Lake, compared to the Lakes discussed .8
in the preceding Sub-Sections, is due to the relatively low rate of dissolution of silica in the mud and the low Si concentration in the interstitial water of the mud associated with that low rate of dissolution. Both these findings are due to the low content of amorphous (i.e. diatomic) silica and the high clay content. The content of sodium carbonate-soluble silica amounted even in deep sediments to only 1.4 to 1.5%/dry substance. That silica consists to a large degree of diatomic silica; however, sodium carbonate treatment results also in the determination of a part of the silica bound in the clay of the mud. The low equilibrium values of silica dissolved in the interstitial water of Schoeh Lake mud, amounting to 10 to 15 mg Si/1., cannot be explained solely on the basis of the low content of sodium carbonate-soluble silica. One mud sample obtained in the Large Ploen Lake at a depth of 15 meters also contained only 1.5% Si_a/dry substance, but the Si concentration of its interstitial water amounted to 26 mg Si/1. The relatively low concentrations of dissolved silica in the Schoeh Lake mud must be attributed rather to absorptive processes and ion exchange processes involving the iron-rich clay sediments.

(c) Pluss Lake - As is demonstrated in Figure 27, the Pluss Lake exhibits a strikingly constant release of Si during the entire year, which is disturbed only during the spring by a brief period of depletion. The average release of Si related to the lake area amounted to 10 to 18 mg $Si/m^2/24$ hrs.

In contrast to the Large Ploen Lake, we did not detect any decrease of Si liberation during the winter. Since the epilimnion of this particular Lake exhibits during summer stagnation only a thickness of about five meters, while the mud starts only at a level below the 5-meter one, we find that constant temperatures between 4 and 6°C prevail in all mud regions. The summer and winter temperatures differ only by 2 to 3°C.

For the period between April 7th and October 15th of 1961 (180 days), we have computed the release of Si for the different layers and related the values obtained to the corresponding areas. These data are presented in Table 28.

<u>Table 28</u> - Si liberation in the Pless Lake

Tabelle 28. Si-Rückführung im Plußsee, 7. 4.—5. 10. 1961

Layer Tiefenstufe m	mg Si/m² · 24 h		
0 — 5	11	10	11
5 — 10	9		
10 — 15	14	18	
15 — 20	25		20
20 — 27	15	15	
0 — 27	12,4	12,4	12,4

Once we take into consideration the exchange processes between the individual layers to be expected also in the well layered Pluss Lake—processes, which in this Lake are, in part, associated with "methane convection" (cf. page 73)—it becomes clear that the most pronounced release of Si takes place from the deep sediments below the 15-meter depth level. The Si release from the intermediate depth regions does not play a predominating role in the Pluss Lake. The conditions prevailing at the mud interface are very uniform due to the high location of the metalimnion, and this with respect to both the temperature and the oxygen situation. During the period of summer stagnation, anaerobic conditions prevail in the entire hypolimnion, so that a higher mud-dwelling fauna (tubificides, chironomides) is absent.

The relatively marked accumulation of Si in the surface water (which .84
accumulation leads to the development of a metalimnic minimum; cf. Figure 26) would be attributable to a release of silica from the leaves deposited in the littoral or from coarse detritus of macrophytes.

In a mud-water exchange experiment—which was carried out using mud layers measuring 20 cm in thickness and, in correspondence with the natural conditions prevailing in this Lake, under anaerobic conditions—we were able to obtain release values very similar to those observed in the Lake (Table 21; Figure 49). The mud samples had been obtained with the aid of a sampler. The experiment was carried out in the usual manner with daily replacement of water. The release of Si from the deep mud (23 meters) amounted to the 1.6- to 1.7-fold of that from mud obtained at a depth of 13 meters. This higher release of Si from the deep mud is due, above all, to the higher saturation concentrations in the interstitial water (Table 29). However, we must be dealing also with a higher rate of dissolution at equal degrees of undersaturation, if we assume equal exchange parameters to be in force. The deep mud was richer in sodium carbonate-soluble silica (3 to 4% Si/dry substance) than the mud obtained at higher depth levels (1 to 2% Si/dry substance).

Table 29

Tabelle 29

Depth Seetiefe m	SW = mud water c_s (mg Si/l SW) 5°	 20°
13	15	19
23	22	25

The release values of 15 to 20 mg Si/m^2/24 hoyrs, determined on the basis of the increase of Si in the hypolimnion, are slightly higher than the experimental values obtained at 5°C. That finding may be attributed to a more pronounced fermentation in the upper mud layers of this Lake. Apart from the latter possibility, we must take into consideration a further .85. increase of Si release with increasing lake depth: The 23-meter mud had been removed from a level still six meters above the maximal depth of the Lake; that mud came from the boundary zone between the humus mud of the more shallow lake regions and the digested sludge of the more deeper ones.

(ζ) Ihl Lake - The maximal average concentration for the entire lake volume amounted to 0.08 mg Si/l.; that concentration was found on January 23, 1963, following prolonged presence of a blanket of ice. The maximal concentration immediately above the sediment amounted to 0.13 mg Si/l. on October 23, 1963, at a depth of 20 meters. The increase of the total Si content of the Lake related to the lake area amounted to 2.2 mg Si/m^2/24 hours during the period between June 8th and September 6th, 1961; to 1.0 mg Si/m^2/24 hours, between September 6th and October 23rd, 1961; and to 1.8 mg Si/m^2/24 hours over the entire interval. Since no diatoms were observed in the lake water during that interval of time and since the Lake has no inflows, we must regard that release value as the average rate of release from the sediment. This is an extremely low rate of release, which amounts to only about 10 per cent of the release observed in both the Pluss Lake and the Schoeh Lake, and to less than one per cent of the release observed in the Large Ploen Lake.

Similar values have been obtained in an exchange experiment using Ihl Lake mud (Table 21, page 67).

The low rate of release of Si from the Ihl Lake mud is due to both the low concentration of Si in the interstitial mud water and the low rates of dissolution of Si compounds contained in the mud (compounds like quartz, silicate minerals, but hardly any diatom remains at all). The Si concentrations in the interstital water—determined immediately after taking the mud samples—are summarized in Table 30.

Table 30 - Si concentrations in the pore waters of the Ihl Lake mud
Tabelle 30. Si-Konzentrationen im Interstitialwasser des Ihlsee-Schlammes

1. Datum der Schlamm-Entnahme	2. Seetiefe m	3. Sedimenttiefe cm	4. mg Si/l SW (ci)
9. 6. 61	5	0—10	2,4
	9	0—5	2,9
		5—10	4,7
	21	0—5	2,4
		5—10	4,9
23. 1. 63	21	0—5	2,4
		5—10	3,5
		10—20	5,4

Key: 1, Date of mud withdrawal; 2, lake depth; 3, sediment depth, 4, SW = mud water.

Due to the low rate of dissolution of Si in the mud of this Lake, we find that the gradient reaches very deep down into the mud; the Si concentrations .86 in the upper mud layer (o-1 cm) would in the entire lake water be only a little higher than those in the water close to the bottom.

The low rate of dissolution of Si in the Ihl Lake mud is due to the deficiency of that mud in amorphous silica. The dry substance of the deep mud consists to 60 to 80 per cent of SiO_2. That mud, however, contains about three per cent of sodium carbonate-soluble silica, which amount represents about one per cent Si of the dry substance. This sodium carbonate-soluble silica contains a high percentage of Si liberated from the silicate minerals as a consequence of sodium carbonate treatment. These silicate minerals can be attacked and broken down only with difficulty under the dissolution conditions prevailing in the mud. The composition of the Ihl Lake mud is reflected also in its rate of dissolution in dependence on the pH value, which—on plotting—represents the mirror image of the curve of dissolution of amorphous silica (Figure 73). We have suspended 1 g of dried Ihl Lake mud finely disintegrated with the aid of a pestle or 1 g of dried amorphous silica, respectively, in 200 ml. of distilled water. The suspensions were adjusted to different pH values with the aid of hydrochloric acid, sodium hydrogen carbonate and sodium carbonate, respectively. These suspensions were kept in polyethylene bottles and continuously agitated in the dark using a rotary mixer. After 24 hours (or after 4 days, respectively), the suspensions were filtered and the silica gone into solution was determined by photometric means. The smallest quantity of silica gone into solution in a given pH series was established as unity (1), and the values obtained at the other pH steps were related to that unit. The numbers appearing on the ordinate [in the Figures], thus, represent multiples of the minimum value. Amorphous silica exhibited a steep rise of the rate of dissolution above pH 4, while that rate decreased in the case of the Ihl Lake mud up to pH 8.6, reaching a minimum at that value (0.13 mg Si/l. in 24 hours, or 0.16 mg Si/l. in four days), in order to rise again above pH 9. (The minimum of the rate of dissolution of amorphous silica at pH 4 amounted to 0.6 mg Si/l.) The high rate of dissolution of the Ihl Lake mud in the acidic region, and the extremely low rate in the weakly alkaline region indicate that the Si gone into solution was present in the mud not in the form of amorphous silica, but in that of either silicates or sorptive complexes. The rise in dissolution at pH 9—which showed a course exactly as steep at pH 10 as in the acidic region at pH 3.6—must also be attributed to disintegration of silicates. This particular steep rise in the rate of dissolution above pH 10 was also observed in the case of the clay-rich Schoeh Lake mud and in that of the mud taken from the Buelt Lake (a sand lake).

The absence of allochthonous supply of dissolved silica must be regarded as the primary cause of the low liberation of Si in the case of the Ihl Lake; that absence prevents the biogenic accumulation of amorphous silica in the sediments. The high quartz and silicate contents are unable to provide the setting for any pronounced release of silica from the sediment.

VII. Factors causing different silica concentrations in different lakes .87.

1. Basis for comparison

The average concentration of dissolved silica prevailing at a certain moment in time in a given lake (determined for the entire water volume) is the result of two reverse processes:

1. The continuous increase of the concentration due to both the autochthonous liberation of silica and the allochthonous inflow or supply of silica; and

2. The biogenic precipitation of silica, which shows great seasonal variations; in inland lakes, that precipitation is due, above all, to the activities of diatoms.

The annual variations in concentration in a given body of water may be just as large as the differences between two different bodies of water exhibiting extremely different Si balances. The silica-rich Heiden Lake, in which the Si concentration may rise as high as 12 mg Si/l., exhibits, following marked diatom development (bloom), the same minimal concentration of 0.02 mg Si/l. as the extremely silica-deficient Ihl Lake, in which the maximal values never exceed 0.13 mg Si/l. even above the mud at the maximal lake depth. The same is valid in the case of other silica-rich lakes, like the Large Ploen Lake (Figure 14) and the Vierer Lake (Figure 28) among other ones (Table 9).

The Si concentration determined at a given moment during the course of the year, thus, reflects always only the current state within a dynamic process; that concentration value cannot be used as a basis for comparative investigations, and this, above all, not in cases where the respective values to be compared have been obtained during different seasons.

In view of the great seasonal variations, we may use as basis for comparison only the maxima attained in each instance prior to the onset of the main period of depletion, i.e. we may use only the peaks of the concentration curves. The differences in the maximal concentrations observed during individual years are significantly smaller than the variations within a given year (cf. Figures 14, 26, 28 and 30). Other concentration values determined in a random manner may be considered only as minimal values.

On the other hand we find that sediment samples can at any time of the year provide valuable information on the Si balance (metabolism) of a given lake. Sediment samples should be taken in all excursion-type investigations, since they at least reveal whether the low Si concentration found in the lake at the time of sampling is characteristic for that lake or has been brought about by an instance of marked diatom development (bloom). Plankton studies do not reveal that aspect due to the frequently rapid occurrence of sedimentation of diatoms. The sediment represents the sole constant factor in the Si metabolism of a given lake, i.e. the sediment represents the storage space for the autochthonous release of Si, and it is formed on the basis of allochthonous inflow of silica and biogenic desilicification (precipitation of silica).

2. Silica concentrations in lakes without inflowing waters .88.

The calcium-deficient sand lakes without either inlets or outlets of Sleswig-Holstein and Jutland exhibited—as long as they did not receive large quantities of leaves—without exception extremely low Si concentrations. The values obtained in these lakes are summarized in Table 31. In the case of these lakes we usually are dealing with small depression lakes (dead-ice lakes) located within sandy surroundings outside of the drainage valleys. The Jutland lakes were investigated during September of 1962; the Buelt Lake, during September and December of 1961; and the Ihl Lake, repeatedly during the years 1961 to 1963. In several of these investigations, we have reported the highest ones of the concentrations determined. The first value given refers in each case to the surface water, and the second one, to the water close to the bottom of the lake at its maximal depth. In addition to the Si concentrations of the water, we have also presented the Si values determined in the sediments. The sediment samples were obtained either at the maximal lake depth (Ihl Lake and Buelt Lake) or at the deepest sites found by us (the Danish lakes). The values refer to the upper 5-cm layer of the sediment columns removed. All the lakes listed in Table 31 measure less than 100 hectares, and are deficient in calcium, with the exception of the Buelt Lake, which exhibits an intermediate calcium content. These lakes contain the plant characteristic for calcium-deficient lakes, viz. Lobelia dortmanna [the Water-Lobelia or the Water-Gladiole]. The Ihl Lake possesses a small outlet, which, however, carries a little water only during the winter.

Table 31

Tabelle 31. Zuflußlose Sandseen Sand lakes without inlets

1. See		2. Tiefe m	3. Seewasser SBV	mg Si/l	4. Sedimente % Si_a/Tr.S.	mg Si/l SW
1	Ihlsee	22	0,3	0,08—0,13	1,0	2,5
2	Bültsee	13	0,6	0,07—0,14	1,5	1
3	Granc Langsö	12	0	0,05—0,05	1,5	6
4	Eggesö	4	0	0,05—0,05	1,7	5
5	Mörkesö	7,5	0	0,05—0,17	1,8	6
6	Skaansö	—	0	0,05	Uferprobe	Shore sample
7	Skörsö	—	0	0,08	"	
8	Kolgardsö	—	0,06	0,12	"	
9	Gjeddesö	—	0	0,15	"	

Key: 1, Lake; 2, depth; 3, lake water; 4, sediments; SBV = acid-binding capacity; SW = mud water.

None of the listed lakes exhibited a Si concentration exceeding 0.2 mg Si/l., although both the Ihl Lake and the Buelt Lake were investigated a number of times and this during different seasons, and also despite the fact that the wind-protected Mörkesö exhibited stable stratification with a hydrogen sulfide-containing hypolimnion. These uniformly low Si concentrations cannot have been caused solely by preceding periods of depletion, since no diatoms were found in the plankton and hardly any diatoms were found in the sediment. Examination of the sediments showed these lakes to be extremely deficient in Si.

The low Si concentrations found in the water of the above-listed lakes must be attributed to a low release of Si from their sediments. The low re- .89.
lease of Si, in turn, is due to the deficiency of the sediments in amorphous

silica, which, in turn again, is due to the absence of allochthonous Si inflow. The hydrolysis of silicates in both the littoral sandbanks and the sand-rich sediments is so low that it is of no significance for the Si metabolism of even these small lakes. In the same way it appears that the exchange between the lake water and the groundwater must be minimal, since the groundwaters in Sleswig-Holstein as well as those in Jutland contain high Si concentrations, which usually exceed 10 mg Si/l. Apart from that, we are able to locate silica-rich waters in the immediate proximity of these lakes. In the ditches draining a swamp forest, we determined during June of 1961 Si concentrations between 4 and 5 mg Si/l. There is hardly any reason to assume that the weakly humous and sand-rich sediments prevent accumulation of silica by means of absorption, but we must rather conclude that the quantity of groundwater penetrating into these lakes is minimal.

In cases where lakes without inflows are surrounded not by heath or coniferous forests, but by either high deciduous forests or mixed forest, we may find "inflows" of amorphous silica by means of aeolian transport of leaves and, to a lesser extent, other plant parts (woody particles, bud scales, fruits, etc.). Leaves of all kinds contain larger or lesser quantities of silica (Handbuch der Pflanzenphysiologie [Handbook of plant physiology], Volume 4, pages 129 - 130, 1958). We have determined in leaves of beech trees growing along the shore of the Pluss Lake concentrations of 1.0 to 1.5% Si/dry substance. That silica was readily soluble and could, exactly like diatomic silica, be dissolved within one hour in a 0.25% sodium carbonate solution heated in a water-bath. Dissolution experiments using lake water samples (from either the Pluss Lake or the Large Ploen Lake) showed that the silica deposited in leaves went relatively readily into solution: One gram of dried leaves was coarsely disintegrated and suspended in one liter of filtered [lake] water. The suspensions were stored in polyethylene bottles at either room temperature or 5°C and agitated once a day. The analytical data obtained in the experiment using Pluss Lake water are summarized in Table 32.

Table 32 – Dissolution experiments with beech leaves

Tabelle 32. Lösungsversuch mit Buchenlaub

Tage Days	μS$_{20}$		1 SBV		2 Hufa		mg Si/l		% Si in Lösg. 3	
	5°	20°	5°	20°	5°	20°	5°	20°	5°	20°
0	225		1,65		8		0,02		0	
5	212	213	1,25	1,30	35	45	0,4	1,2	3	9
16							0,5	4,0	4	30
33	212	236	1,40	1,70	40	60	1,7	7,0	13	52
56							2,7	9,9	20	73
97							7,0	13,3	52	99
115	220	256	1,40	2,05	60	60	8,0	13,5	59	100

Key: 1, acid-binding capacity; 2, cf. Table 1; 3, in solution.

The bicarbonate content (i.e. the acid-binding capacity) and, thus, also .90 the electrolytic conductivity decreased in a transitory manner due to absorption of the dissolved calcium; however, the Si content of the lake water sample increased greatly right from the start of the experiment. At room temperature that increase of Si continued until complete dissolution of Si had taken place; at 5°C, however, the dissolution of Si had not yet been completed when the experiment was discontinued. The experiment carried out using Large Ploen Lake water revealed the same course of events, so that there is no need to describe these results. On the basis of the relatively rapid dissolution of the silica deposited in the leaves, we are forced to assume that silica is released into lake water from leaf masses dropping into forest lakes, which masses there are initially deposited in the littoral. In addition, there occurs in these lakes also an accumulation of amorphous silica in the deep sediments, so that we must count on an increased autochthonous liberation of Si.

The Si contents found in both the lake water and the sediments of the forest lakes under consideration are presented in Table 33 (cf. the explanations offered in connection with Table 31 on page 88). These lakes are deficient in calcium; their surface measures less than five hectares; they are surrounded by forests; and they possess neither inflows nor outflows. Lakes No. 1 and No. 2 are surrounded by mixed forests; Lakes No. 3 and No. 4, by beech forests. The influence exerted by the factor forest appears to be in evidence in particular in the case of Lakes No. 3 and No. 4 surrounded by beech forests; the Si concentrations in the water of these Lakes are higher, in part, by more than the ten-fold than those of the heath lakes without inflows.

Table 33 - Si contents of forest lakes without inlets. Key: 1, Lake; 2, depth; 3, lake water; 4, (wiederholt) = (repeated); 5, forest lake near . . .; 6, Tr.S. = dry substance; 7, ges. Si. = total Si; 8, SW = mud water.

1. Name des Sees		2. Tiefe	3. Seewasser	
		m	SBV	mg Si/l
1	Kl. Ukleisee 3. 7. 63	11	0,1—0,2	0,1—0,7
4. 2	Pinnsee (wiederholt)	9	0	0,3—0,4
4. 3	Kolksee/Eutin (wiederholt)	5,5	0,4	0,9—3,0
5. 4	Waldsee bei Silkeborg (Jütland, Sept. 62)	2	0,15	2,0

Lake See	Sediments (0—5 / 5—10 cm)		
	6. % Si_a/Tr.S.	7. % Si_a/ges. Si	8. mg Si/l SW
1	0,1—0,05	3—5	8—11
2	1,4—1,6	16—16	9—13
3	1,6—4,0	26—44	19—27
4	1,7	37	13

The relations between humus content and silica content found by both Gessner (1934) and Ohle (1940) in the calcium-deficient lakes in southern Sweden, perhaps, could also be attributed to the varying allochthonous influence. High

humus contents are due to marked introduction of plant remains into the lake; these remains, however, contain as a rule amorphous silica as structural constituent. In cases where humous substances reach a given lake by way of in- .91
flowing waters, that event, of course, simultaneously represents an inflow of dissolved silica. However, it remains to be investigated whether humus content and Si concentration parallel each other also in flowing waters, since it appears well probable that hydrolysis of silicates is influenced by humic acids.

3. Silica concentrations in lakes with inflows and continuous outflows

Discharging lakes (i.e. lakes having both inflows and outflows) differ in principle from lakes without inflows (and outflows, respectively) with regard to their Si metabolism, and this also in cases where the direct increase in concentration due to the inflow of dissolved silica (import surplus) plays a subordinate role in the annual course of the Si concentrations. It should .92
be noted in this connection that lakes extremely deficient in silica may be located in the immediate proximity of lakes extremely rich in silica. Of decisive importance in this regard is the silica introduced into the lake per unit volume over a relatively long period of time. Notwithstanding the fact that the accumulation of silica takes place in the sediment and that this accumulation depends on the quantity of silica introduced per unit surface (or area) and precipitated by biogenic means, we find that it is suitable to proceed on the basis of the unit volume in comparisons of silica concentrations in lake water. The volume of the lake enters into considerations dealing with direct increases of concentration due to inflows as well as into those dealing with increases of concentration taking place on the basis of release of Si from the mud. This release of Si from the mud is influenced indirectly by the inflow of Si per unit area.

Table 34 - Dependence of autochthonous Si removal from the mud on the allochthonous Si supply of the lakes. Key: 1, allochthonous Si supply for 24 hours; 2, summer Si removal, average for 24 hours; 3, maximum Si concentration in the lake (average); 4, mud taken at a depth of; 5, d. Tr. S. = of the dry substance; 6, Si liberation in the experiment; [8] Si liberation after KCN treatment; [9] Si liberation at approximately natural colonization of the mud with chironomid larvae.

See Lake	1. allochthone Si-Zufuhr f. 24 h mg Si/m²	1. allochthone Si-Zufuhr f. 24 h mg Si/m³	2. sommerliche Si-Rückfg. ⌀ f. 24 h mg Si/m²	3. max. Si-Konz. im See ⌀ mg Si/l
Ihlsee	0	0	1—2	0,08
Plußsee	ca. 5	ca. 0,5	10—18	0,45
Schöhsee	ca. 5	ca. 0,5	ca. 20	0,40
Gr. Plöner See	15—30	1—2	200—300	3,2
Vierersee	35—50	5—7	300—330.	7,8
Heidensee	120—160	60—80	(400)	12,0

See Lake	4. Schl.-Entn. m Seetiefe	5. % Si$_a$ d. Tr.S.	6. Si-Abgabe im Experiment mg Si/m² · 24 h 5°	6. Si-Abgabe im Experiment mg Si/m² · 24 h 15—20°
Ihlsee	21	1	0,5—1	1,5—2,5
Plußsee	13	1,5	9	20
	23	3	14	34
Schöhsee	13		10	45—50
	21	1—2	15	50—55
Gr. Plöner See	21	2,6	—	100[8])—400[9])
	34	15	40	100 —
Vierersee	11	6	—	—
	17	12	—	—
Heidensee	3	2,5	25[8])—60—200[9])	100[8])—200—600[9])

The particular interrelationship existing between allochthonous introduction of Si into the lake water, autochthonous return (liberation) of Si, and the average maximal concentration of the lake water is illustrated in Table 34.

The values determined in the experiment for Si released from the mud as well as the values for re-introduction (liberation) of Si in the lake and the maximal Si concentrations observed in the lake water during complete winter circulation show courses which parallel the values for Si introduced into the lake. In this connection we find that the direct increase of concentration always amounts only to a fraction of the total release, and it frequently is significantly lower than is indicated by the values given in Columns 1 and 2 [of Figure 34], since the concentration of the lake water is not taken into consideration in these computations. The allochthonous supply reaching the lake is determined by repeated measurements of the Si loads of all inflowing waters.

Stangenberg (1961), too, has found that the Si values found in drainage lakes usually are higher than those found in seepage lakes.

Loeffler (1960) found in Chilian lakes a distinct correlation between the size of the catchment area and the Si concentrations of the respective lakes. However, neither Stangenberg nor Loeffler has reported on studies of the waters flowing into the lakes or of the sediments.

The importance of allochthonous introduction of Si for the autochthonous Si metabolism is particularly clearly in evidence in the case of the Jutland sand lakes. These lakes have been studied during the summers of 1909 and 1910 by Broensted and Wesenberg-Lund (1911-1912), who found in several lakes (Almindsö, Slaansö and Sundsö among other ones) Si concentrations between 11 and 17 mg Si/l. These authors associated these high Si concentrations directly with the sandy character of the lake shores and the "geological structure of the region." On page 482, they stated in this connection: "It is rather interesting to find that the typical heath lakes having bottoms consisting entirely of gravel exhibit silica contents exceeding the calcium contens."

Our re-investigations carried out during September of 1962 showed that
all the silica-rich lakes investigated by Broensted and Wesenberg-Lund .93.
receive inflowing waters or, at least (Slaansö) possess an outlet with continuous outflow[10]. We were able to find significantly higher Si concentrations in all lakes exhibiting (apparently) continuous, even if frequently weak, outflows than in lakes without (inflows and) outflows (cf., Tables 31 and 35). However, the difference between these lakes is particularly impressive when we consider their sediments and, in particular, the silica contents of the interstitial water of these sediments.

Table 35 - Jutland sand lakes with inflows. Key: 1, Lake; 2, ouflow; 3, depth; 4, lake water; SBV = acid-binding capacity (or bicarbonate content; Tr.S. = dry substance; ges. = total; SW = mud water.

1. See	2. Ausfluß	3. Tiefe	4. Seewasser		Sediments, 0—5 cm		
	l/sec	m	SBV	mg Si/l	a	b	c
Söbysö	20—30	5,5	0,4	1,0	12	40	40
Sundsö	750	2,5	0,55	4,0	6	35	50
Almindsö	60	15	0,56	1,7—4,8	14	54	50
Slaansö	80	10	1,2—1,3	5,5—8,4	10	46	50
Torsö	200	5	0,9	1,8	16	58	50
Salten Langsö	ca. 1000	—	1,2	5,1			
Örnsö		—	0,9	6,4			
Stubbergdsö		—	1,3	8,3			
Flyndersö		—	1,5	3,5			
Hellesö	—	—	1,8	7,4			
Torupsö	20	—	0,95	5,0			

a = % Si_a/Tr.S.
b = % Si_a/ges. Si
c = mg Si/l SW

The Si concentrations of lake waters as well as the peculiar qualities of the sediments of the heath lakes having no inflows, on the one hand, and the heath lakes having both inflows and outflows, on the other one, demonstrate that the high silica contents of the lakes investigated by Broensted and Wesenberg-Lund must be attributed not to the gravel present at the

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[10] The Slaansö contains sublimnic springs.

lake bottom, but to the introduction of dissolved silica from the surroundings. The disintegration and degradation of silicates takes place not in the lake, but in the soils of the surrounding region. Only the connection of a given lake with these sites of silicate degradation be means of flowing waters creates the precondition required for accumulation of silica in a given lake. Degradation of silicates is promoted in sandy soils, in particular, by the low pH values of the subsurface waters (cf. Section III). The chemical data obtained in the waters flowing into the lakes considered are presented in Table 16, on page 47.

The extremely high Si concentrations of between 11 and 17 mg Si/l. reported by Broensted and Wesenberg-Lund in the case of the Slaansö, Almindsö and Sundsö could not be confirmed by us during our investigation carried out in September of 1962. The maximal concentration in these three lakes found by us amounted to 8.4 mg Si/l.; that value was found in the Slaansö at a depth of 10 meters (above the sediment) (cf. Table 35).

It is well possible that the Si concentrations found in the lakes in question during the summer or the late summer, respectively, may be significantly lower at the present time due to increased depletive activities than .94.
at the beginning of this century.

However, we found during September of 1962 also that all Si concentrations determined in both the waters flowing into these lakes and other flowing waters in Jutland were below 10 mg Si/l. Since there exists no reason to assume that the Si concentrations in the flowing waters have changed since the beginning of the century to such a great extent, there arises the question whether, for instance, the Sundsö could attain a Si concentration of 17 mg Si/l., when the

Si concentrations of the inflowing waters amount only to 6 to 7 mg Si/l. In view of both the uncommonly high Si concentrations in the interstitial water of 50 mg Si/l. and the low average depth of this lake of about three meters, there certainly exists the possibility of a transitory rise of the Si concentration in the lake by way of its inflowing waters. At a Si release from the mud of 300 to 400 mg Si/m^2/24 hours—a release observed by us in the sediments of other lakes (i.e. the Heiden Lake and the Large Ploen Lake) in the experiment as well as in the lake waters in situ—we would be faced in the case of a lake measuring three meters in depth with a rise in concentration amounting to 9 to 12 mg Si/l. already within three months.

Although continuous allochthonous inflow (supply) of Si and biogenic accumulation of silica in the sediments both represent the most important requirements for any marked autochthonous release of silica from the sediments and determine to a large degree the level (intensity) of the Si metabolism, we find that absorptive and ion-exchanging processes may influence greatly both the solubility (c_s) and the rate of dissolution of silica deposited in the sediment (cf. Sections III and IV). These processes play a role, above all, in those lakes, which receive either no or only insignificant inflows and, thus, exhibit sediments deficient in diatomic silica, but rich in absorptive substances (cf. the Schoeh Lake, page 83). Allochthonous inflow of suspended inorganic substances ('clay-induced turbidity') would—above all, in the case of calcium-rich lakes—make difficult the release of diatomic silica accumulated in the sediment as a consequence of the autochthonous metabolic activity.

In cases where allochthonous inflow of dissolved silica and biogenic presipitation of silica in the lake are intensive to an extent that autochthonous, silica-rich muds are formed—as in the Large Ploen Lake, the Vierer Lake, the Heiden Lake and the Danish lakes listed in Table 35—we find that the inorganic binding of Si in the sediments decreases more and more. All sediments listed in Table 4 (on page 20) having a Si content exceeding 5% Si_a/dry substance also were found to contain more than 25 mg Si/l. in their interstitial water. However, the fact that we may encounter also in these muds large differences in the Si concentrations of the interstitial waters and, thus, also of the release of Si from the muds is demonstrated by a comparison of the respective lakes in Sleswig-Holstein and Jutland. This particular difference, which amounts to 100 per cent in the case of the interstitial waters, must be attributed to the different calcium contents of the sediments. High calcium .95.
contents represent in sediments as well as in soils the precondition for the increased efficiencies of absorptive and exchanger substances.

This particular view, which has been reached on the basis of both experimental and limnological investigations, appears to contradict the parallelity between calcium and silica deficiencies occasionally observed. However, that parallelity exists only in lakes without inflows—lakes receiving no supplies of either calcium or silica; it is not of autochthonous origin.

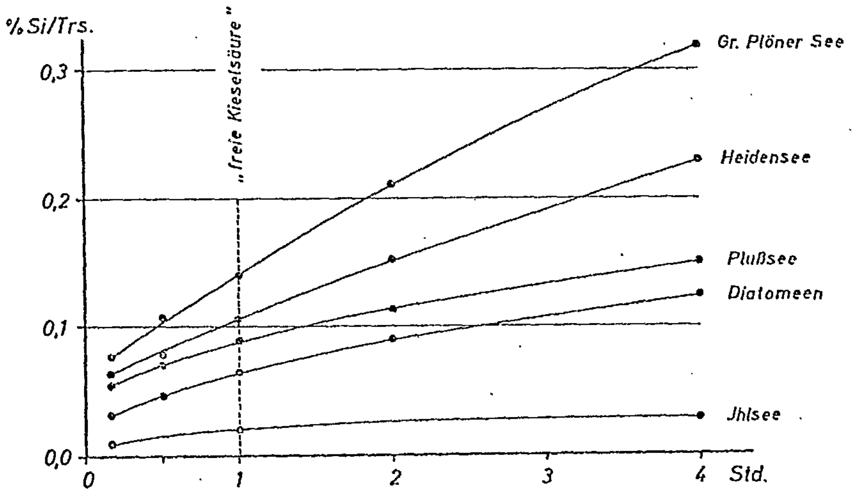

Figure 1 - Solution of silica from sessile diatoms (*Cymbella* and *Gomphonema*, among other ones) and different muds in n Na_2CO_3. "Free silica" determined after Zuellig, 1956. Key: Trs. = dry substance; Std. = hours; See = lake; Diatomeen = diatoms.

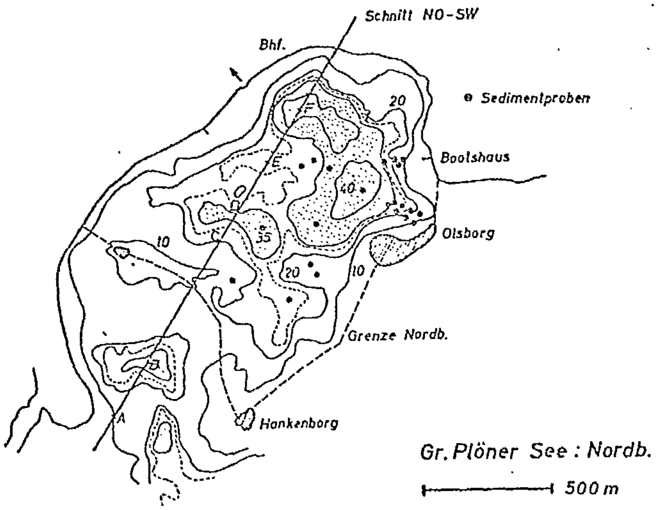

Figure 2 - Bathymetric map of the Large Ploen Lake, north basin, drawn after a preliminary sounding map (after Dr. Utermoehl). Depths above 30 m are indicated by dotted lines. The black dots indicated the sediment sampling sites (Figures 62 to 67). NE-SW plane, cf. Figure 56. Key: Sedimentproben = sediment sampling sites; Bootshaus - boat-house; Grenze = border; Bhf. = railway station; Nordb. = north basin.

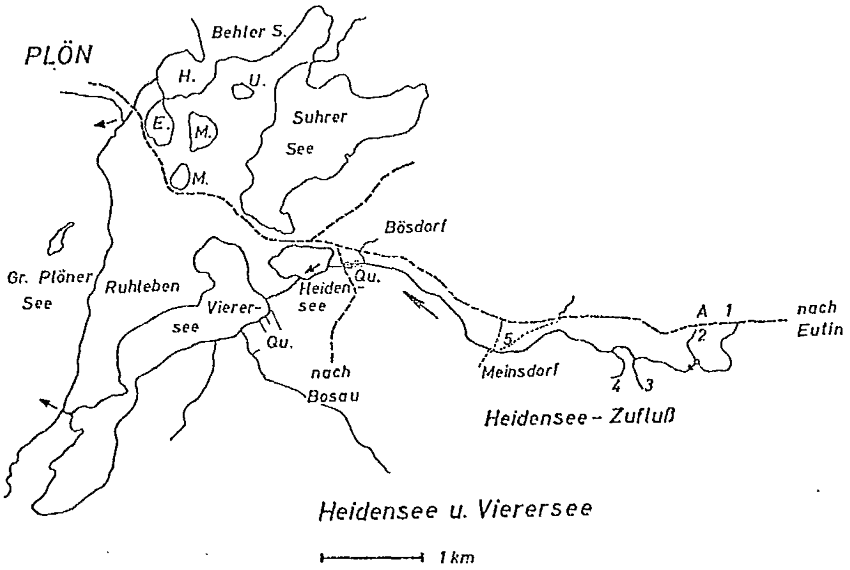

Figure 3 - Catchment area of the Heiden and Vierer Lakes. Key: nach = to; Zufluss = inlet or inflow; Qu.=spring.

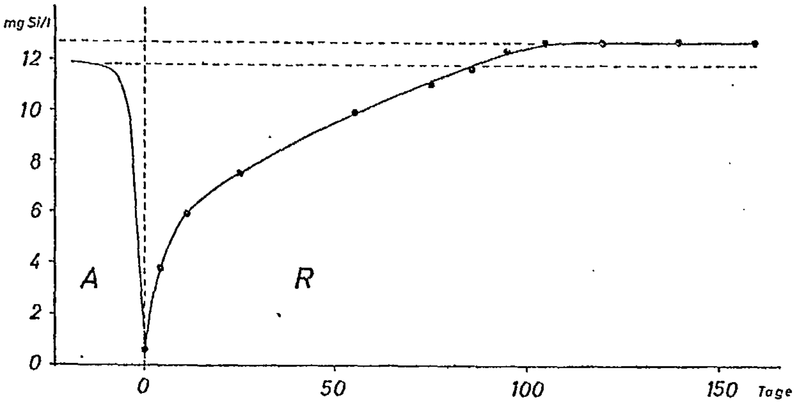

Figure 4 - First percolation experiment: Leaching (A) and regeneration (R) of dissolved silica in the soil-water system. Key: Tage = days.

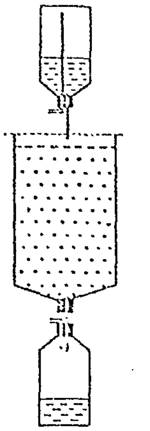

Abb. 5. 2. Perk
A. d.: A
A_1 und
B_1 und

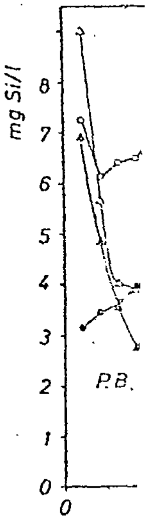

Abb. 6. 2. Pe
lytis
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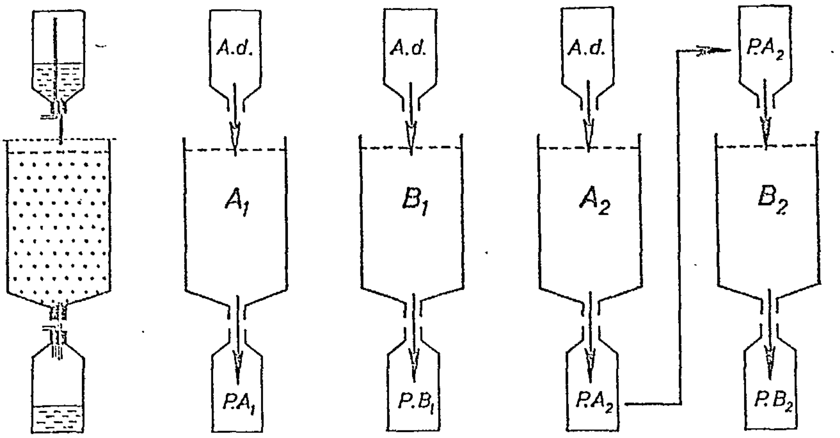


Figure 5 - Second percolation experiment: Experimental design. A.d. = distilled water; A_1 and A_2, upper soil layer; P.A_1 and P.A_2, their percolates; B_1 and B_2, lower soil layer; P.B_1 and P.B_2, their percolates.

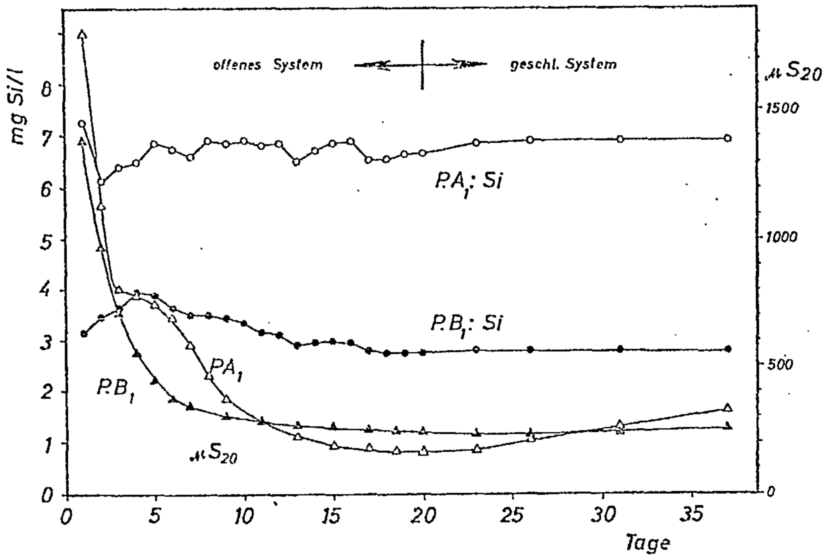


Figure 6 - Second percolation experiment: Silica concentrations (circles) and electrolytic conductivity (triangles) of Percolate P.A_1 (open symbols) and Percolate P.B_1 (black symbols) on percolation in open and closed systems. Key: offenes = open; geschl. = closed; Tage = days.

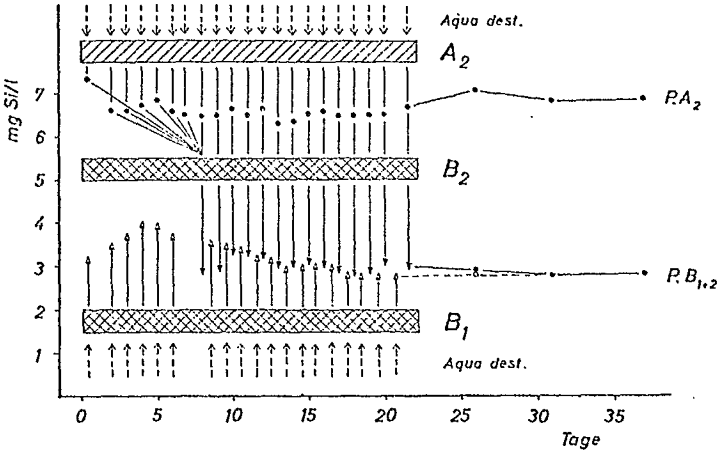


Figure 7 - Second percolation experiment: Equilibrium concentrations of dissolved silica in the percolates of the upper soil layer (P.A_2) and of the lower soil layer (P.B_1 and P.B_2) on percolation in an open system (up to day 22) and a closed system. B_1, distilled water percolation; B_2, continuous percolation: distilled water → A_2 → B_2. Key: Aqua dest. = distilled water; Tage = days.

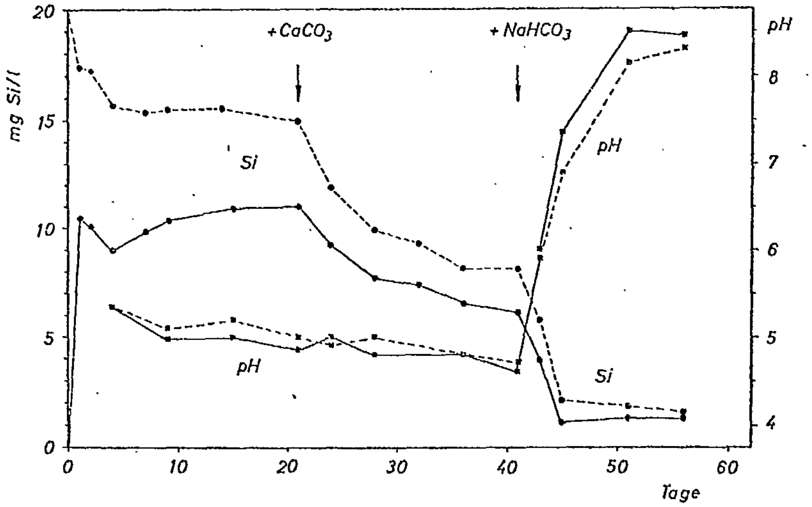


Figure 8 - Third percolation experiment: Behavior of the silica solution equilibrium in the soil-water system on artificial modification of the reaction conditions: Key: Tage = days.

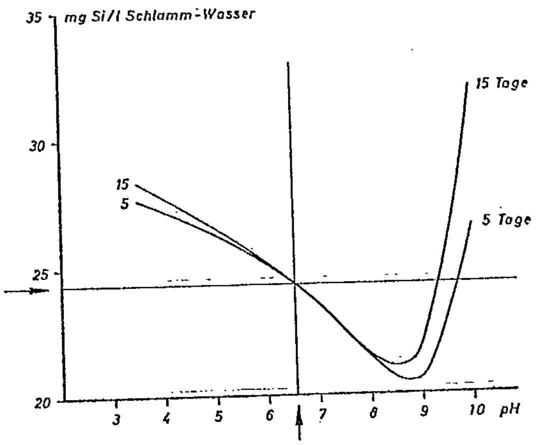


Figure 9 - Dependence of the silica solution equilibrium in Kolk Lake mud on the pH of the mud. The arrows indicate the initial values. Key: Tage = days; Schlamm-Wasser = mud-water.

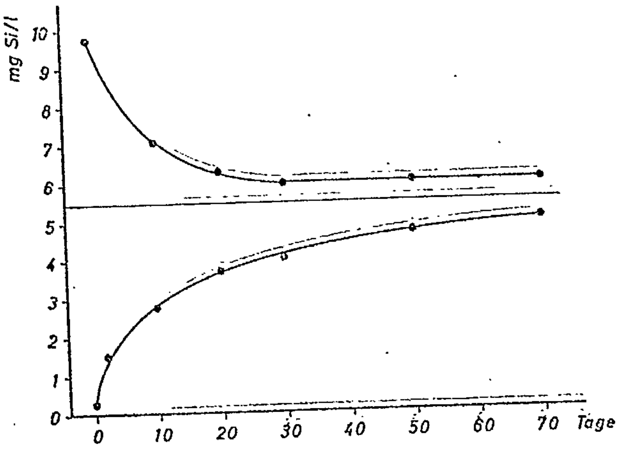


Figure 10 - Attainment of equilibrium of dissolved silica in the overlaying water of a mud-water system (Schoeh Lake). Key: Tage = days.

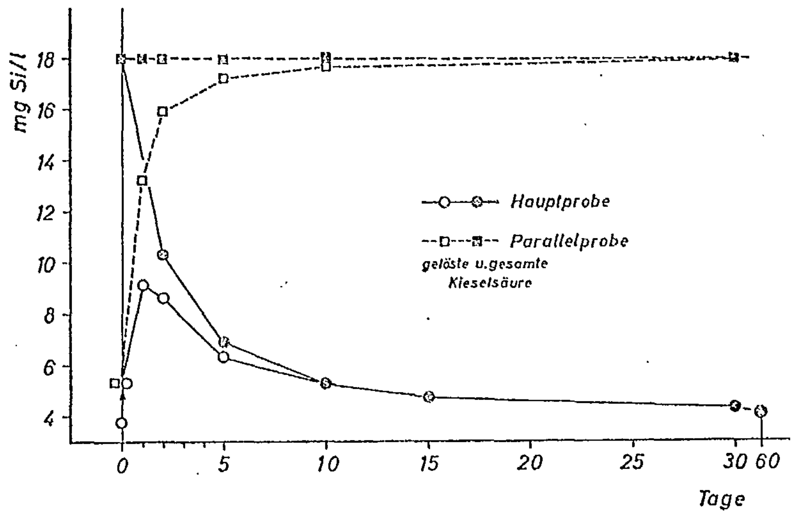


Figure 11 - Silica solution equilibria in the overlaying water of a mud-water system (Schoeh Lake), which (a) was in contact with the mud (Main Sample, circles), and (b) was isolated from the mud (Parallel Sample, squares). Open symbols: dissolved silica; black symbols: total silica (i.e. dissolved plus colloidal). Key: Hauptprobe = Main Sample; Parallelprobe = Parallel Sample; gelöste und gesamte Kieselsäure = dissolved and total silica; Tage = days.

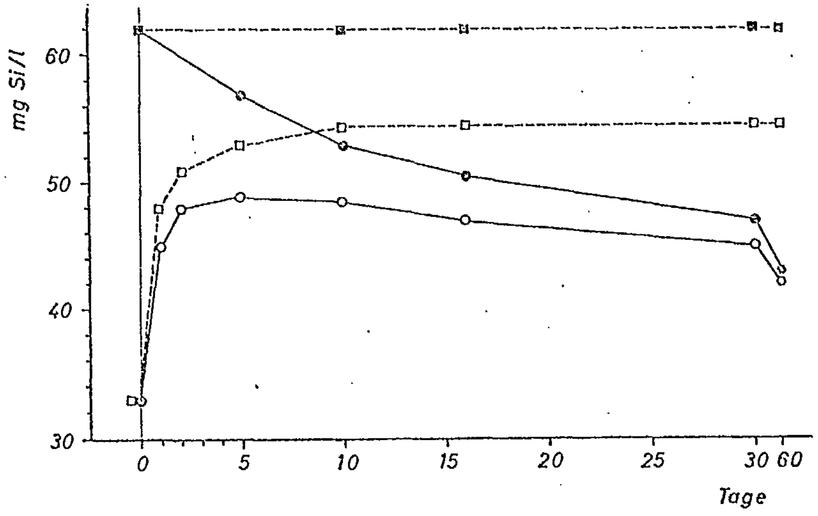


Figure 12 - Mud-water system: Large Ploen Lake; cf. Figure 11 for legend.

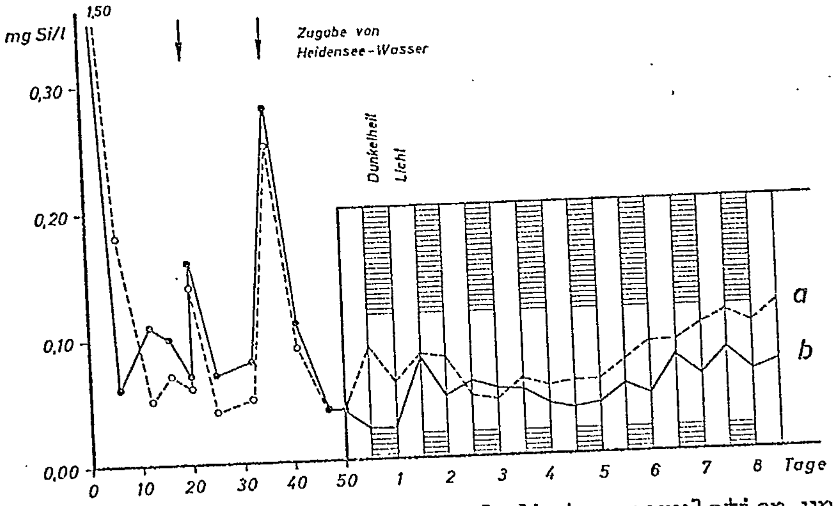


Figure 13 - Silica uptake by a natural diatom population under conditions of light-dark changes. Key: Tage = days; Zugabe von Heidensee-Wasser = addition of water from the Heiden Lake; Dunkelheit = darkness; Licht = light.

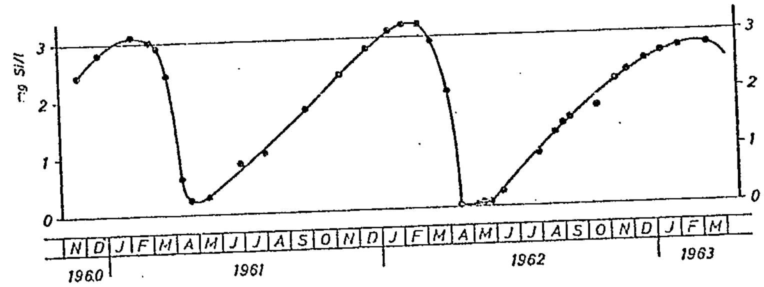


Figure 14 - Annual course of the average concentration of dissolved silica calculated for the north basin of the Large Ploen Lake.

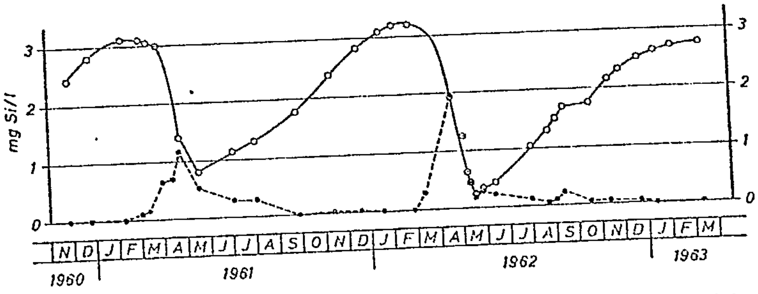


Figure 15 - Cf. Figure 14: Total silica (continuous line) and suspended silica (broken line).

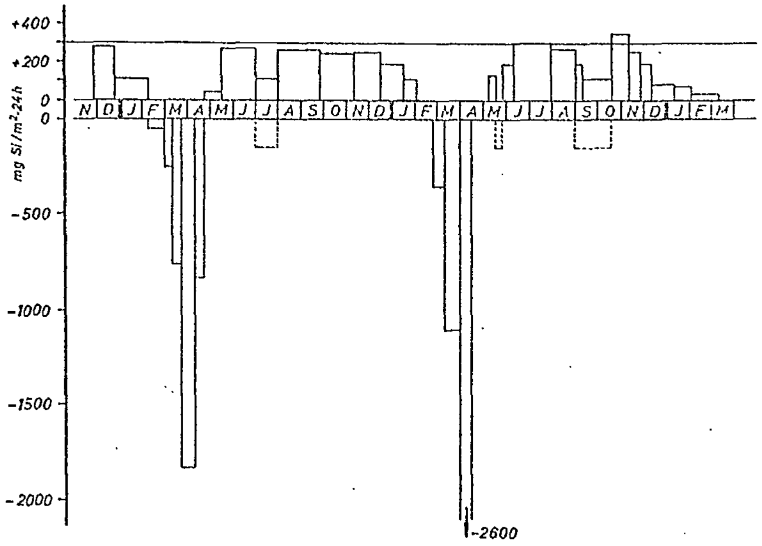


Abb. 16. Gr. Plöner See, Nordbecken, November 1960 bis März 1963:

Figure 16 - Large Ploen Lake, north basin, November 1960 to March 1963: Modifications in the total content of dissolved silica related to area units. "+", liberation; "-", depletion.

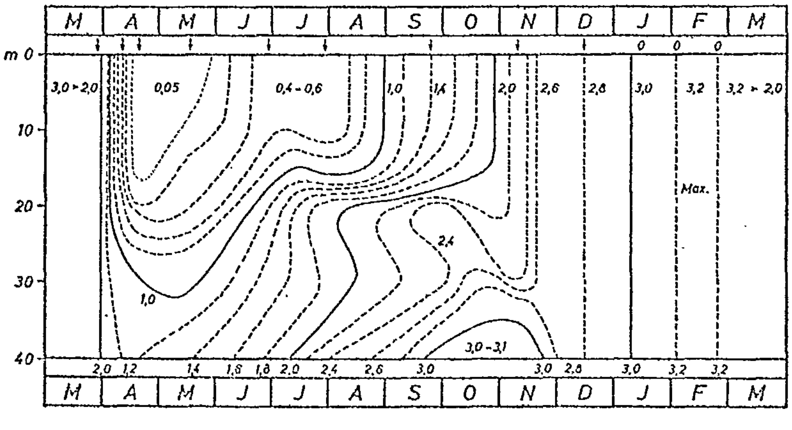


Figure 17 - Large Lake Ploen, north basin, March 1961 to March 1962: Concentrations of dissolved silica over the point of maximal depth (Figures 18 to 25 deal with the same sampling site; cf. Figure 2, Site F). Arrows: Stratification studies; 0: surface samples.

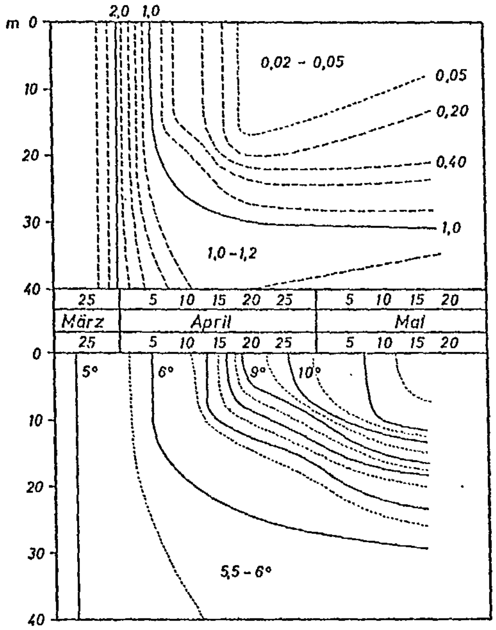


Figure 18 - Large Ploen Lake, north basin, spring of 1961: Course of Si depletion (upper part) in relation to the development of temperature stratification (lower part). Cf. Figure 17. Key: März = March; Mai = May.

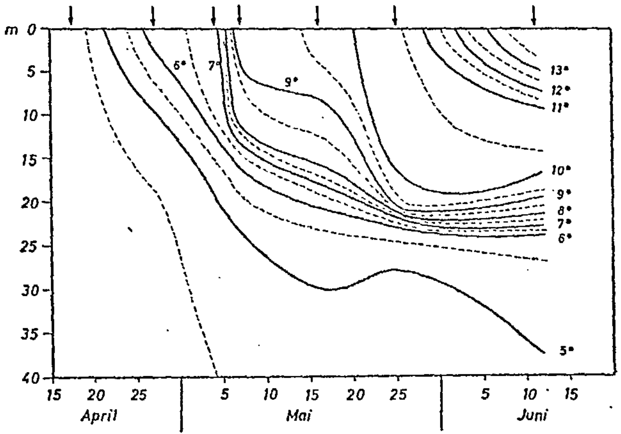


Figure 19 - Large Ploen Lake, north basin, spring of 1962: Development of temperature stratification. Cf. Figure 17. Key: Mai = May; Juni = June.

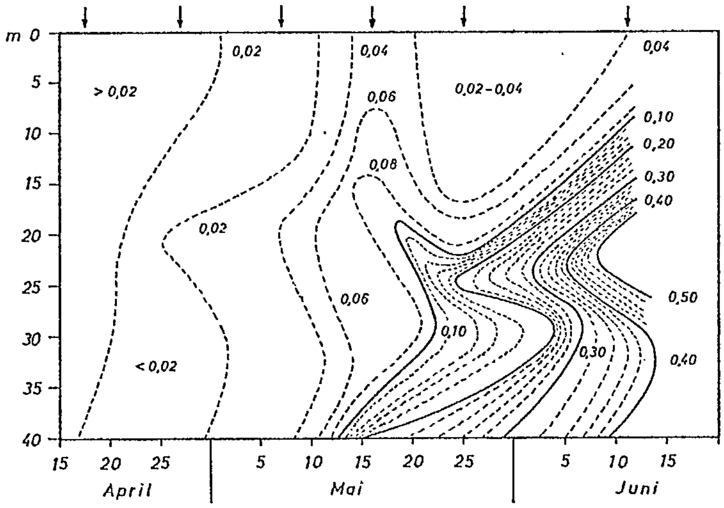


Figure 20 - Large Ploen Lake, north basis, the same interval shown in Figure 19: Total depletion and onset of liberation. Isopleths: Concentrations of dissolved silica. Cf. Figures 17 and 19 (for Key).

Abb 21

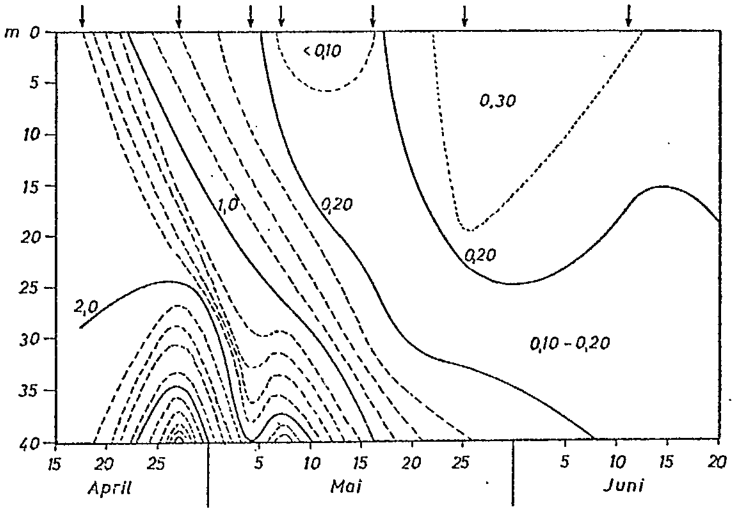


Figure 21 - Large Ploen Lake, north basin, the same interval as shown in Figures 19 and 20: Sedimentation of the spring diatom population. Isopleths: Concentrations of suspended diatomic silica. Cf. Figure 17 and 19 (for Key).

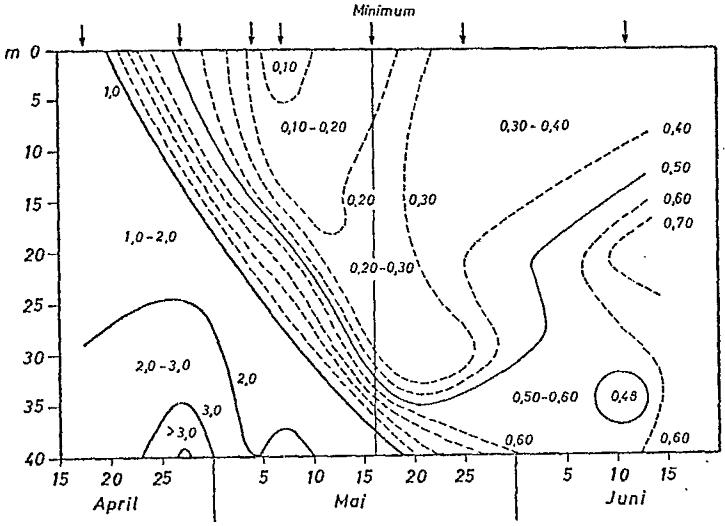


Figure 22 - Large Ploen Lake, north basin, the same interval as shown in Figures 19 to 21: Course of total Si loss to the sediment. Isopleths: Concentrations of dissolved and suspended silica. Cf. Figures 17 and 19 (for Key).

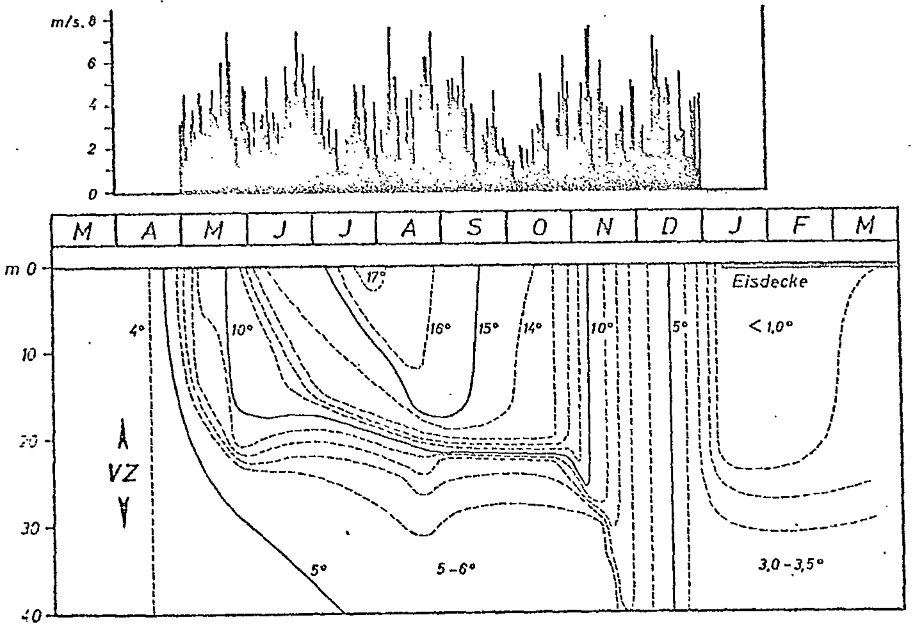


Figure 23 - Large Ploen Lake, north basin, March 1962 to March 1963: Temperature stratification and daily average wind velocities (the latter data were collected by Dr. Vaupel). VZ = full circulation. Cf. Figures 17 and 19. Key: Eisdecke = ice cover.

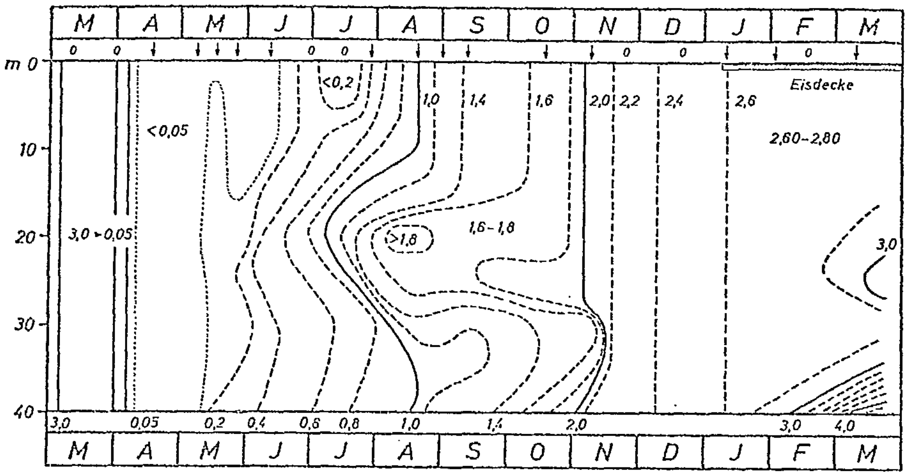


Figure 24 - Large Ploen Lake, north basis, March 1962 to March 1963: Concentrations of dissolved silica. Cf. Figures 17 and 23 (for Key).

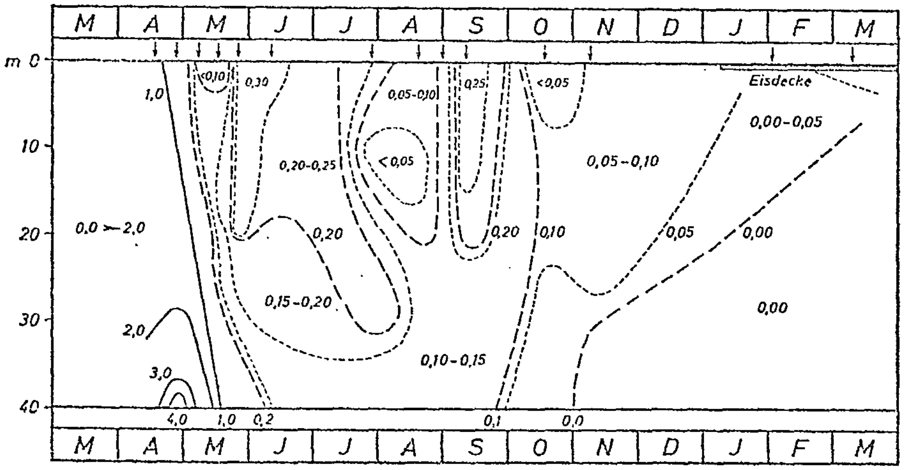
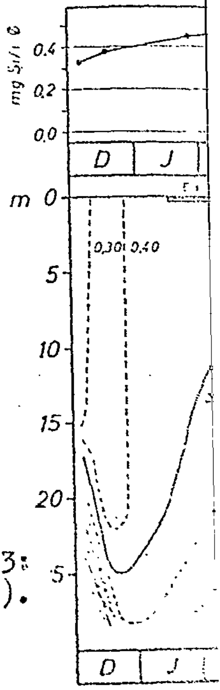


Figure 25 - Large Ploen Lake, north basin, March 1962 to March 1963: Concentrations of suspended silica. Cf. Figures 17 and 23 (for Key).



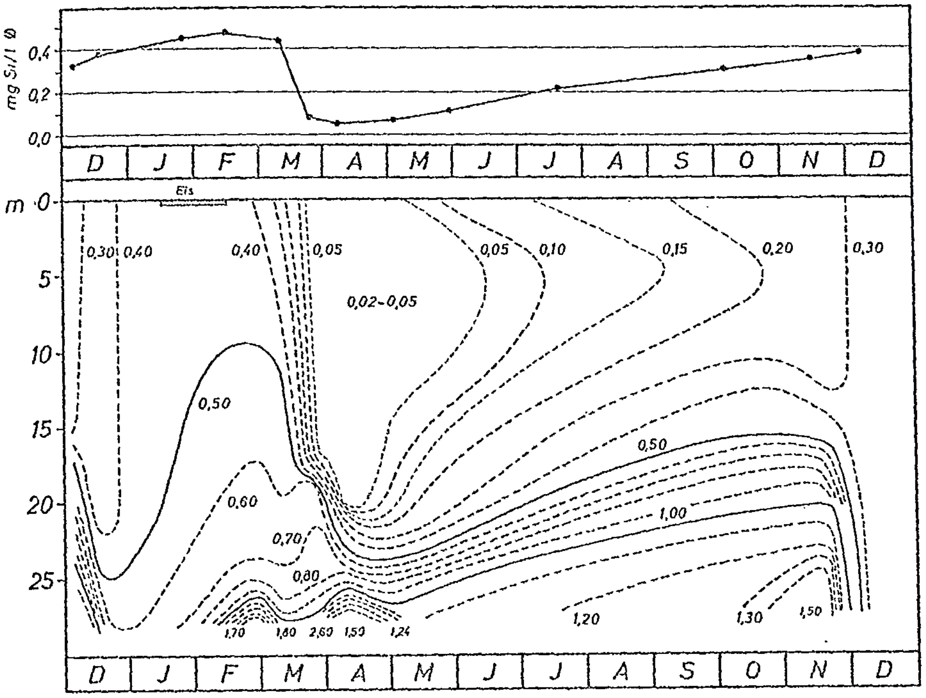


Figure 26 - Pluss Lake, December 1960 to December 1961: Dissolved silica. Upper part: Course of average concentration calculated for the entire lake volume. Lower part: Stratification over the site of maximal depth. Key: Eis = ice cover.

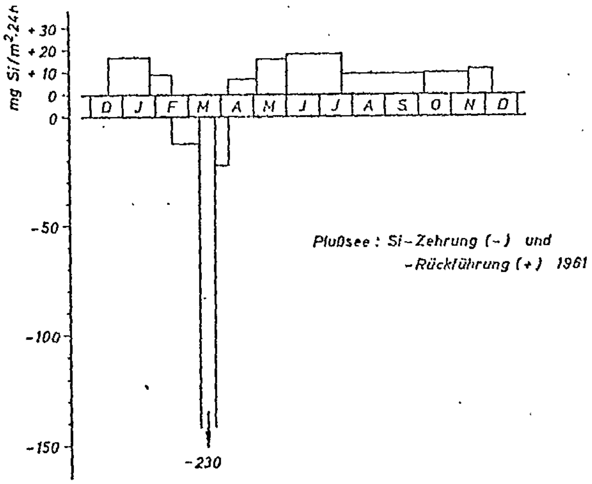


Figure 27 - Pluss Lake, same interval as in Figure 26: Modification in the total content of dissolved silica related to area units. Key: Zehrung (-) = depletion; Rückführung (+) = liberation.

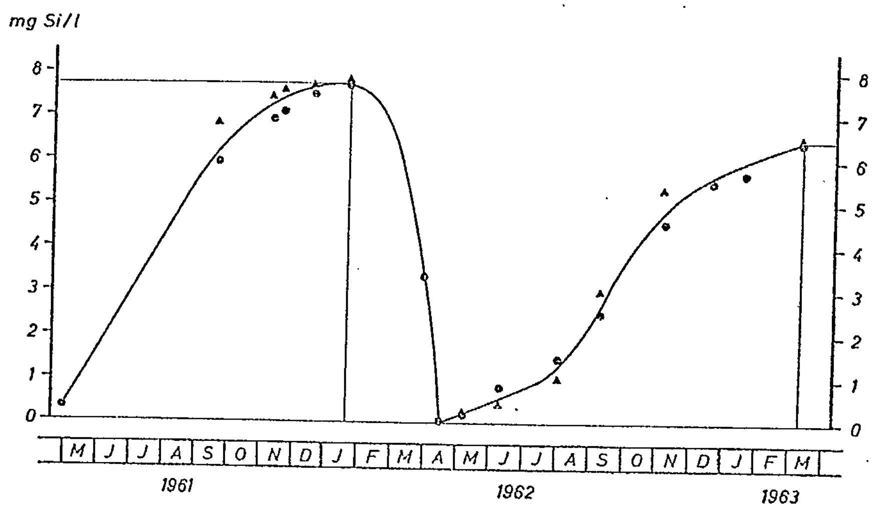


Abb. 28. Vierersee, Mai 1961 bis März 1963:

Figure 28 - Vierer Lake, May 1961 to March 1963: Course of average concentration of dissolved silica calculated for the entire lake volume. Triangles, north basin; circles, south basin.

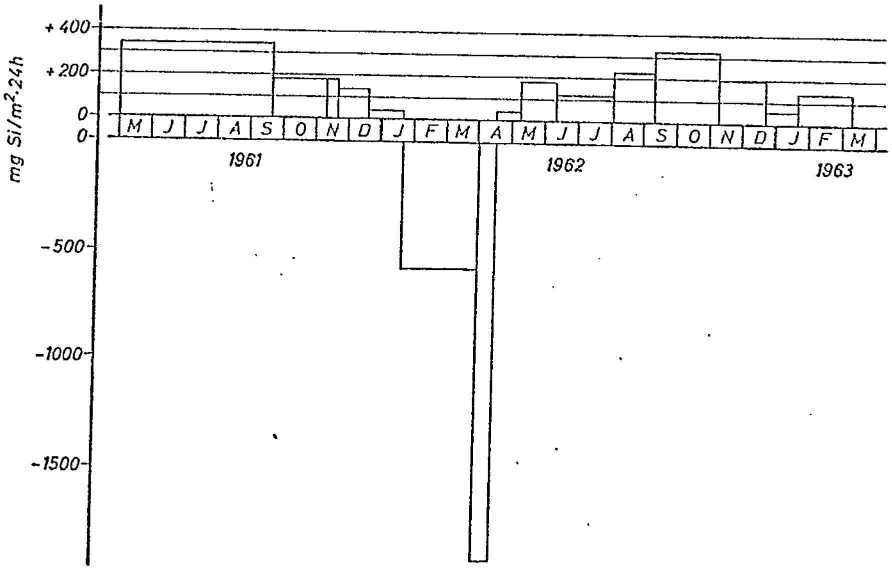


Figure 29 - ViererLake, south basin, same interval as in Figure 28: Modifications in the total content of dissolved silica related to area units.

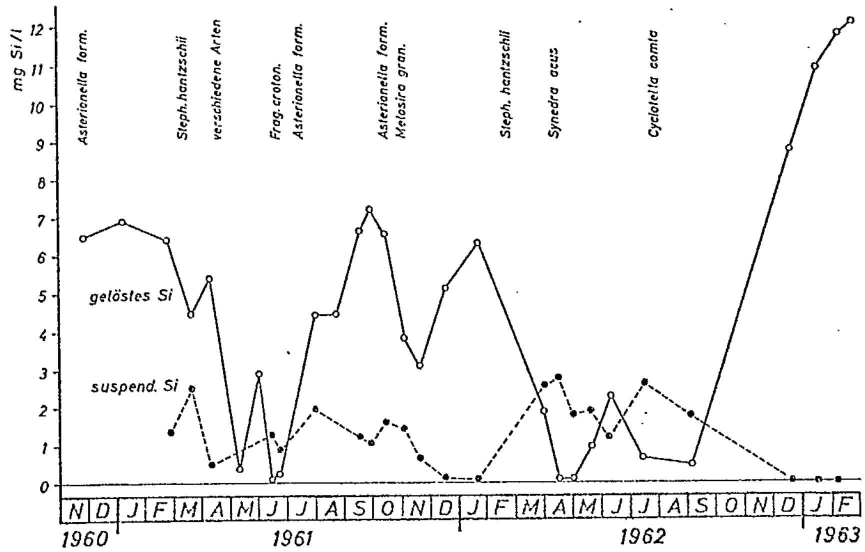


Figure 30 - Heiden Lake, November 1960 to February 1963: Course of the concentrations of dissolved and suspended silica. Upper part: Predominating diatom forms. Key: gelöst = dissolved.

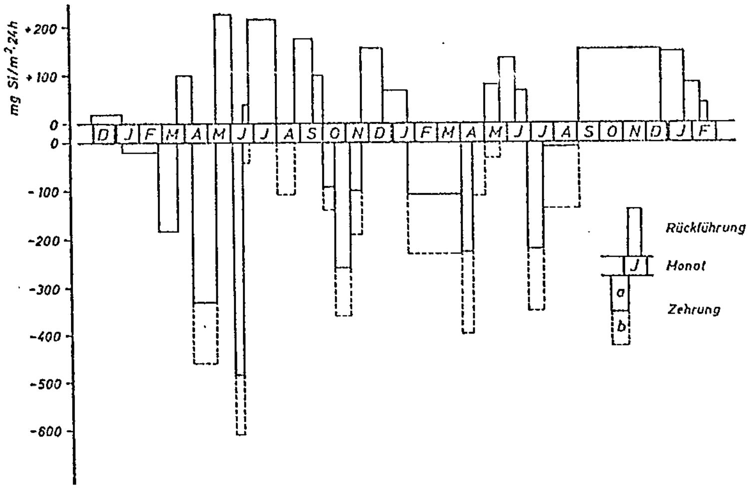


Figure 31 - Heiden Lake, November 1960 to February 1963: Depletion and liberation of silica. Continuous lines: Modification of the total content of dissolved silica related to area units. Broken lines: Depletion, taking into consideration the depleted allochthonous supply fraction. Key: Rückführung (+) = liberation; Zehrung (-) = depletion.

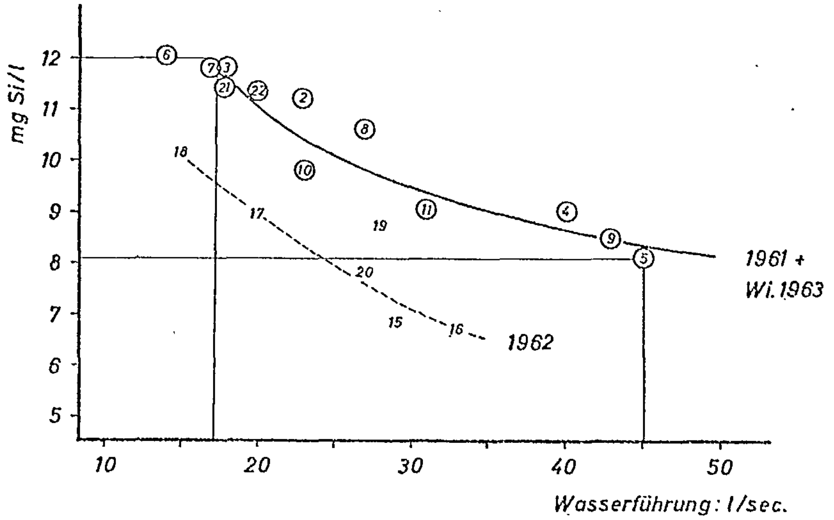


Figure 32 - Heiden Lake inflow, at the mouth: Relation of Si concentration to inflowing water masses (cf. Table 12 for data). Numbers inside circles: 1961 and winter 1963; the remaining numbers (Nos. 15 to 20): Spring and summer of 1962. Key: Wasserführung = inflowing water masses, l./sec.

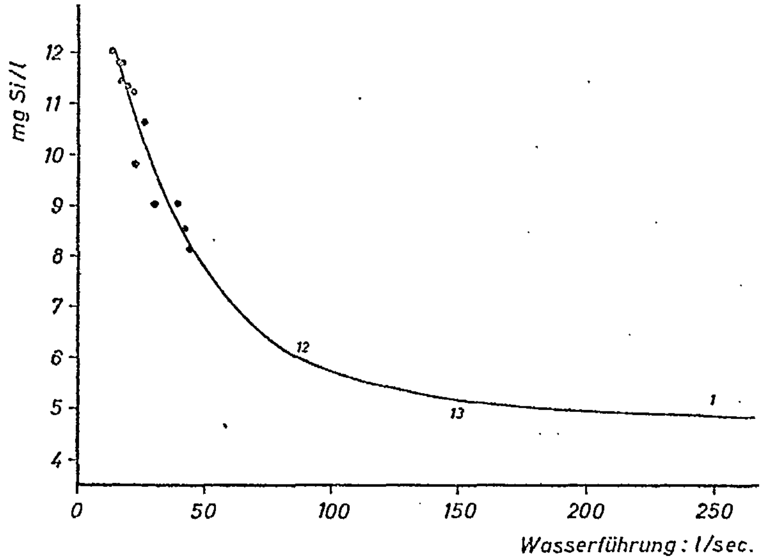


Figure 33 - Heiden Lake inflow, at the mouth: As in Figure 32, but extended to an inflow of 250 l./sec (continuation of the continuous curve of Figure 32). Cf. Figure 32 for Key.

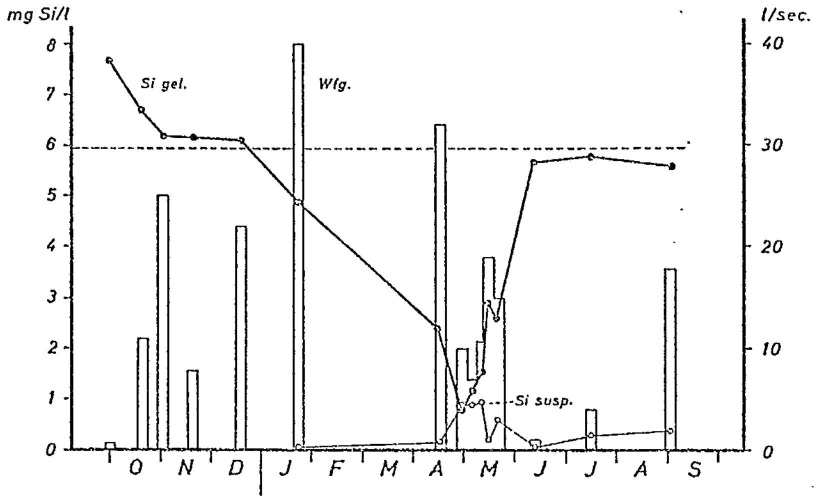


Figure 34 - Heiden Lake inflow, spring inlets, October 1961 to September 1962: Concentrations of dissolved and suspended silica, and water masses inflow. Key: gel. = dissolved; Wfg. = water-mass inflow.

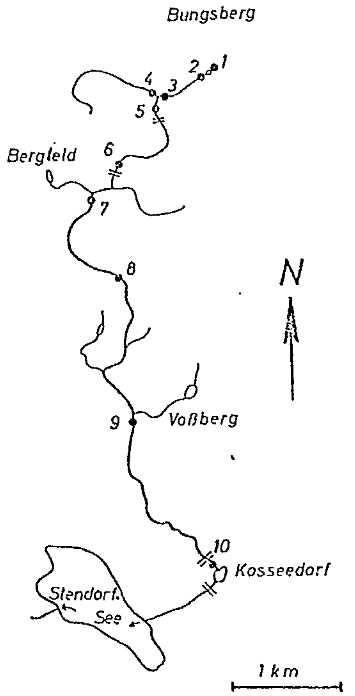


Figure 35 - Upper course of the Bungsberg Schwentine" showing sampling sites.

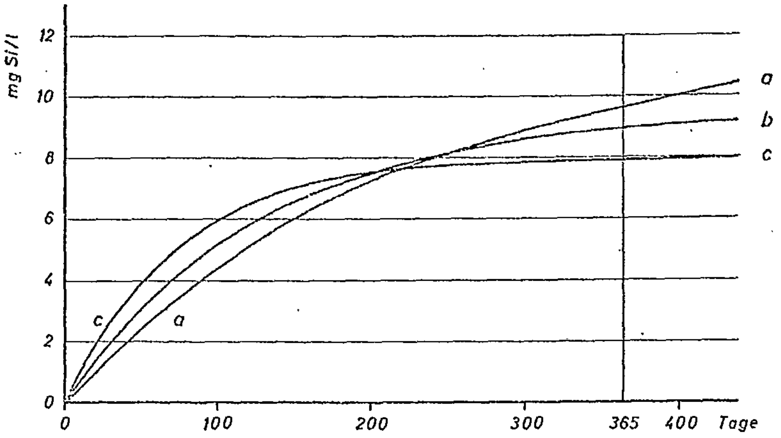


Figure 36 - Theoretical course of Si concentration in the Heiden Lake on the basis of the allochthonous inflow of dissolved silica (cf. Table 17). Key: Tage = days.

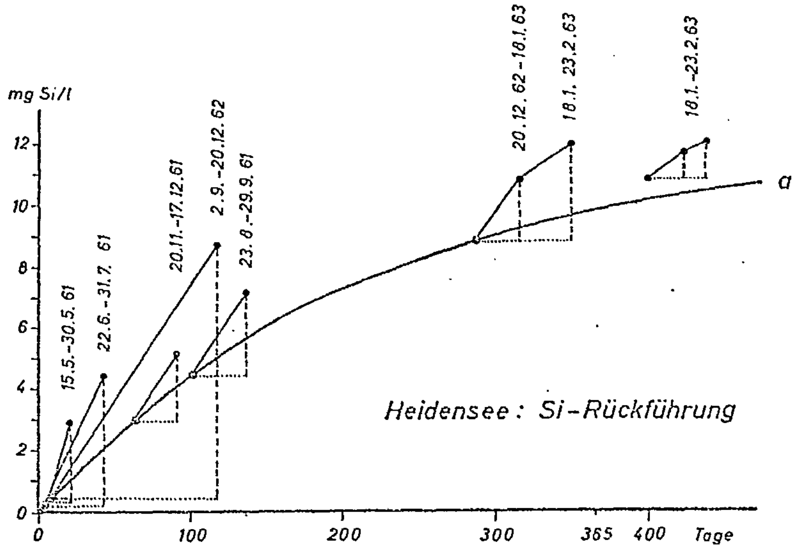


Figure 37 - Heiden Lake: Allochthonous Si inflow (Curve A of Figure 36) and increases of concentrations measured. Key: Rückführung = liberation; Tage = days.

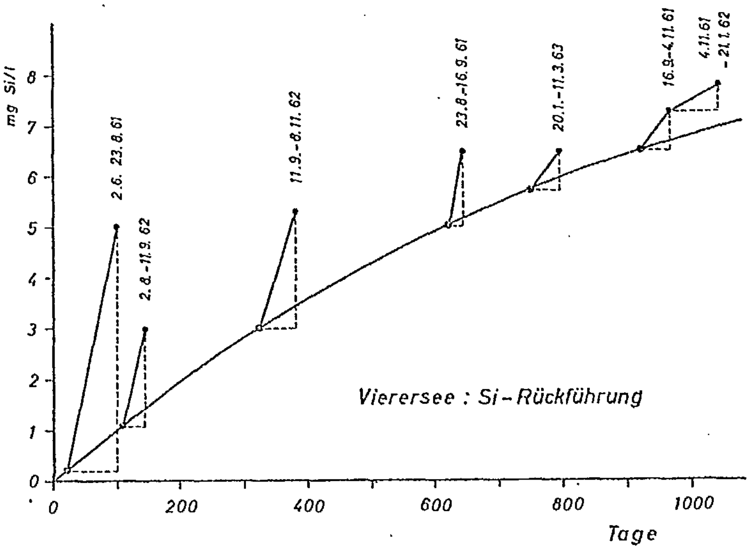


Figure 38 - Vierer Lake, north basin, corresponding to Figure 37 (Heiden Lake): Continuous curve: Increase in concentration expected on the basis of average allochthonous Si inflow. Key: Rückführung = liberation; Tage = days.

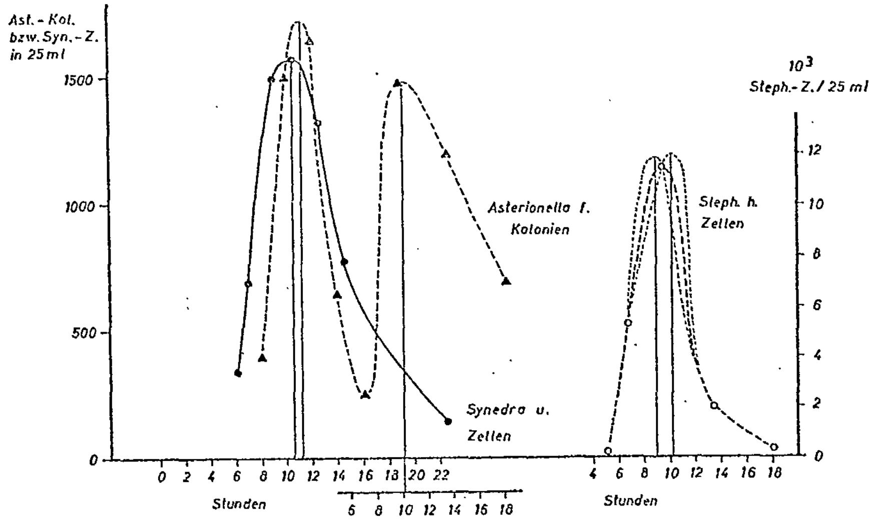


Figure 39 - Sedimentation rates of living diatoms (in the experiment). Settling distance: 90 cm. Key: Kol and Kolonien = colonies; Z. and Zellen = cells; Stunden = hours.

N.B. - Figures 40 and 41 are shown on Plate 1.

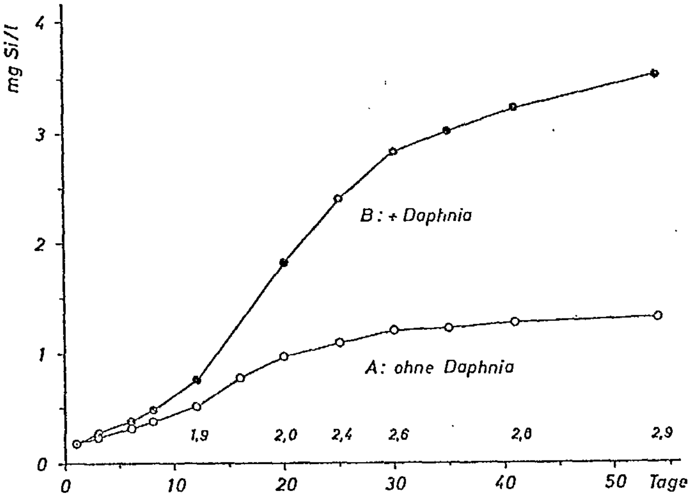


Figure 42 - Dissolution of diatomic silica in an Asterionella suspension in the presence (B) and in the absence (A) of Daphnia magna. Lower series of numerical values: Ratios of the respective increases of the concentration of dissolved silica, (B):(A). Key: ohne = without; Tage = days.

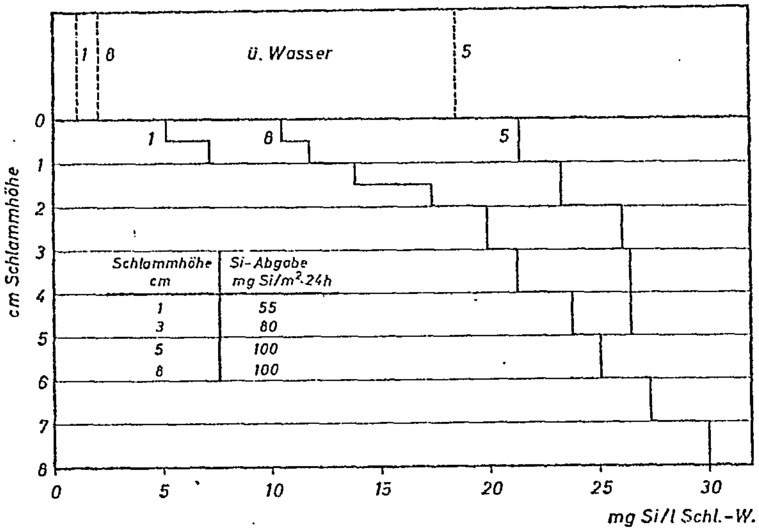
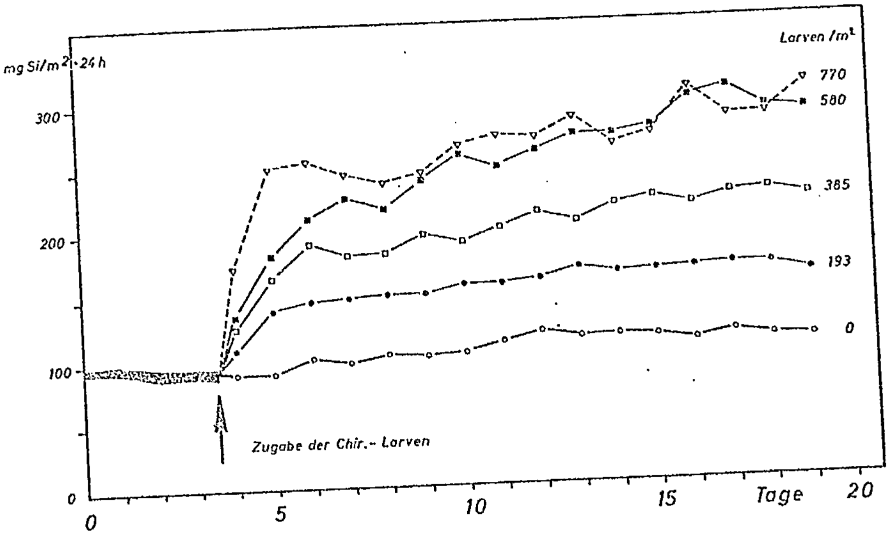
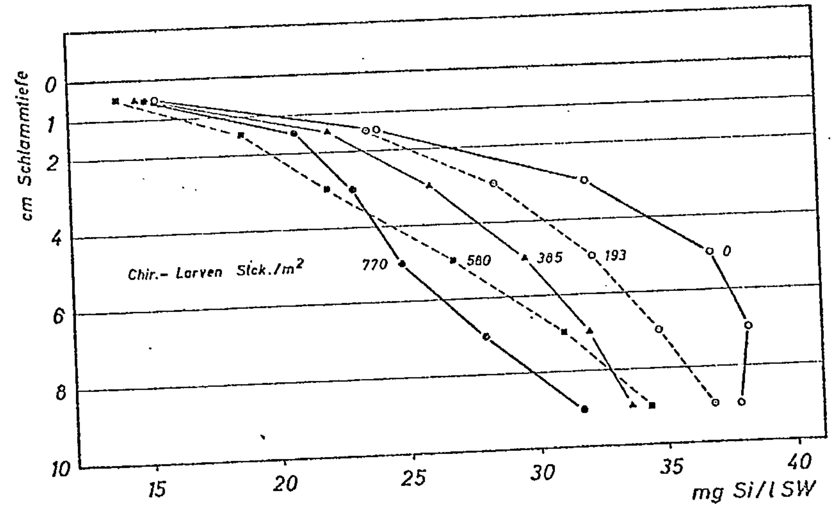


Figure 45 - Mud layer experiment: Broken lines: Si concentrations (at "1" and at "8", average values for the experimental period; at "5", at the discontinuation of the experiment) in the overlaying water. Continuous lines: Concentration gradient of dissolved silica in the mud at the time of discontinuation of the experiment. Key: ü. Wasser = overlaying water; Schlammhöhe - mud layer level; Si-Abgabe = Si release; Schl-W. = mud-water.

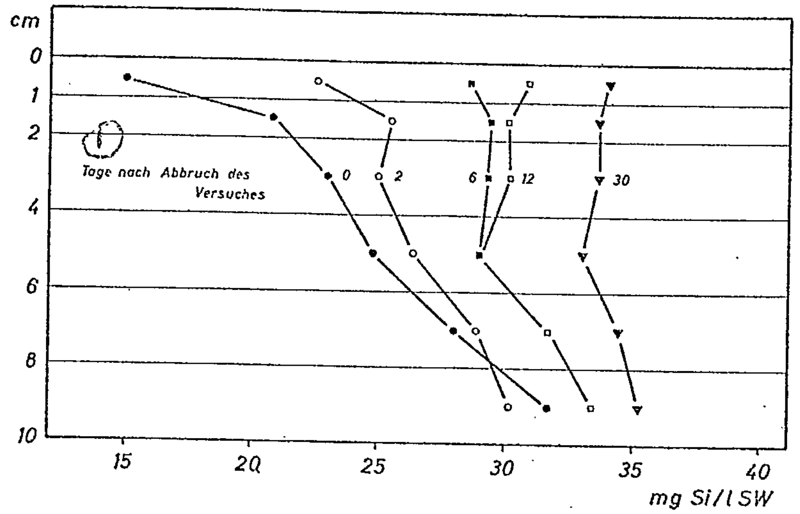
N.B. Figures 43 and 44 appear on Plate 2.



<u>Figure 46</u> - Experiment on the removal of Si from the mud by larvae of <u>Chironomus plumosus</u>. Modification of Si release following addition of larvae. <u>Key:</u> Larven = larvae; Zugabe der . . = addition of the . . .; Tage = days.



<u>Figure 47</u> - (relating to Figure 46): Concentration gradient of dissolved silica in the mud at different colonization densities at the time of discontinuation of the experiment. <u>Key:</u> Schlammtiefe = mud depth; Larven = larvae; Stck = individuals per square meter; SW = lake water.



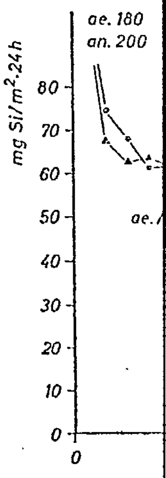


Figure 48 - (relating to Figure 47): Regenration of dissolved silica in the isolated mud layers. Key: 1, days after discontinuation of the expt.

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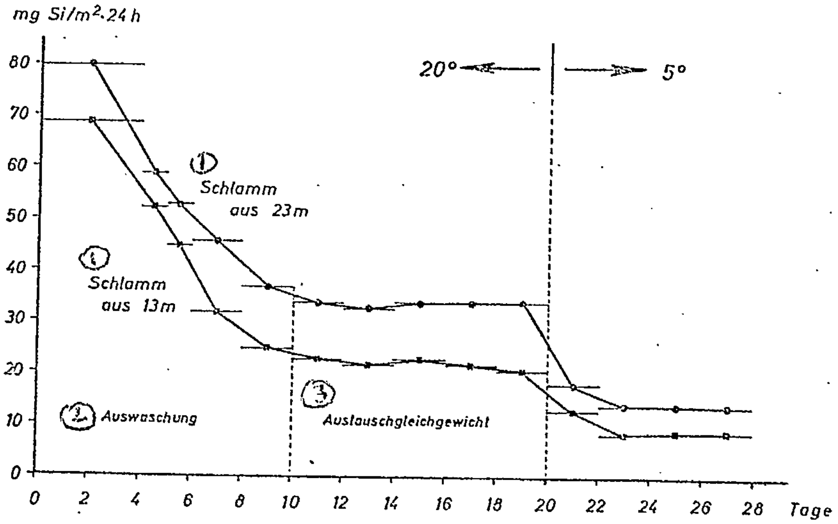

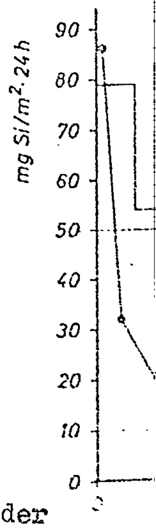

Figure 49 - Si release from Pluss Lake mud at 5°C and at 20°C, resp., under anaerobic conditions. Key: 1, mud from a depth of . . .; 2, leaching; 3, exchange equilibrium; Tage = days.

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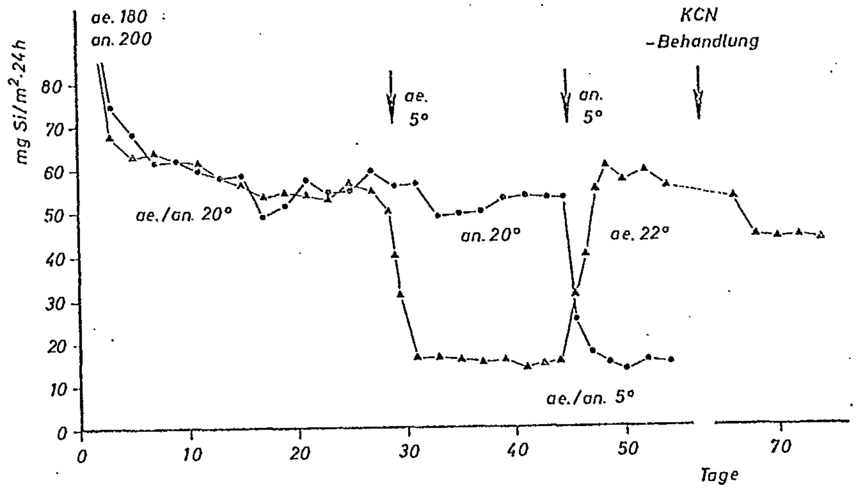


Figure 50 - Si release from Schoeh Lake mud taken at a depth of 21 meters, at 5°C and at 20°C, resp., under aerobic (ae) and anaerobic (an) conditions. Triangles, aerobic; circles, anaerobic conditions. Key: Behandlung = treatment; Tage = days.

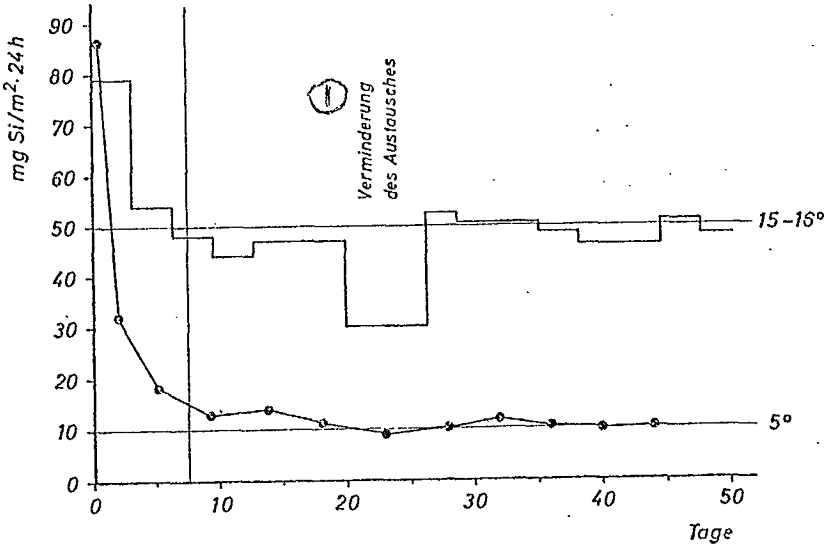


Figure 51 - Si release from Schoeh Lake mud taken at a depth of 13 meters, at 5°C and at 15 - 16°C, resp., under aerobic conditions. Key: Decrease in exchange; Tage = days.

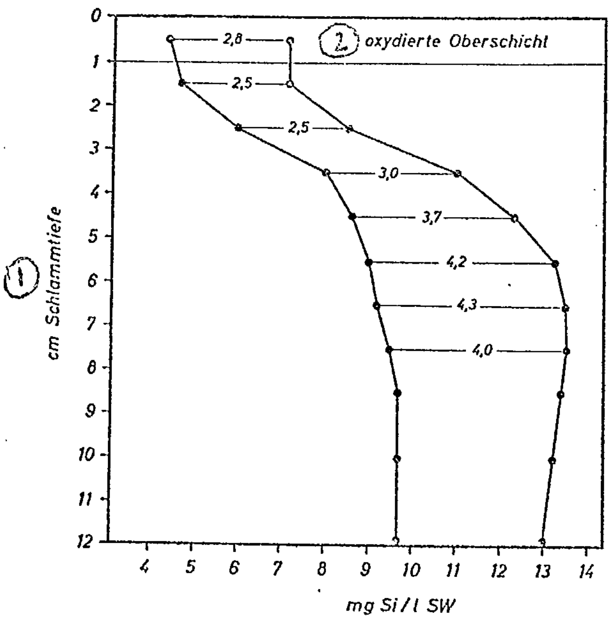


Figure 52 - Concentration gradient of dissolved silica in the mud after discontinuation of the experiment (cf. Figure 51). Left curve, 5°C; right curve, 15 - 16°C. Key: 1, Mud depth, in cm; 2. oxidized upper layer.

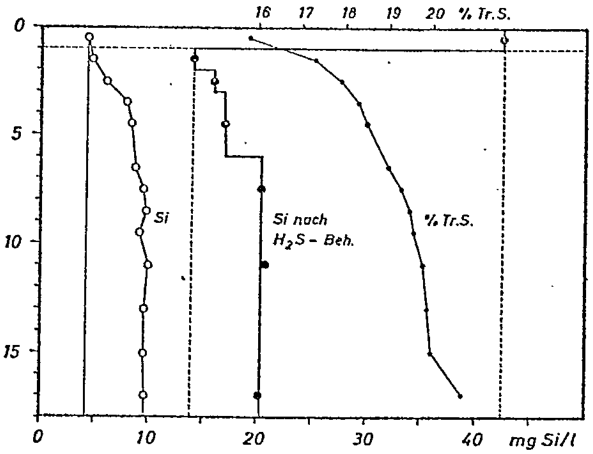


Figure 53 - Concentration gradient of dissolved silica in the 5°-C experiment (presented in Figure 51) before and after treatment of the mud with H_2S. Key: % Tr.S. = dry substance of the wet mud; nach = after; Beh. = treatment.

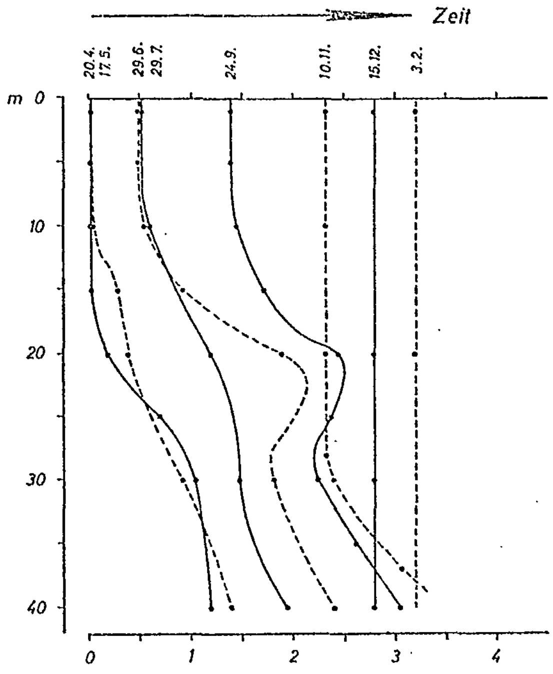


Figure 54 - Large Ploen Lake, north basin: Stratification of dissolved silica, Apr 20, 1961, - Feb 3, 1962 (cf. Fig. 17).

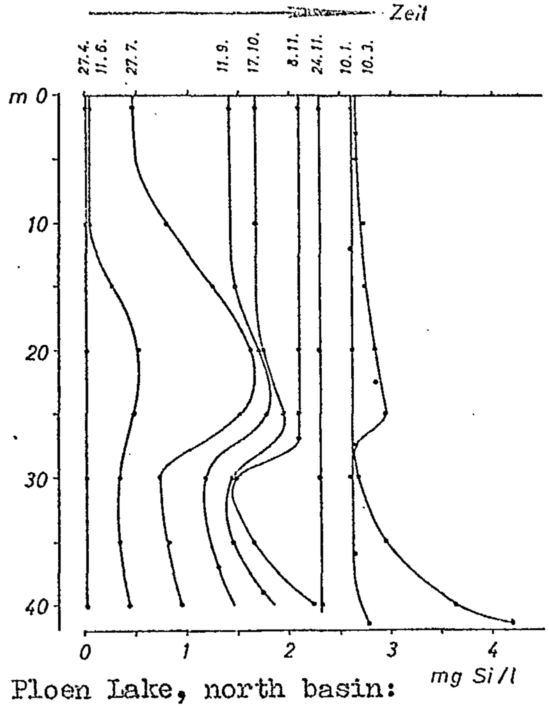


Figure 55 - Large Ploen Lake, north basin: Stratification of dissolved silica, April 27, 1962, to March 10, 1963 (cf. Figure 24). Key: Zeit - time.

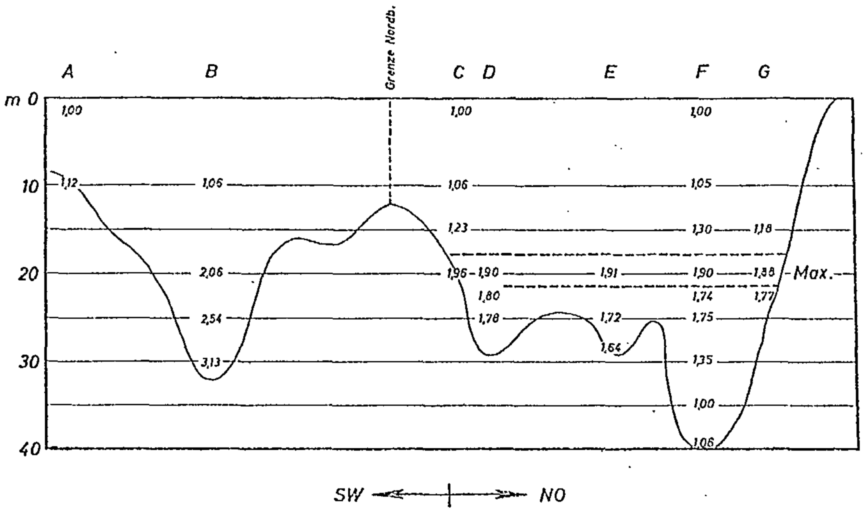


Figure 56 - Large Ploen Lake: Horizontal stratification of dissolved silica during the summer (August 19, 1962). Numerical values: mg Si/l. NE-Sw plane (cf. Figure 2). Key: Grenze Nordb. = north basin border; NO = NE.

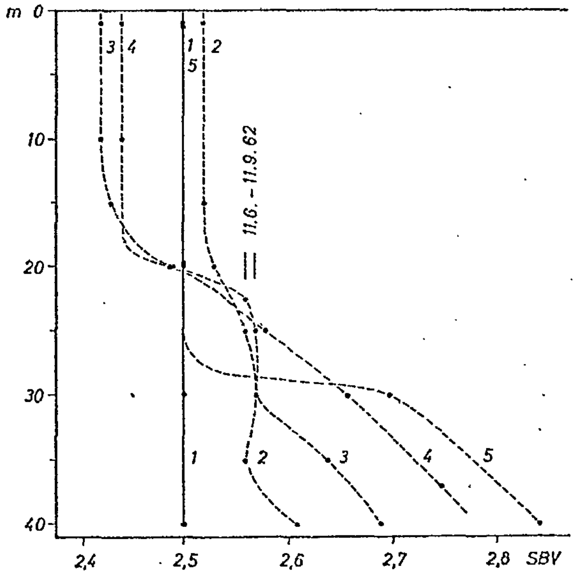


Figure 57 - Large Ploen Lake, north basin. Acid-binding capacity (SBV) in mEq./l., during 1962 summer stagnation.

1: 17.4. 2: 11.6. 3: 19.8. 4: 11.9. 5: 8.11.

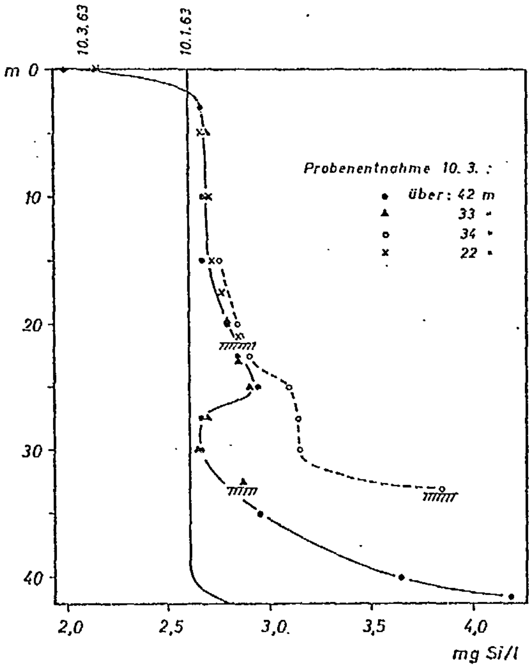


Figure 58 - Large Ploen Lake, north basin: Development of heterograde silica stratification underneath a closed ice cover. January 10 - March 10, 1963 (cf. Figure 24). Key: Probenentnahme - sampling on . .; über = at a depth of . . .

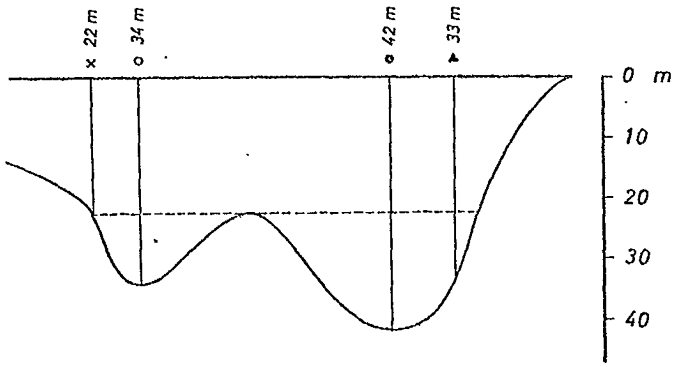


Figure 59 - Schematic representation of the sampling levels indicated in Figure 58. The two basins correspond to the dotted areas of Figure 2 (sampling sites near D and F).

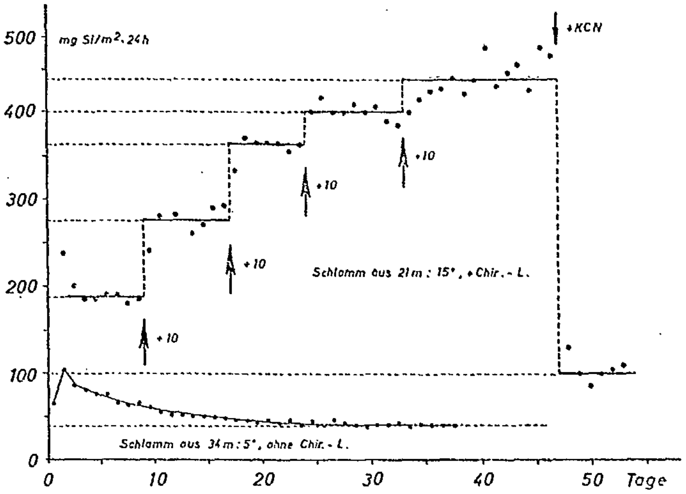
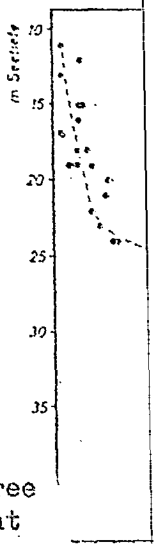


Figure 60 - Large Ploen Lake: Comparison of Si release from chironomid-free deep mud, at 5°C, with mud from the upper profundal, at 15°C, and different chironomid larval colonization densities. Key: Schlamm aus = mud from a depth of . . .; ohne = without; L. = larvae; Tage = days.



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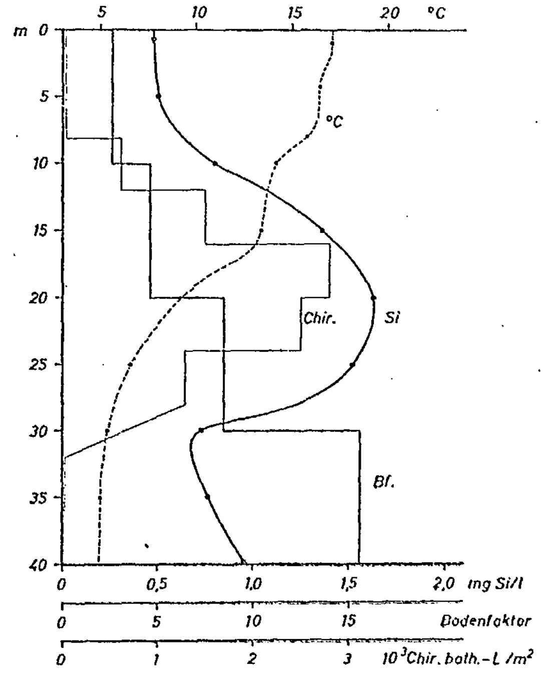


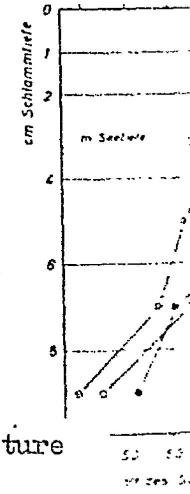
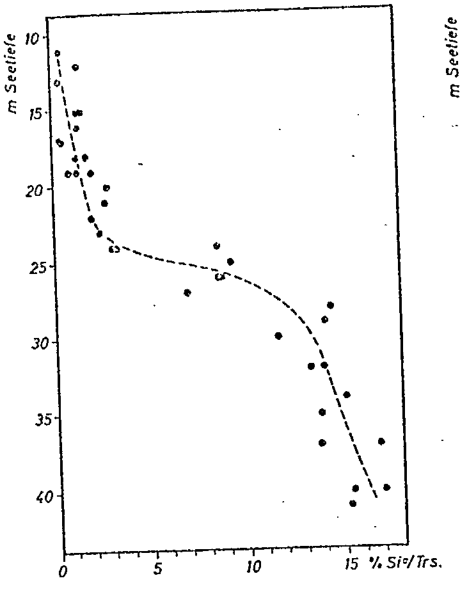


Figure 61 - Large Ploen Lake, north basin: Si stratification and temperature stratification on July 7, 1962. Chironomid colonization on July 31, 1924 after Lundbeck, 1926). Key: Bf. = Bodenfaktor = bottom factor (Bf = $\frac{\text{area}}{\text{volume}}$ x 100, after Elster and Schmolinsky, 1954; L. = larvae.



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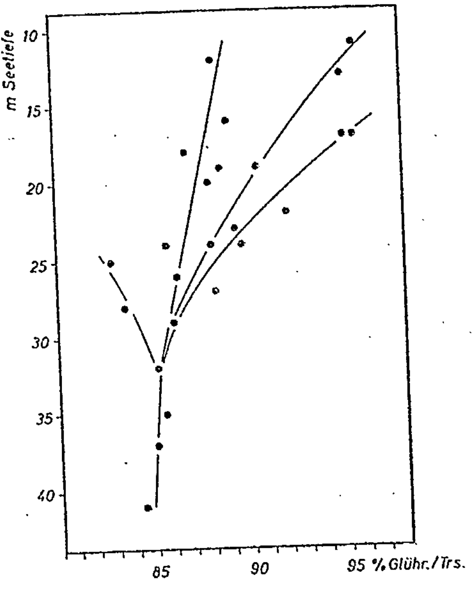
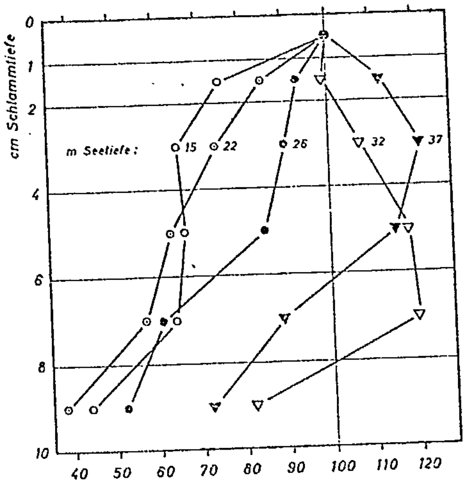


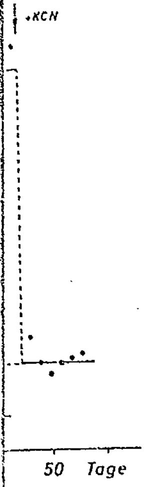
63

<u>Figure 62</u> - Large Ploen Lake, north basin. Mud (upper 10 cm) content of amorphous silica (cf. the microphotographs, Figures 65 to 67, Plate 3) in dependence on lake depth (cf. Figure 2 for sampling sites).

<u>Figure 63</u> - (relating to Figure 62): Residue obtained on ignition of the same mud samples. Glühr.=residue on ignition; Trs.=dry substance; Seetiefe = lake depth.



<u>Figure 64</u> - (relating to Figure 62): Mud Si contents (% Si_a/dry substance) in % of the surface (0-1 cm) layer in mud samples taken at different lake depths.
<u>Key:</u> Schlammtiefe = mud depth; Seetiefe = lake depth.



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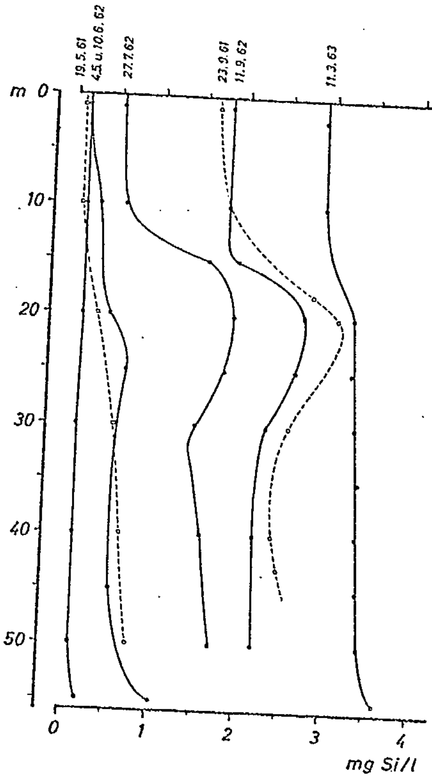

← Figure 68 - Large Ploen Lake, south basin: Stratification of dissolved silica; broken curves, 1961; continuous curves, 1962 - 1963.

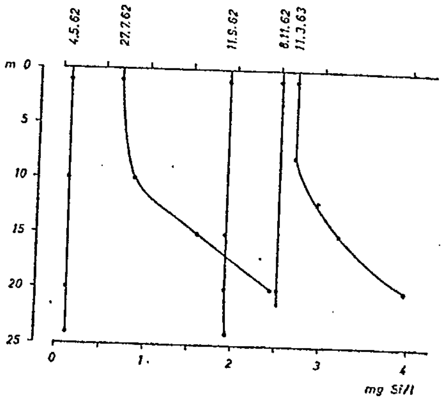

Figure 69 - Large Ploen Lake, Ascheberg area: Stratification of dissolved silica, 1962 - 1963.

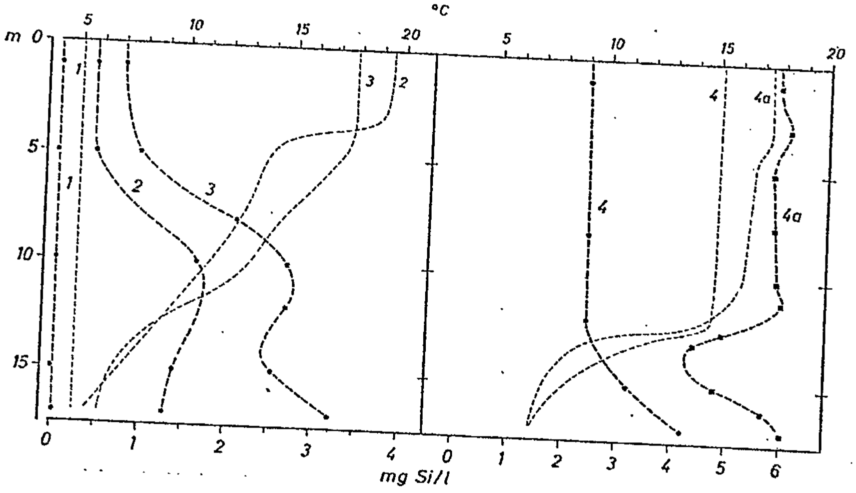

Figure 70 - Vierer Lake, south basin: Stratification of dissolved silica (heavy curves) and of temperature (light curves).

1: 16.4.62 2: 10.6.62 3: 2.8.62 4: 11.9.62 4a: 20.9.61

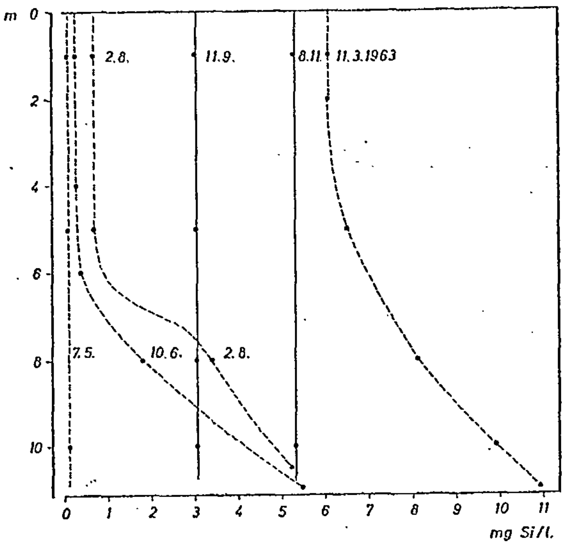

Figure 71 - Vierer Lake, north basin: Stratification of dissolved silica, May 7, 1962 to March 11, 1963.

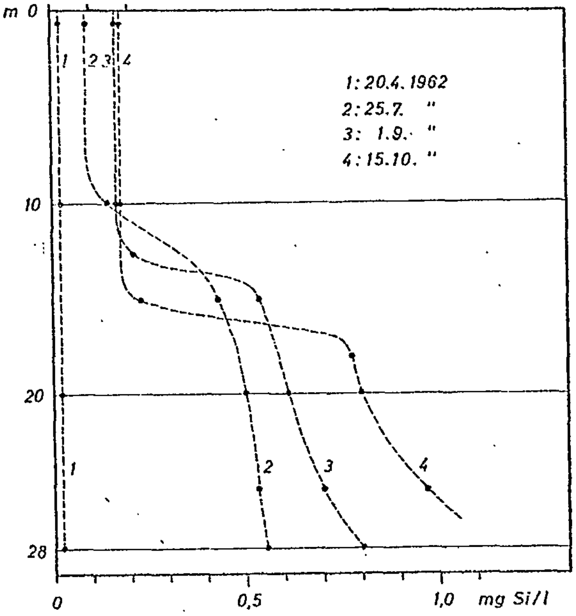

Figure 72 - Schoeh Lake: Stratification of dissolved silica, during the summer 1962 stagnation period.

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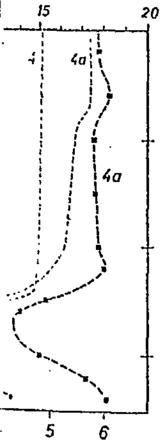

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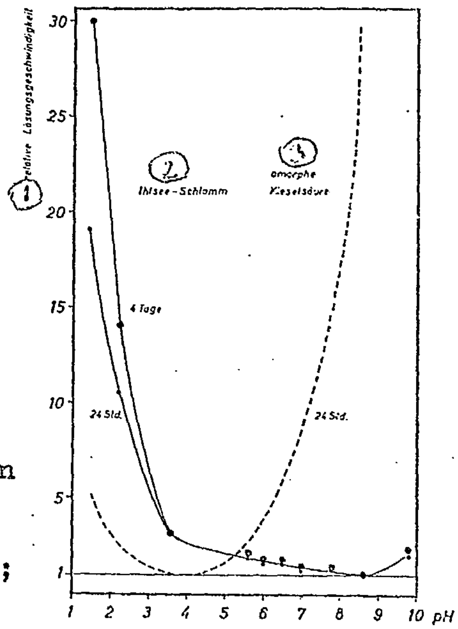


Figure 73 - Relative dissolution rates of Ihl Lake mud and of amorphous silica in dependence on the pH. Key: 1, relative dissolution rate; 2, Ihl Lake mud; 3, amorphous silica; Tage = days; Std. = hours.

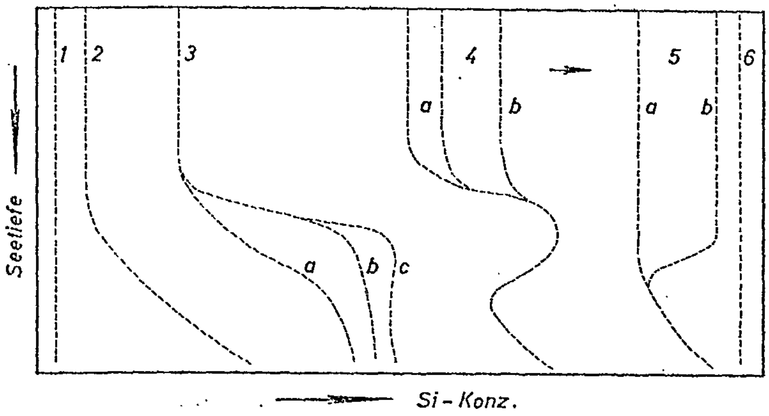


Figure 74 - Schematic representation of the types of stratification of dissolved silica observed in eastern Holstein lakes. Key: Seetiefe = lake depth; Konz. = concentration.

(1) Orthograde Si stratification (homogeneous distribution) following marked depletion during the spring; cf. Figures 20, 55, 68 to 72.

(2) Klinograde stratification curve (running toward the mud surface) obtained in lakes with weakly developed thermokline; cf. Figures 69 and 71.

(3) Klinograde stratification found in lakes with well developed thermokline: (a) Pluss Lake (Figure 26), Large Ploen Lake, April 20, 1961 (Fig. 54); (b) Schoeh Lake (Figure 72); (c) Grebin Lake, weakly developed metalimnic maximum.

(4) Heterograde stratification with metalimnic maximum (summer stratification): (a) Figures 54, 68, 70; (b) Figures 55, 61, 68.

(5) Heterograde stratification of late summer or fall: (a) developing from (4a) (Figures 54 and 70); (b) developing from (4b) (Figures 55 and 70).

(6) Orthograde stratification of complete fall and winter circulation with high Si content. Figures 17, 24, 26, 54, 55, 69 and 71.

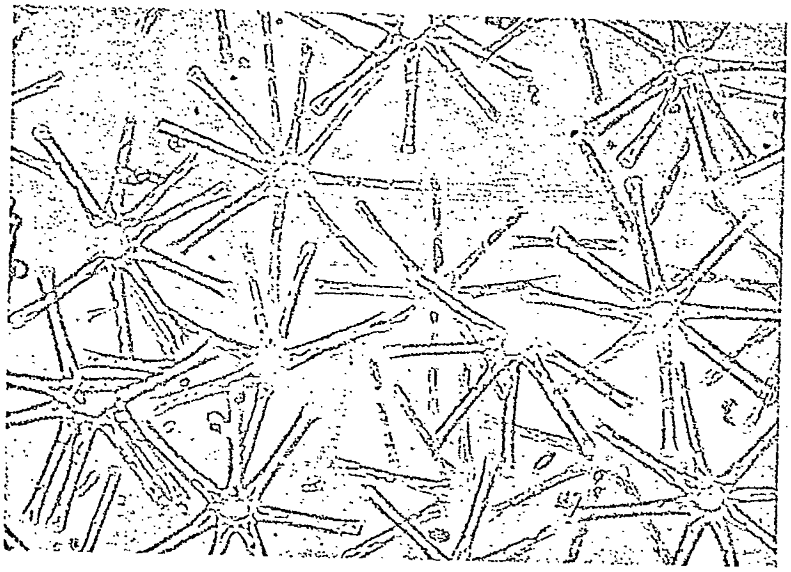


Figure 40 - Mechanical disintegration of *Asterionella formosa* by *Daphnia magna*. Initial situation (or final situation on absence of *Daphnia*).

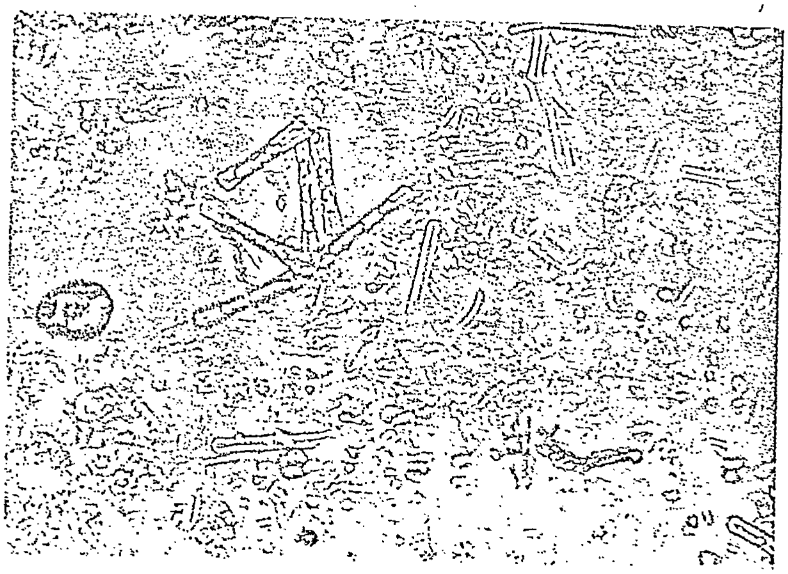


Figure 41 - As Figure 40, following exposure to *Daphnia* for six days.

Uwe Tessenow: Untersuchungen über den Kieselsäurehaushalt
der Binnengewässer

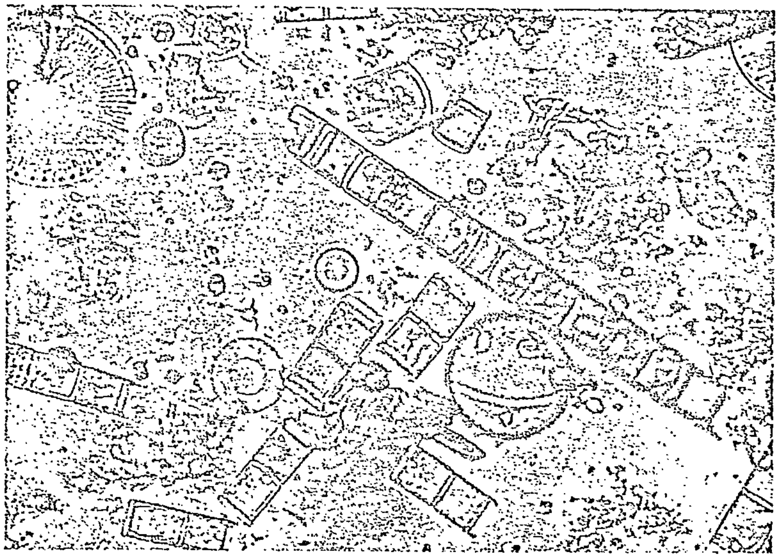
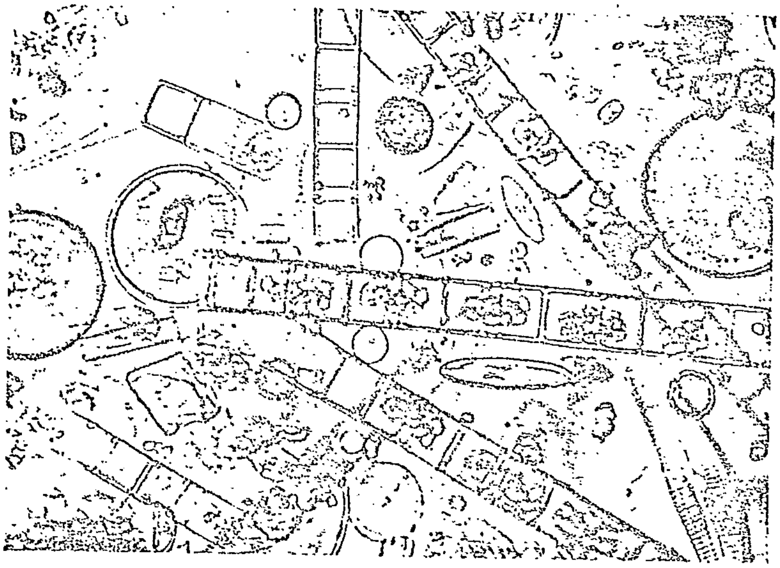


Figure 43 - Mechanical disintegration of Stephanodiscus astrae and Melosira islandica of a diatomic gyttja (Large Ploen Lake) by Daphnia magna. Initial situation (or final situation on absence of Daphnia).

Figure 44 - As Figure 43, after exposure to Daphnia for five days.

Plate 3 Tafel 3



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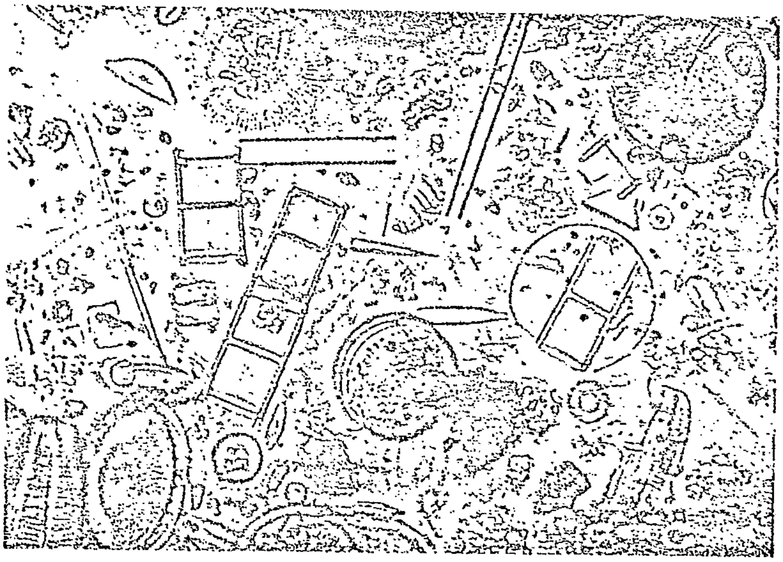

Abb. 66

Abb. 67

Figures 65 to 67 - Microphotographs of mud suspensions (0.5 g of wet mud in one liter of water), using mud samples taken at lake depth of 41, 26, and 23 meters, resp. (sedimented in 25-ml. plankton chambers).

Bibliography

ALEXANDER, G. B., HESTON, W. M., & ILER, R. K. (1954): The solubility of amorphous silica in water. — J. phys. Chem. 58: 453—455.

ALEXANDER, G. B. (1957): The efect of particle size on the solubility of amorphous silica in water. — J. phys. Chem. 61: 1563—1564.

1. ALSTERBERG, G. (1927): Die Sauerstoffschichtung der Seen. — Bot. Not. 1927: 255—274. Lund.

2. — (1928): Neue Beiträge zur Sauerstoffschichtung der Seen. Gleerupska Univ.-Bokhandeln 1928: 1—17.

3. — (1930): Die thermischen und chemischen Ausgleiche in den Seen zwischen Boden und Wasserkontakt sowie ihre biologische Bedeutung. — Int. Rev. Hydrobiol. Hydrogr. 24: 290—327.

4. BAUMANN, H. (1955): Über die Auflösung von SiO_2 im Wasser. — Beitr. Silikose-Forsch., H. 37: 45—71.

BERG, K. (1938): Studies on the bottom animals of Esrom Lake. — Kgl. Danske Vidensk. Selsk. Skr., Naturv. Math. Afd. 9,8: 1—255.

5. BERTALANFFY, L. von (1942): Theoretische Biologie. Bd. 2: 1—362. Berlin-Zehlendorf 1942.

BIRGE, E. A. & JUDAY, C. (1911): The inland lakes of Wisconsin. — Wisc. Geol. Nat. Hist. Surv. Bull. No. 22: 1—259.

6. BRÖNSTED, J. N. & WESENBERG-LUND, C. (1911/12): Chemisch-physikalische Untersuchungen der dänischen Gewässer. — Int. Rev. Hydrobiol. Hydrogr. 4: 251—290 (1911), 437—492 (1912).

7. BRUEVICH, S. V. (1953): Zur Geochemie der Kieselsäure im Meer (russ.). — Izv. Akad. Nauk. SSSR, Ser. Geol. 4: 67—79.

BUDD, S. M. (1961): The mechanism of chemical reaction between silicate glass and attacking agents. Part 1: Electrophilic and nucleophilic mechanisms of attack. — Phys. Chem. Glasses 2: 111—114.

CLARKE, F. W. (1924): The data of geochemistry. 5th Ed., Bull. U.S. geol. Surv. 770.

8. CORRENS, C. W. (1940): Über die Löslichkeit von Kieselsäure in schwach sauren und alkalischen Lösungen. — Chemie Erde 13: 92—96.

9. — (1950): Faktoren der Sedimentbildung, erläutert an Kalk- und Kieselsedimenten. — Dt. hydrogr. Z. 3: 83—88.

10. — (1951): Zur Geochemie der Diagenese. I. Das Verhalten von $CaCO_3$ und SiO_2. — Geochim. cosmochim. Acta 1: 49—54.

11. DEHN, M. VON (1931): Untersuchungen über die Verdauung bei Daphnien. — Z. vergl. Physiol. 13: 334—358.

12. EINSELE, W. & GRIM, J. (1938): Der Kieselsäuregehalt einiger planktischer Diatomeen. — Z. Bot. 32: 545—590.

13. EINSELE, W. & VETTER, H. (1938): Untersuchungen über die Entwicklung der physikalischen und chemischen Verhältnisse im Jahreszyklus in einem mäßig eutrophen See (Schleinsee). — Int. Rev. Hydrobiol. Hydrogr. 36: 285—324.

14. ELSTER, H. J. & EINSELE, W. (1937): Beiträge zur Hydrographie des Bodensees (Obersee). — Int. Rev. Hydrobiol. Hydrogr. 35: 522—585.

15. — (1938): Beiträge zur Kenntnis der Hydrographie des Untersees (Bodensee). Int. Rev. Hydrobiol. Hydrogr. 36: 241—284.

16. ELSTER, H. J. (1939): Beobachtungen über das Verhalten der Schichtgrenzen nebst einigen Bemerkungen über die Austauschverhältnisse im Bodensee (Obersee). — Arch. Hydrobiol. 35: 286—346.

17. ELSTER, H. J. & SCHMOLINSKY, F. (1954): Morphometrie, Klimatologie und Hydrographie der Seen des südlichen Schwarzwaldes. I. — Arch. Hydrobiol. Suppl. 20: 157—211.

18. ELSTER, H. J. (1955 a): Beiträge zur Limnochemie der Hochschwarzwaldseen I. — Arch. Hydrobiol. Suppl. 22: 1—64.

19. — (1955 b): Limnologische Untersuchungen im Hypolimnion verschiedener Seetypen. — Mem. Ist. Ital. Idrobiol., Suppl. 8: 83—119.

20. — (1959): Beiträge zur Limnochemie der Hochschwarzwaldseen III. — Arch. Hydrobiol. Suppl. 24: 361—384.

Emery, K. O. & Rittenberg, S. C. (1952): Early diagenesis of California Basin sediments in relation to origin of oil. — Am. Ass. Petrol. Geol. Bull. 36: 735—806.

21. Findenegg, I. (1935): Limnologische Untersuchungen an Kärntner Seen. — Int. Rev. Hydrobiol. Hydrogr. 32: 369—423.

22. Fritz, Fr. (1935): Über die Sinkgeschwindigkeit einiger Phytoplanktonorganismen. — 32: 424—431.

Gardner, L. U. (1938): Reaction of the living body to different types of mineral dusts with and without complicating infection. — Amer. Inst. Min. Metall. Engrs., tech. Publs. 929: 1—15.

23. Gessner, F. (1934): Nitrat und Phosphat im dystrophen See. — Arch. Hydrobiol. 27: 131—161.

24. — (1959): Hydrobotanik II: 1—701. Stoffhaushalt. — VEB Deutscher Verlag der Wissenschaften, Berlin.

Goltermann, H. L. (1960): Studies on the cycle of elements in fresh water. — Acta bot. neerl. 9: 1—58.

Greenberg, S. A. & Price, E. W. (1957): The solubility of silica in solutions of electrolytes. — J. phys. Chem. 61: 1539—1541.

25. Grim, J. (1939): Beobachtungen am Phytoplankton des Bodensees (Obersee) sowie deren rechnerische Auswertung. — Int. Rev. Hydrobiol. Hydrogr. 39: 193—314.

Hart, T. J. (1934): On the phytoplankton of the south-west Atlantic and the Bellingheusen Sea 1929—31. — Discovery Reports 8: 1—268.

— (1942): Phytoplankton periodicity in Antarctic surface waters. — Discovery Reports 21: 261—356.

26. Helmcke, J. G. (1954): Die Feinstruktur der Kieselsäure und ihre physiologische Bedeutung in Diatomeenschalen. — Naturwiss. 41: 254—255.

Hughes, I. C. & Lund, J. W. G. (1962): The rate of growth of Asterionella formosa Hass. in relation to its ecology. — Arch. Mikrobiol. 42: 117—129.

Hutchinson, G. E. (1938): Chemical stratification and lake morphology. — Proc. National Acad. Sci. 24: 63—69.

— (1941): Limnological studies in Connecticut: IV. Mechanism of intermediary metabolism in stratified lakes. — Ecol. Monogr. 11: 21—60.

— (1957): A Treatise on Limnology, 1: 1—1015. Geography, Physics and Chemistry. — John Wiley and Sons, Ind., New York; Chapman and Hall, Ltd., London.

Iler, R. K. (1955): The colloid chemistry of silica and silicates: 1—324. Ithaca, New York: Cornell University Press 1955.

27. Jander, H. & Heukeshoven, W. (1931): Über amphotere Oxydhydrate, deren wäßrige Lösungen und kristallisierende Verbindungen. 8. Mitt.: Über Kieselsäuren und gelöstes Siliciumdioxydhydrat in alkalischen und sauren Lösungen. — Z. anorg. allg. Chemie 201: 361—382.

28. Järnefelt, H. (1955): Über die Sedimentation des Sestons. — Verh. Int. Verein. Limnol. 12: 144—158.

29. — (1963): Zur Limnologie einiger Gewässer Finnlands XIX. — Ann. Zool. Soc. zool. bot. fenn. „Vanamo" 24: (No. 7): 1—118.

Jones, L. H. P. & Handreck, K. A. (1963): Effects of iron and aluminium oxides on silica in solution in soils. — Nature 198: 852—853.

Jörgensen, E. G. (1953): Silicate assimilation by diatoms. — Physiologica Plantarum 6: 301—315.

— (1955 a): Solubility of the silica in diatoms. — Physiologica Plantarum 8: 846—851.

— (1955 b): Variations in the silica content of diatoms. — Physiologica Plantarum 8: 840—845.

— (1957): Diatom periodicity and silicon assimilation. — Dansk. bot. Ark. 18: 6—54.

30. Kann, E. (1940): Ökologische Untersuchungen an Litoralalgen ostholsteinischer Seen. — Arch. Hydrobiol. 37: 177—269.

31. Kautsky, H., Pfleger, H., Reise, R. & Vogell, W. (1962): Lepidoide, 7. Mitteilung: Lösungsgleichgewicht, Lösungsvorgang und Kolloidstruktur der Kieselsäure. — Z. Naturforsch. 17b: 491—499.

King, E. J. & Lucas, C. C. (1928): The use of picric acid as an artificial standard in the colorimetric estimation of silica. — J. Amer. Chem. Soc. 50: 2395—2397.

King, E. J. (1939): The biochemistry of silicid acid. VIII. The determination of silica. — Biochem. J. 33: 944—954.

Kobayashi, J. (1960): A chemical study of the average quality and characteristics of river waters of Japan. — Ber. Ohara Inst. landw. Biol., Okayama Univ. 11: 313—357.

Krauskopf, K. B. (1956): Dissolution and precipitation of silica at low temperatures. — Geochim. cosmochim. Acta 10: 1—26.

Laaksonen, R. (1956): On variations in the silica content of some ponds. — Arch. Soc. Zool. Bot. Fenn. „Vanamo“ 10: 161—163.

Lenher, V. & Merrill, H. B. (1917): The solubility of silica. — J. Amer. Chem. Soc. 39: 2630—2638.

Lewin, J. C. (1954): Silicon metabolism in diatoms. I. Evidence for the role of reduced sulfur compounds in silicon utilization. — J. gen. Physiol. 37: 589—599.

— (1955): Respiration and silicon uptake in Navicula pelliculosa. — J. gen. Physiol. 39: 1—10.

— (1961): The dissolution of silica from diatom walls. — Geochim. cosmochim. Acta 21: 182—198.

Lier, J. A. van, Bruyn, P. L. de, & Overbeek, J. T. G. (1960): The solubility of quartz. — J. phys. Chem. 64: 1675—1682.

32. Löffler, H. (1960): Limnologische Untersuchungen an chilenischen und peruanischen Binnengewässern. — Ark. Geofys. 3: 155—254.

33. Lundbeck, J. (1926): Die Bodentierwelt norddeutscher Seen. — Arch. Hydrobiol. Suppl. 7: 1—473.

Marshall, S. M. & Orr, A. P. (1962): Food and feeding in Copepods. — Rapp. Procès-Verbaux des Réunions 153: 92—98.

McKeague, J. A. & Cline, M. G. (1963): Silica in soil solutions, I and II: Can. J. Soil Sci. 43: 70—96.

Meloche, V. W., Leader, G., Safranski, L., & Juday, C. (1938): The silica and diatom content of Lake Mendota water. — Trans. Wisc. Acad. Sci., Arts and Lett. 31: 363—376.

Morey, G. W., Fournier, O., & Rowe, J. J. (1962): The solubility of quartz in water in the temperature interval from 25° to 300° C. — Geochim. cosmochim. Acta 26: 1029—1043.

Mortimer, C. H. (1941/42): The exchange of dissolved substances between mud and water in lakes. — J. Ecol. 29: 280—329; 30: 147—201.

Mullin, I. B. & Riley, I. P. (1955): The colorimetric determination of silicate with special reference to sea and natural waters. — Analytica chim. Acta 12: 162—176.

34. Nauwerck, A. (1963): Die Beziehungen zwischen Zooplankton und Phytoplankton im See Erken. — Symb. bot. Upsal. 17; 5: 1—163.

O'Connor, T. L. & Greenberg, S. A. (1958): The kinetics for the solution of silica in aqueous solutions. — J. phys. Chem. 62: 1195—1198.

35. Ohle, W. (1931): Eine Selbstauslösevorrichtung zur Entnahme von bodennahen Wasserproben in Seen. — Arch. Hydrobiol. 23: 690—693.

36. — (1934): Chemische und physikalische Untersuchungen norddeutscher Seen. — Arch. Hydrobiol. 26: 386—658.

37. — (1940): Chemische Eigenart der smäländischen Seen. — Verh. Int. Verein Limnol. 9: 145—159.

38. — (1952): Die hypolimnische Kohlendioxydakkumulation als produktionsbiologischer Indikator. — Arch. Hydrobiol. 46: 153—285.

39. — (1953 a): Phosphor als Initialfaktor der Gewässereutrophierung. — Jb. Vom Wasser 20: 11—23.

40. — (1953 b): Der Vorgang rasanter Seenalterung in Holstein. — Naturwiss. 40: 153—162.

41. — (1955 a): Die Ursachen der rasanten Seeneutrophierung. — Verh. Int. Verein. Limnol. 12: 373—382.

42. — (1955 b): Beiträge zur Produktionsbiologie der Gewässer. — Arch. Hydrobiol. Suppl. 22: 456—479.

43. — (1958 a): Typologische Kennzeichnung der Gewässer auf Grund ihrer Bioaktivität. — Verh. Int. Verein. Limnol. 13: 196—211.

44. — (1958 b): Die Stoffwechseldynamik der Seen in Abhängigkeit von der Gasausscheidung ihres Schlammes. — Jb. Vom Wasser 25: 127—149.

45. — (1959): Die Seen Schleswig-Holsteins, ein Überblick nach regionalen, zivilisatorischen und produktionsbiologischen Gesichtspunkten. — Jb. Vom Wasser 26: 16—41.

46. — (1962): Der Stoffhaushalt der Seen als Grundlage einer allgemeinen Stoffwechseldynamik der Gewässer. — Kieler Meeresforsch. 18: 107—120.

47. — (1964): Kolloidkomplexe als Kationen- und Anionenaustauscher in Binnengewässern. — Jb. Vom Wasser 30: 50—64.

Okamoto, G., Okura, T., & Goto, K. (1957): Properties of silica in water. — Geochim. cosmochim. Acta 12: 123—132.

48. Olszewski, P. (1963): Wirbelströmungen in den Hypolimnien der Seen. — Schweiz. Z. Hydrol. 25: 1—8.

49. Rogall, E. (1939): Über den Feinbau der Kieselmembran der Diatomeen. — Planta 29: 279—291.

50. — (1959): Betrachtungen über den Feinbau der Diatomeen. — Nova Hedwegia 1: 309—313.

51. Ruttner, F. (1931): Hydrographische und hydrochemische Beobachtungen auf Java, Sumatra und Bali. — Arch. Hydrobiol. Suppl. 8: 197—454.

52. Schmidt, K. G. & Lüchtrath, H. (1955): Vergleich der Wirkungen von Quarz-, Cristobalit- und Tridymitstaub im intratrachealen Tierversuch mit Ratten. — Beitr. Silikose-Forsch. 37: 1—43.

53. Sioli, H. (1950): Das Wasser im Amazonasgebiet. — Forsch. Fortschr. 26: 274—280.

Stangenberg, M. (1961): Some remarks on the determination and the content of silica in lake waters. — Mem. Ist. Ital. Idrobiol. 13: 17—42.

54. Stöber, W. (1956): Über die Löslichkeit und das Lösungsgleichgewicht von Kieselsäuren. — Kolloid Z. 147: 131—141.

55. — (1957): Zur Berechnung des Polykondensationsgleichgewichtes der Kieselsäuren. — Kolloid Z. 151: 42—47.

56. Struckmann, C. (1855): Über die Zersetzung der alkalischen Silicate durch Kohlensäure und über die Löslichkeit der Kieselsäure in reinem Wasser sowie bei Gegenwart von Salzsäure, Kohlensäure, Ammoniak, Salmiak und Bicarbonaten. — Ann. Chem. Pharm., N. R. 18: 337—347.

57. Tessenow, U. (1964): Experimentaluntersuchungen zur Kieselsäurerückführung aus dem Schlamm durch Chironomidenlarven (Plumosus-Gruppe). — Arch. Hydrobiol. 60: 497—504.

58. Thienemann, A. (1928): Der Sauerstoff im eutrophen und oligotrophen See. — Die Binnengewässer 4: 1—175.

59. Ule, W. (1891): Die Tiefenverhältnisse der ostholsteinischen Seen. — Jb. k. preuß. geol. Landesanst. 1890: 102—127. Berlin.

60. Ungemach, H. (1960): Sedimentchemismus und seine Beziehungen zum Stoffhaushalt in 40 europäischen Seen. — Dissertation, Kiel. 1—420.

61. Utermöhl, H. (1925): Limnologische Phytoplanktonstudien. — Arch. Hydrobiol. Suppl. 5: 1—527.

62. Vetter, H. (1937): Limnologische Untersuchungen über das Phytoplankton und seine Beziehungen zur Ernährung des Zooplanktons im Schleinsee bei Langenargen am Bodensee. — Int. Rev. Hydrobiol. Hydrogr. 34: 285—324.

63. Wotinzew, K. K. (1948): Die Rolle der Schwämme in der Dynamik der Kieselsäure im Baikalsee (russ.). — Dokl. Akad. Nauk. SSSR 62: 661—663.

64. Wattenberg, H. (1931): Die Bestimmung von Phosphat, Nitrat, Nitrit, Ammoniak und Silikat im Meerwasser. — Ann. Hydrogr. Berlin: 95—106.

65. Wawrik, F. (1960 a): Kieselsäurehaushalt und Diatomeenvegetation im Lunzer Untersee und in benachbarten Fließgewässern, einschließlich der Ybbs. — Wasser und Abwasser 2: 108—132.

66. — (1960 b): Die Jaidhof-Teiche. — Sitzungsber. Österr. Akad. Wiss., Math.-nat. Kl., Abt. I, 169: 341—381.

67. — (1962): Zur Frage: Führt der Donaustrom autochthones Plankton? — Arch. Hydrobiol. Suppl. 27: 28—35.

68. Wegemann, G. (1915): Die Seen Mittelholsteins. — Abh. k. preuß. geol. Landesanst., N. F., H. 64: 108—116.

69. — (1922): Die Seen Ostholsteins: 1—48. Verl.: W. G. Mühlau Kiel.

70. Weitz, E., Franck, H. & Schuchard, M. (1950): Über die Kieselsäure und die Silikate. — Chemikerzeitung 74: 256—257.

Yoshimura, S. (1939): Seasonal variations in the silica- and diatom-contents of the water of Takasuka Pond, Saitama, Japan. — Jubilee Publication in the Commemoration of Prof. H. Yabe's 60th Birthday: 261—282.

71. Züllig, H. (1956): Sedimente als Ausdruck des Zustandes eines Gewässers. — Schweiz. Z. Hydrol. 18: 5—143.

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