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Aus dem Institut für Meereskunde an der Universität Kiel

A Study of the Variability in the Hydrochemical Factors in the Baltic Sea on the Basis of two Anchor Stations September 1967 and May 1968

by

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(Summary): The present study was undertaken to investigate the physical and chemical variability in the eastern Gotland Basin. This can serve as an example for the variability in the inner part of an adjacent sea with small tidal influence. Two anchor stations of about four days duration were made, with R.V. „Alkor" in September 1967 and with F.R.V. „Anton Dohrn" in May 1968. On the basis of variations in the physical parameters, and also from continuous recordings of salinity and temperature, c.f., of oxygen and temperature, the presence of internal waves is demonstrated. The variability in the chemical data not only indicate internal waves but also proves the patchlike structure of the water masses with regard to biochemical parameters. The two anchor stations were made during periods of partial and of total stagnation in the deeper parts of the Gotland Basin.

Beobachtungen über die Veränderlichkeit in den hydrochemischen Parametern auf Basis zweier Ankerstationen in der Ostsee im September 1967 und im Mai 1968 (Zusammenfassung): Ziel dieser Arbeit ist eine Beschreibung der physikalisch chemischen Veränderlichkeit im östlichen Gotland-Becken, und zwar als Beispiel für die Veränderlichkeit im inneren Teil eines gezeitenarmen Nebenmeeres. Zwei viertägige Ankerstationen wurden durchgeführt, im September 1967 und Mai 1968, mit „Alkor" und „Anton Dohr". Auf Grund der Variationen in den physikalischen Parametern und auch von den kontinuierlichen Registrierungen von Salzgehalt und Temperatur, bzw. von Sauerstoff und Temperatur, werden interne Wellen nachgewiesen. Von der Veränderlichkeit der chemischen Parameter werden neben internen Wellen auch wolkenartige Strukturen der Wassermassen im Bezug auf biochemische Eigenschaften demonstriert. Beide Dauerstationen fielen in einer Periode von teilweiser und von voller Stagnation im Gotland-Becken.

Introduction

For the study of the physical and the chemical parameters in the Baltic Sea it is necessary to have information on the short time variations in space and time of these parameters. DIETRICH (1966) pointed at the necessity to make such studies in the open ocean, but, of course, in basins like the Baltic Sea the study of the variability is equally important. Especially in the Baltic Sea large variations can be expected, as was amply shown by WÜST (1957), BANSE (1957), and KREY (1957). Wüst indicated that a continuous registration of the vertical distribution of temperature and salinity is of great importance in order to gain insight in the various processes that cause the layering of the water masses in the Baltic Sea.

DIETRICH (1961), KRAUSS and MAGAARD (1961), SIEDLER (1961), and JACOB (1961) studied the short time variations in the layering of the Baltic Sea in the summer of 1960. The results showed large variations in the vertival structure of the water masses with regard to temperature, salinity, and also the chemical data, especially in the Arkona Basin and in the Bornholm Basin. In the western Gotland Sea, however, the temperature profile also shows a detailed structure (SIEDLER, 1961).

The anchor stations, that were made for the studies, as mentioned in the above paragraph, were generally of short duration. HELA and KRAUSS (1959) made longer stations in the Arkona Basin. In this area large variations occur not only due to internal

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waves, but also because of the complicated mixing processes that characterize this area of the Baltic Sea. In the Gotland Deep no anchor stations of longer duration have been made for the study of the variability of hydrochemical factors. The Gotland Deep is particularly suited for a study of the time dependent variability of these factors, because no great changes due to mixing processes as, e.g., in the Arkona Basin, can be expected. Another reason for choosing this area for an anchor station is that in the Gotland Deep periodic stagnation occurs (FONSELIUS 1962, 1967a, KALEIS et AL 1968). A study of the variability in the area of the Gotland Deep can serve as an example for the variability in the inner part of an adjacent sea with small tidal influence.

The first anchor station was made in the late summer of 1967 and the second in the early spring of 1968. The general location of the anchor stations and of two relevant sections across the Gotland Deep are presented in Figure 1 (Plate 1).

Methods

Both continuous registrations of oxygen and temperature, and of salinity and temperature were made. Furthermore water samples were obtained with classical Nansen casts. These samples were analysed for nutrient components, as well as for the pH, alkalinity, and dissolved oxygen.

The oxygen temperature probe has been descibed by GRASSHOFF (1963), and the present modification is discussed in this volume by GRASSHOFF (1969).

The salinity temperature sensor is based on the sensor developed by KOSKE (1963, 1964). The accuracy of the sensor has been discussed by GIESKES (1967), and has been confirmed in these surveys.

Nutrient analysis was carried out for the following components: nitrate, nitrite, ammonia, dissolved inorganic phosphate, and silicate. All determinations were made with the Auto-Analyser system. The methods used are described by GRASSHOFF (1969b).

Dissolved oxygen was determined by means of the Winkler method.

Hydrogen sulphide was measured with the method described by FONSELIUS (1962).

Salinity was measured with a Brown and Hamon type (1961) extended range salinometer. The accuracy of this methods is not better than ± 0,01 $^{0}/oo$, as has been pointed out by PARK (1968) an GRASSHOFF (1968).

In general the reproducibility of the methods is larger than the accuracy. The accuracy is not better than that discussed by the various authors in their reports on the recent intercalibration exercises of the ICES countries (UNESCO 1968).

Work schedule at the anchor stations

The anchor stations were made at a depth of about 240 meters. Every three hours a hydrographic cast taken for the analysis of the salinity, the dissolved oxygen, and the nutrient components. Also hydrogen sulphide was determined, whenever present. The automatic analysis makes a rythm of three hours very well possible, because this way of

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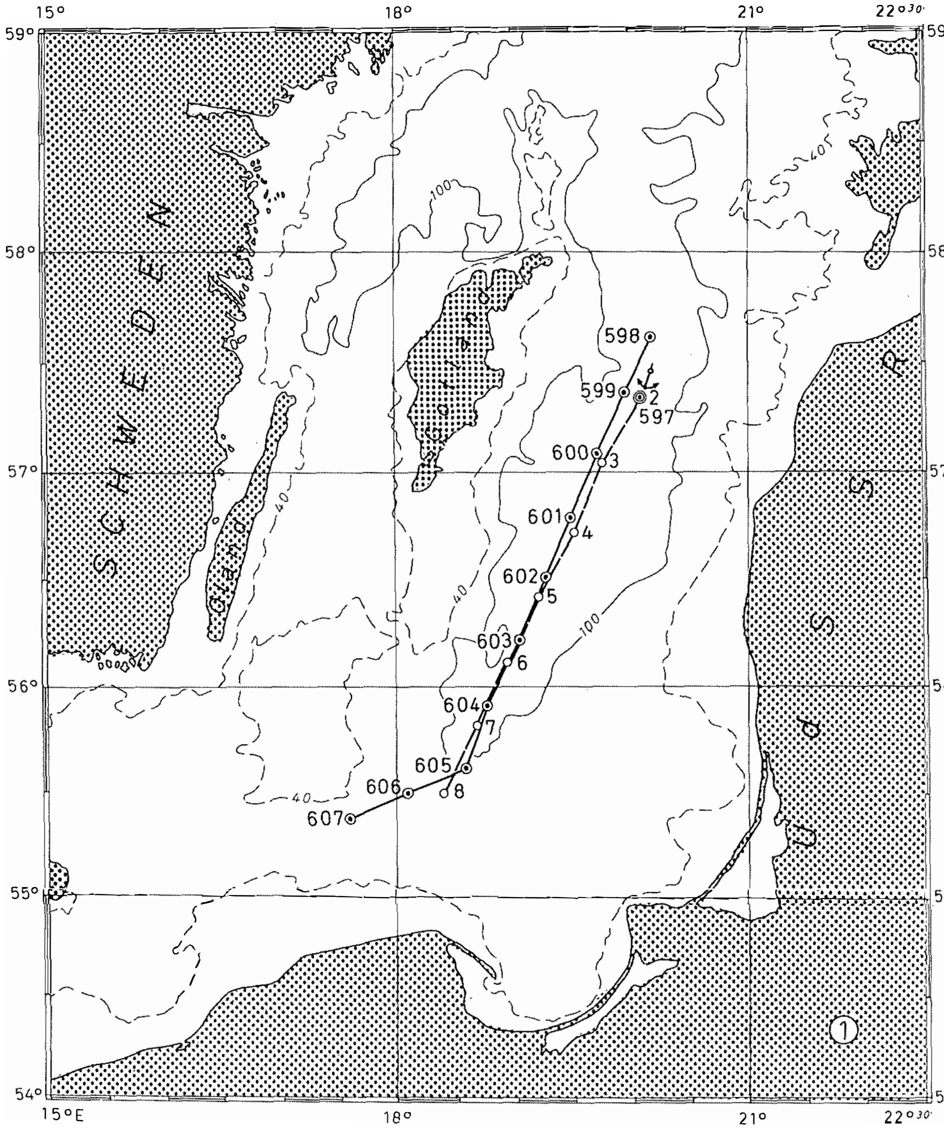
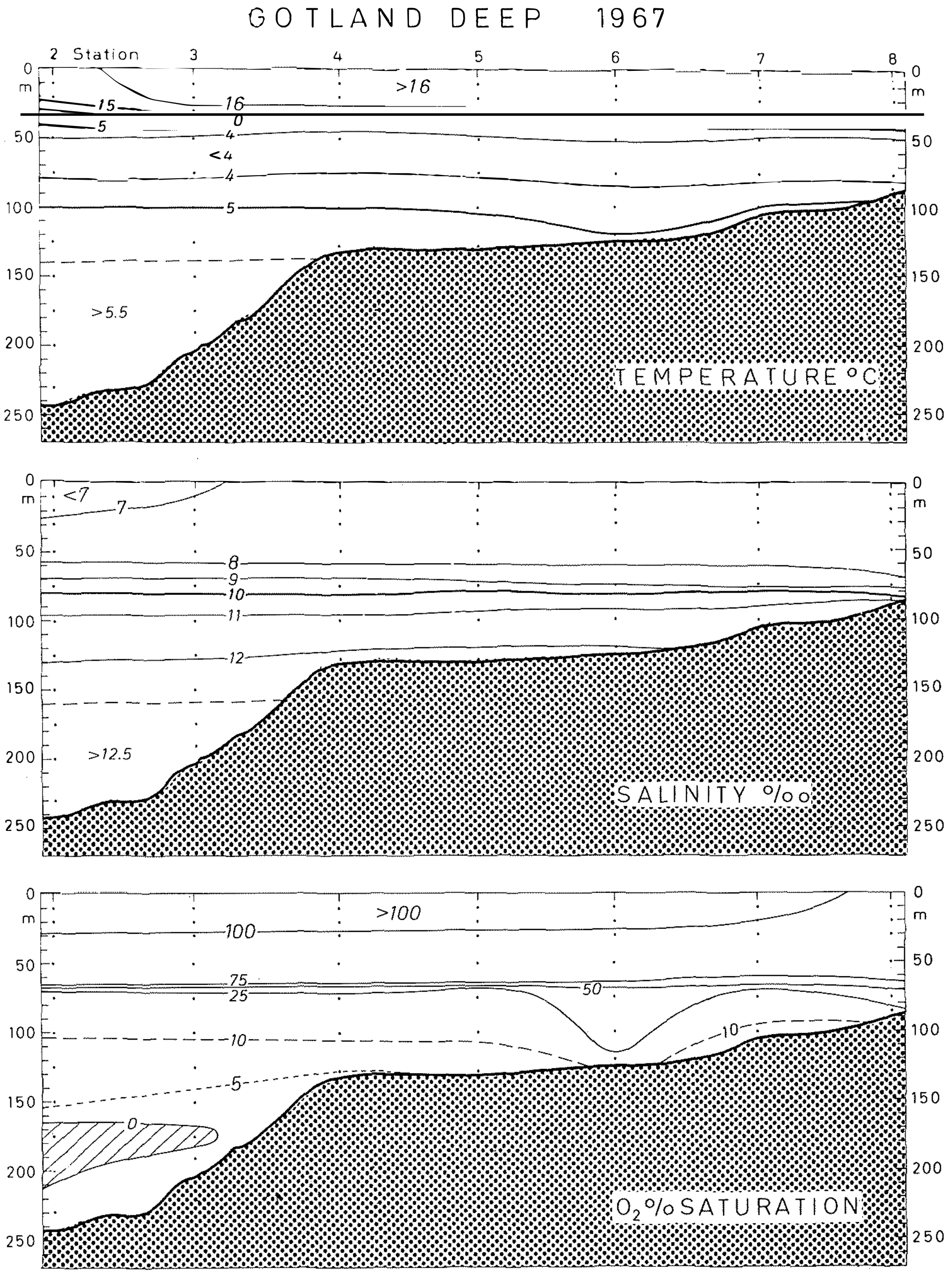
Plate 1
Figure 1: Map of the area of investigation

Plate 2
Figure 2: Hydrographic section across the Gotland Deep September 1967
The dashed area indicates the zone with hydrogen sulphide



Tafel 1 (zu Gieskes/Graßhoff)



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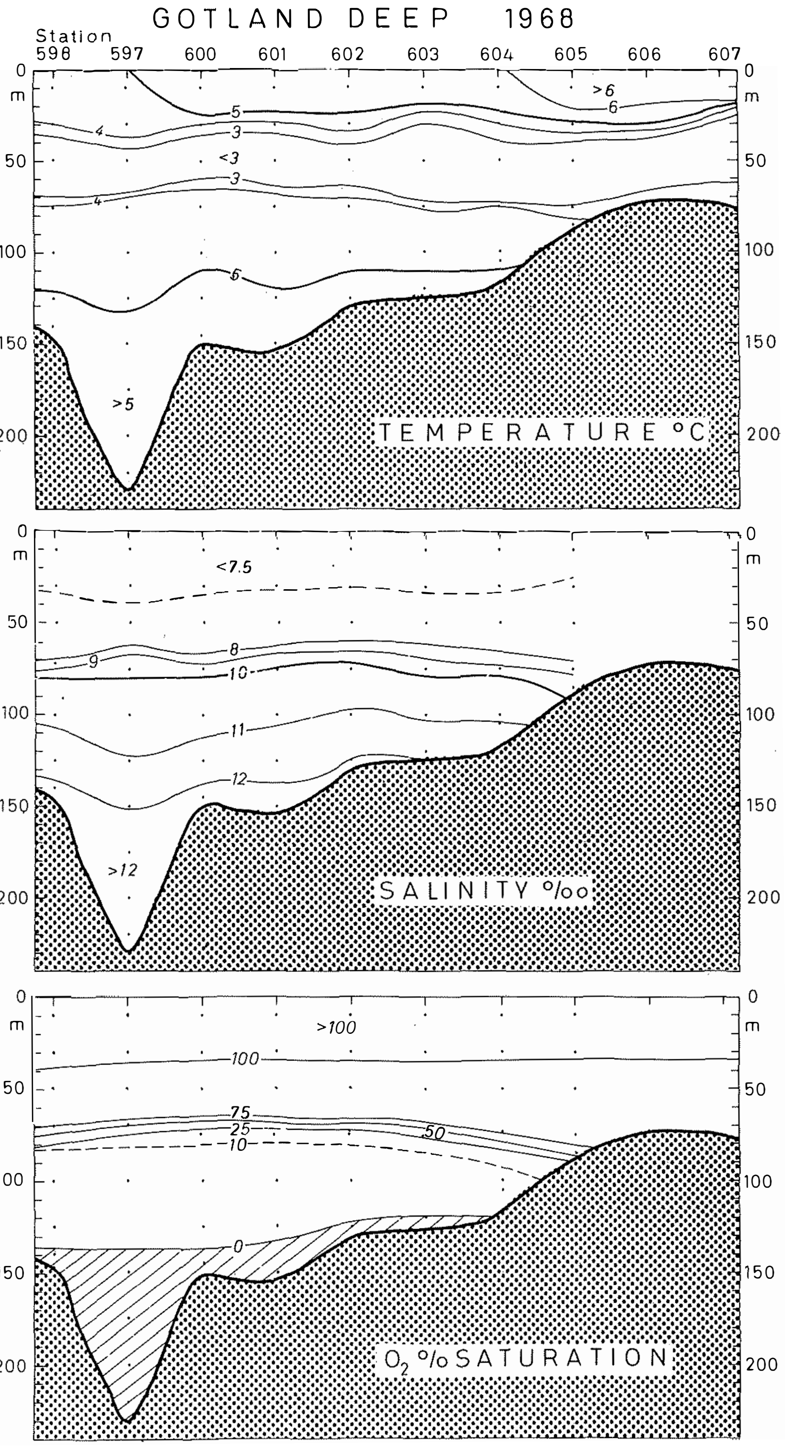

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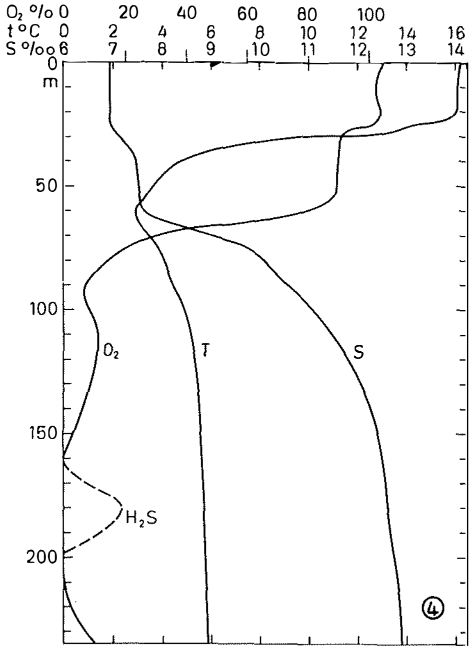
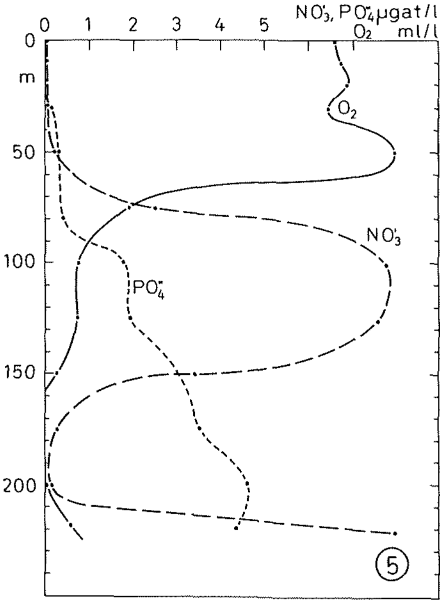
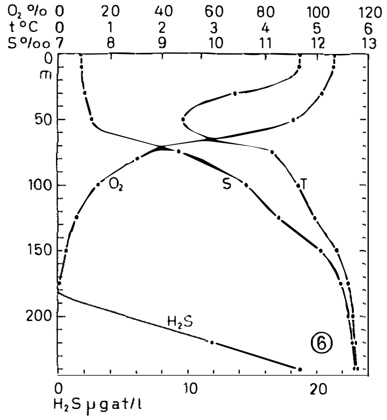
Tafel 3 (zu Gieskes/Graßhoff)

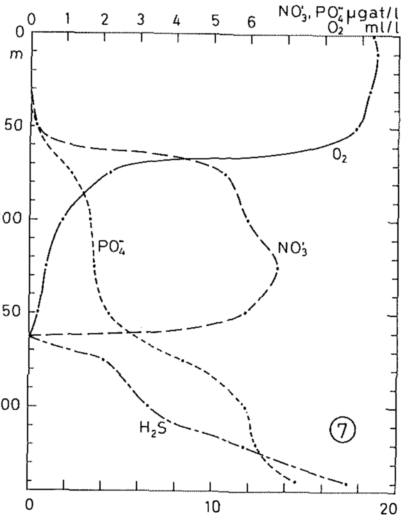
GOTLAND DEEP 1967





GOTLAND DEEP 1968





Tafel 4 (zu Gieskes/Graßhoff)

analysis is much less cumbersome and time consuming than the traditional manual methods.

At the other full hours either an oxygen temperature registration, or a salinity temperature registration were carried out.

In this manner we obtained 46 hydrographic casts, oxygen temperature, and salinity temperature records in September 1967, and 35 of these in May 1968.

Simultaneously a set of six current meters were moored near the ship in September 1967. On the data obtained with these instruments will be reported by HOLLAN (1969) in this volume.

Furthermore analyses were carried out for dissolved and particulate organic carbon and nitrogen. The results of these measurements will be presented by EHRHARDT (1969).

The results of the two anchor stations will be discussed in such a manner, that for every topic under discussion an attempt will be made to compare the results of the two anchor stations.

A. Hydrography

Here we shall discuss the results obtained with the Nansen casts. Only the distribution of the parameters, that are of importance for the characterization of the water masses, shall be taken into consideration.

1. The hydrographic sections

During the spring and summer of 1967 the hydrographic situation is characterised by the disappearance of the hydrogen sulphide in the layers just above the bottom in the Gotland Deep, as was shown by FONSELIUS (1967 a, loc.cit.). Fonselius noticed a tongue shaped distribution of hydrogen sulphide in the Gotland Deep basin, and this same situation was found in September 1967. In Figure 2 (Plate 2) the data ara presented for the hydrographic section as given in Figure 1, Station 2 to 8. The tongue shaped distribution was explained by Fonselius as due to the inflow of new, slightly oxygenated water. It seems that in September this same situation still persists.

In May 1968 the situation has changed radically. Again we observe stagnation, as is amply demonstrated in Figure 3 (Plate 3). From a depth of 135 meters to the bottom hydrogen sulphide is present in ever increasing quantities. The inflow of new bottom water must have stopped. Interesting to note is, that the salinity in the depth of 230 meters has decreased from an average of 12.85 $^{o}/oo$ to 12.68 $^{o}/oo$, and also the temperature has decreased from $5.83^{o}C$ to $5.75^{o}C$. From this it would appear that during

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Plate 3
Figure 3: Hydrographic section across the Gotland Deep May 1968
The dashed area indicates the zone with hydrogen sulphide

Plate 4
Figure 4: Vertical Distribution of t, S, H_2S, and oxygen saturation September 9th, 1967, 15.00 h at Station 2
Figure 5: Vertical Distribution of O_2, NO^{-}, and PO_4^{---} September 9th, 1967, 09.00 h at Station 2
Figure 6: Vertical Distribution of t, S, H_2S, and oxygen saturation May 8th, 1968, 06.00 h at Station 597
Figure 7: Vertical distribution of O_2, H_2O, NO_3^{-}, and PO_4^{---} May 11, 1968, 18.00 h at Station 597

winter a gradual mixing has taken place in the lowest layers in the Gotland Deep. Presumably, after the gradual reduction of the inflow along the bottom, this mixing process has gained in importance. After this the conditions for total stagnation became again ideal.

For both of the anchor stations there were, therefore, two quite different states in the Gotland Basin. Also large differences in the vertical distribution of the various physical and chemical parameters are apparent. In Figure 4 (Plate 4) a typical vertical distribution of temperature, salinity, and oxygen saturation, c.f. hydrogen sulphide, is presented. The hydrographic cast was taken on September 9th, 1967 at 15.00 h. A very large and pronounced thermocline is present in a depht of about 30 meters, and this is accompanied by a weak halocline. At a depth of about 65 meters the large halocline becomes apparent, together with the less pronounced thermocline. From this we can clearly discern the usual three different water masses (WÜST, 1957), that characterize the Gotland Basin in summer: the warm summer water layer of low salinity, the Baltic winter water layer with a cold temperature and a slightly higher salinity, and finally the Baltic deep water with an increasing salinity and temperature right to the bottom. The dissolved oxygen shows supersaturation in the surface layer, 90 % saturation in the winter water layer, followed by a rapid decrease below the main halocline. At a depth of 120 meters a small maximum can be observed, but the dissolved oxygen disappears below 160 meters, to be replaced by hydrogen sulphide (no quantitative scale given in Fig. 4). Below a depth of 200 meters the dissolved oxygen reappears, thus indicating an inflow of relatively well oxygenated water. In Figure 5 (Plate 4) the distribution of the chemical parameters, as found on September 9th, 1967 at 09.00 h, is presented. The distribution of the nitrate and also of the phosphate show that these parameters are useful for the characterization of the water masses. Just below the main halocline a sharp rise in nitrate and phosphate can be observed. It should be noted that nitrite does only occur in the winter water layer, indicating a possible oxidation of ammonia or of organic nitrogen compounds. The slight minimum in the nitrogen/carbon ratio of particulate matter as reported by EHRHARDT (1969, loc.cit.) in this layer, may well indicate the beginning of a nitrification process, one of the first products being nitrite. In the lower layers, where the dissolved oxygen disappears completely, also the nitrate vanishes. At the same time the phosphate content increases in this layer. This is, of course, due to the denitrification processes, which are involved in the anoxic oxidation of organic matter. Similarly the sulphate reduction is accompanied by an increase in the phosphate. RICHARDS (1965) discusses these processes in detail, but we shall return to this subject later. Near the bottom simultaneous with the increase in the dissolved oxygen also the nitrate concentration rises again very sharply. The concentration of the dissolved inorganic phosphate shows a very slight decrease.

The situation on May 8th, 1968 at 06.00 h is presented in Figure 6 (Plate 4). The summer surface layer is forming already, with again a slightly lower salinity than the winter water layer. The difference in salinity, however, is much less than in September 1967. It seems that with the gradual increase in temperature of the surface layers also a gradual decrease in the salinity of the surface water may develop during the summer period. Presumably this is due to the net outflow in the southerly direction. In winter this southward flowing water would mix with the winter water layer. In May, however, the

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Plate 5

Figure 8: Variations in time of the temperature at Station 2 at various depths

Figure 9: Variations in time of the salinity at Station 2 at various depths

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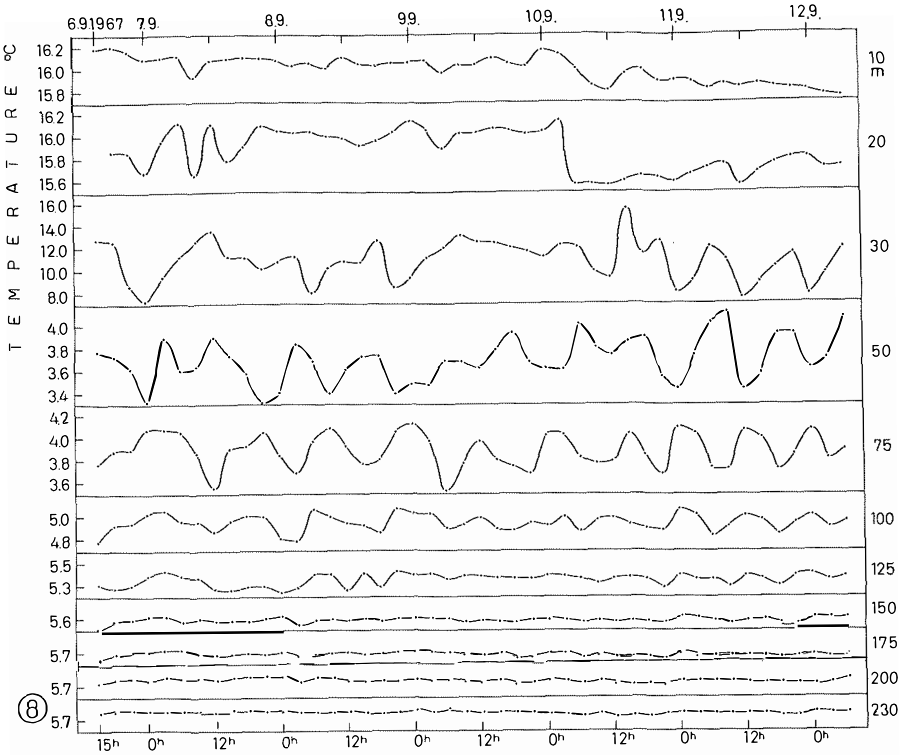

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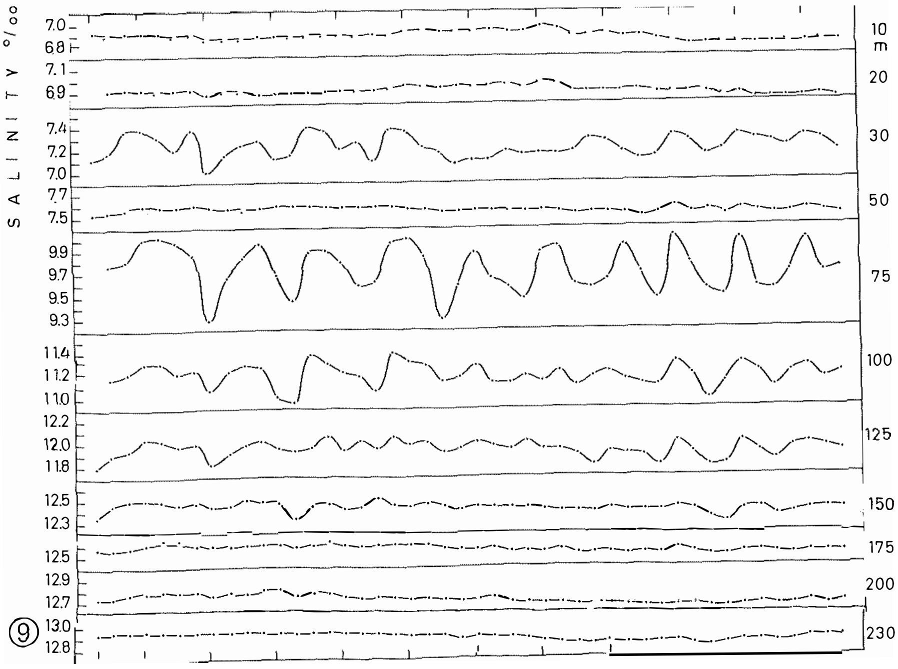
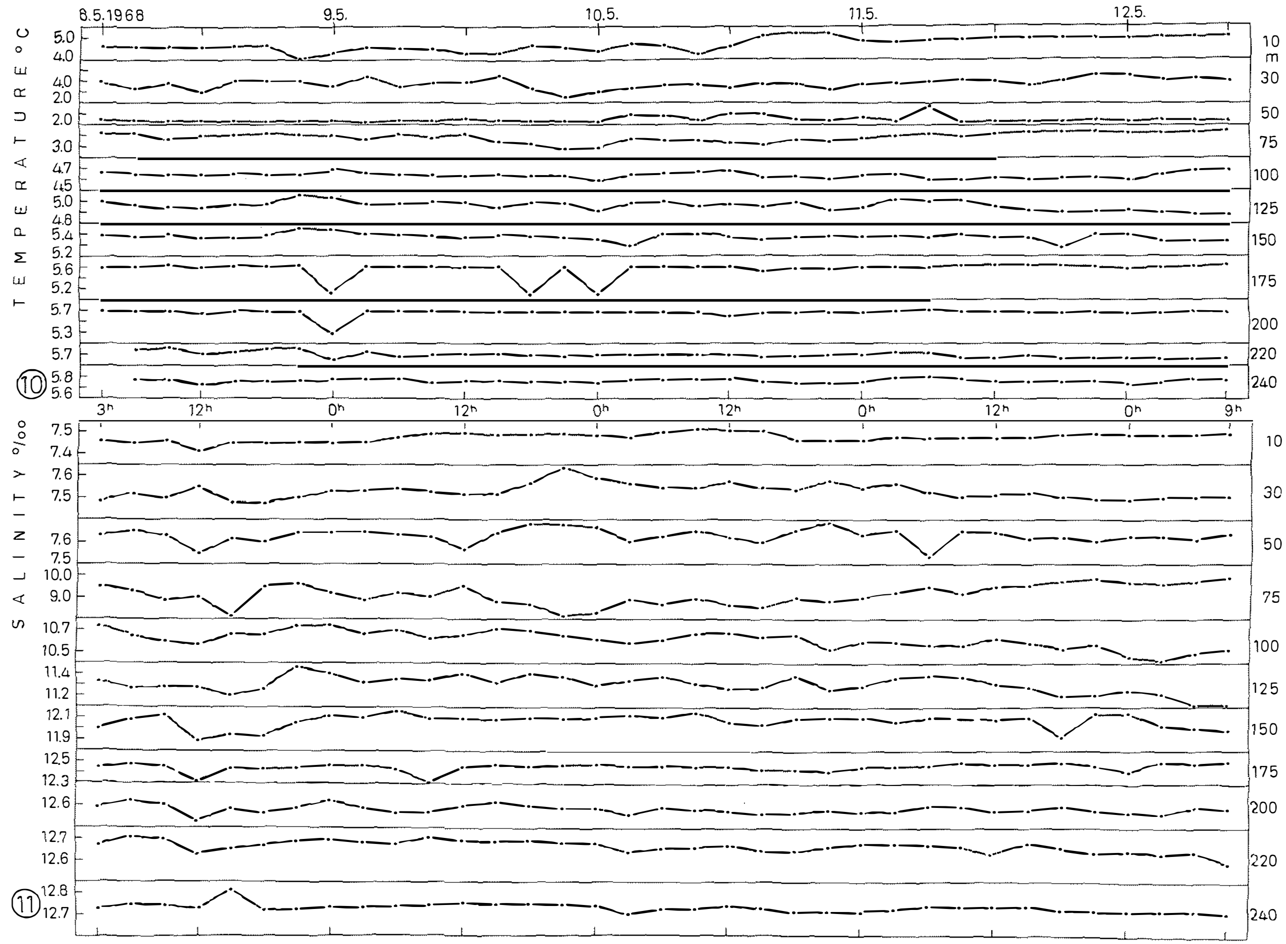


Tafel 5 (**zu** Gieskes/Graßhoff)

Tafel 6 (zu Gieskes/Graßhoff)



three water masses, as discussed previously, can already be discerned. Below a depth of 150 meters the dissolved oxygen disappears completely, to be replaced by hydrogen sulphide. The distribution of the chemical parameters with depth is presented in Figure 7 (Plate 4). The samples were collected on May 11th, 1968 at 18.00 h. Again nitrate disappears, when hydrogen sulphide makes its appearance. Also, as in September 1967, the winter water layer shows a maximum in nitrite, which is not shown in Figure 7.

2. Short time variations in physical parameters

During both anchor stations hydrographic casts were taken at 3 hours intervals. Always the samples were taken at standard depths. In this way we are able to construct diagrams, that show the variation with time of the temperature and salinity at the various levels, where the samples were taken.

The results of the September anchor station are presented in Figure 8 (Plate 5) for the temperature, and in Figure 9 (Plate 5) for the salinities.

The changes of the temperature in the levels above 100 m depth show very regular fluctuations in the temperature distribution. In the levels of 10 m and 20 m we note the appearance of a new, slightly colder water mass on September 10, at 06.00 h. This water mass must have moved in from an easterly or north-easterly direction. The changes in the 30 m level show a rather irregular pattern. We should realize, that at this level the gradient of the thermocline is very large, so that a very regular pattern can hardly be expected. The changes in the 50 m and 75 m levels, however, show a remarkable regularity. A definite feature is, for instance, the apparent phase difference between the peaks and the troughs of the two wave forms. From Figure 4 we notice that a downward movement of the water would cause an increase in temperature in the 50 m level, but a decrease in the 75 m level. The apparent phase difference, therefore, confirms the view that the regular changes are due to internal waves in the water masses. The lower levels show much less variability, but, of course, the temperature changes with depth are much less pronounced in these levels.

The salinity profiles confirm these observations. In Figure 9 (Plate 5) the salinity changes with time in the various levels are presented. In the 30 m level again the changes are rather irregular, but in the 75 m level an extremely regular pattern of a wavelike form is clear. Again a slackening of the variations with increasing depth can be seen.

The regular changes in the distribution of the temperature and the salinity in the 75 m level suggest strongly the presence of internal waves in the Gotland Basin. HOLLAN (1969, loc.cit.) finds from his current measurements during the September anchor station, that internal waves with periods of 13.3. hours do play a major role in the internal movements of the water masses. We, therefore, made a very simple harmonic analysis of the density data in this level, based upon u period of 13.3 hours. For this analysis use was made of the formula

$$f(t) = a_c \qquad f(t) = a_o + \sum_{v=1}^{\infty} a_v \cos vt + \sum_{v=1}^{\infty} b_v \sin vt$$

Plate 6

Figure 10: Variations in time of the temperature at Station 597 at various depths

Figure 11: Variations in time of the salinity at Station 597 at various depths

in which the constants are

a_o = median value of f(t)

$$a_v = \frac{1}{\pi} \int_0^{2\pi} f(t) \cos vt \, dt$$

$$b_v = \frac{1}{\pi} \int_0^{2\pi} f(t) \sin vt \, dt \qquad \text{and}$$

f(t) = the density as a function of time

By mean of a simple computer programme and using interpolated data for the density o_t, the amplitude of the harmonic wave can be calculated from

$$A = \sqrt{a_v^2 + b_v^2}$$

Based upon these data we obtain the simple harmonic form of the wave in Figure 12 (Plate 7). The amplitude of this calculated wave is $\delta\sigma_t = 0.162$. In Figure 12 this wave form has been superimposed upon the values of σ_t as calculated from our measurements. We have done this by indicating the boundaries of the wave peaks and troughs, and also by drawing vertical lines at 13.3 hours intervals. A remarkably good agreement can be observed over the period of September 7, 12.00 h to September 10, 12.00 h. Thereafter a phase shift seems to occur in the internal wave. The reason of this phase shift ist not quite clear. One should note, however, that the change in phase occurs about 6 – 8 hours after a pronounced change in the temperature structure in the 10 m and 20 m levels is observed. Possibly the arrival of a new water mass in the surface layers in an easterly or northerly direction has caused a catastrophic change there, which is only noticed in the Gotland Deep at some later time. The changes in the densities in the 30 m level are also represented in Figure 12. A vague correlation with the phenomena in the 75 m level can be seen. The apparent phase shift is confirmed also.

The situation in May 1968 is quite different as is demonstrated in Figure 10 (Plate 6) and Figure 11 (Plate 6). The temperature and the salinity changes in all levels are very irregular. The irregularities in the various layers down to the 100 m level can be explained by the phenomena that will be discussed in a following pragraph on continuous registrations.

3. Temperature Salinity diagrams

The large amount of data, that were collected during the anchor stations, make possible the construction of detailed temperature salinity diagrams. In Figure 17 (Plate 9) the T-S-diagram for the September anchor station is presented. The open circles are

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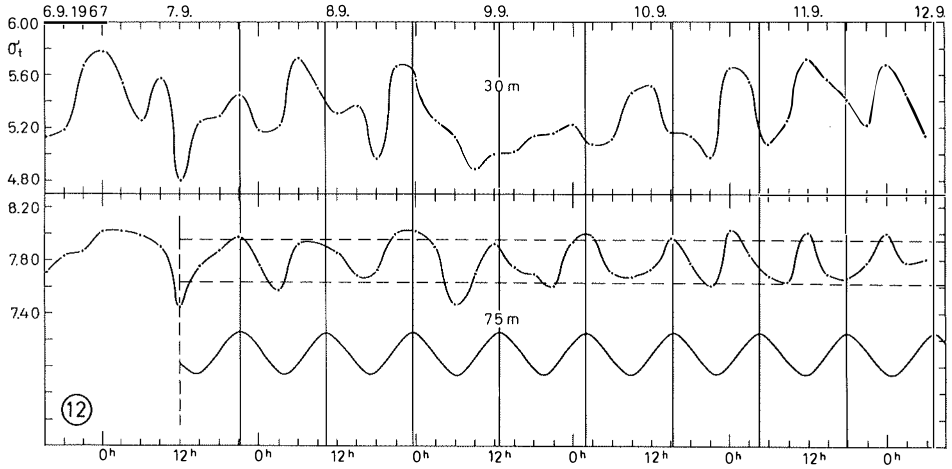
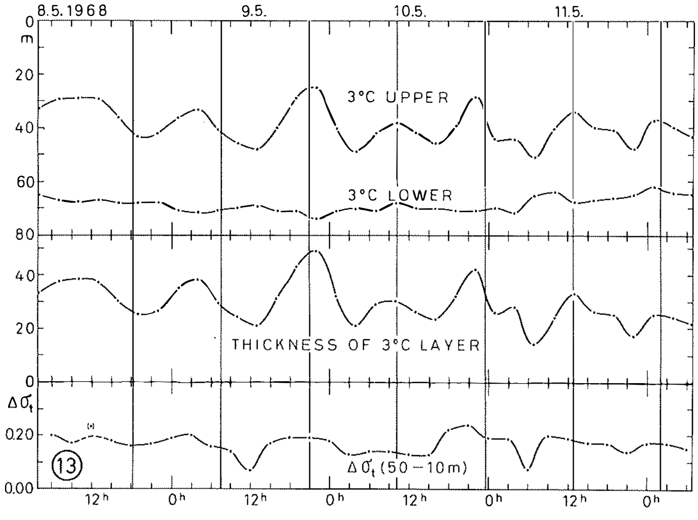
Plate 7

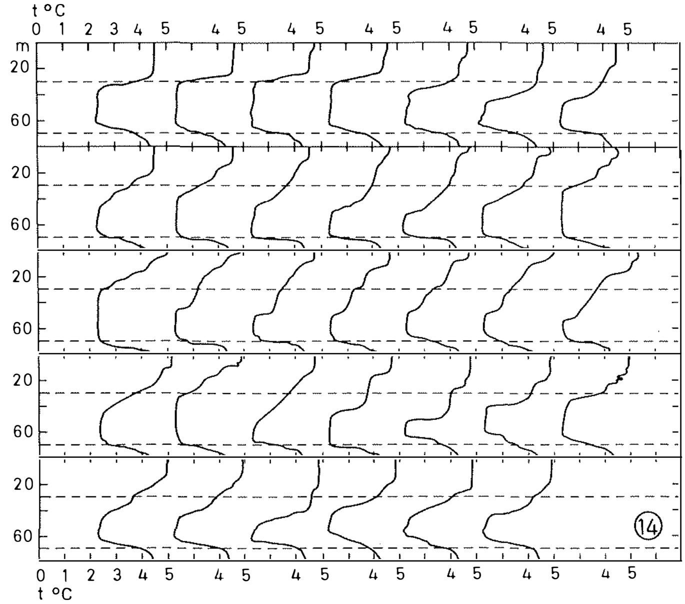
Figure 12: Analysis of the time dependence of the density in the 75 m level at Station 2

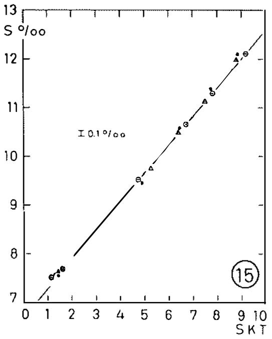
Figure 13: Analysis of the fluctuations in the thickness of the winter water layer in May 1968 at Station 597



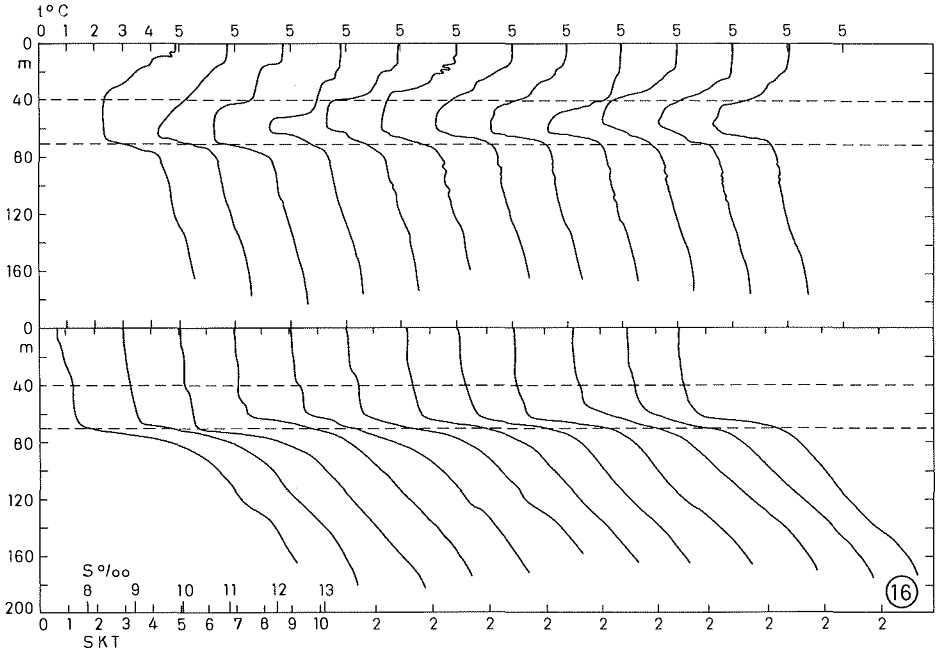


Tafel 7 (zu Gieskes/Graßhoff)





GOTLAND DEEP 10.5.68 22.00h – 12.5.68 07.00h



Tafel 8 (zu Gieskes/Graßhoff)

derived from the temperature salinity registrations with the in situ membrane salinometer. A very accurate diagram i obtained in this way. Similarly the T-S-diagram for the anchor station in May 1968 is presented in Figure 18 (Plate 9). The points indicate data from this station, and the dashed curve represents the T-S-diagram for September 1967.

We observe that from a depth of 125 m the two curves are identical. Furthermore, an envelope seems to exist between the diagrams for May 1968 and September 1867 for the depths between 50 and 125 meters. This envelope seems to have a more or less permanent nature, but the lines for May and September are not necessarily the extreme boundaries thereof. If, however, we plot the data of FONSELIUS (1968 a), and of KALEIS (1968) for the year 1966 in this diagram we see that nearly all data between 70 m and 125 m fall within this envelope, whereas the data for depths below 125 m fall exactly on the diagram. GIESKES (1967, loc.cit.) noticed, that down to a depth of 140 m a certain unrest in the water structure exists.

This phenomenon is very striking and we think that T-S-diagrams are particularly useful for the characterization of water masses in the Baltic Sea. From the T-S-diagram one observes that in the deep water of the Gotland Deep changes in salinity and temperature at certain levels of depth below 150 m must be due to mixing, but cannot be due to advection. In May 1968 the salinity as well as the temperature in the bottom layer have decreased as compared with September 1967. The T-S characteristic has not changed at all. Therefore, we conclude, that mixing must have occurred in the deep water layers, presumably after the stoppage of the inflow of oxygenated water. Due to this mixing conditions may have become favourable again for stagnation to develop, so that in May 1968 the lower layers of the Gotland Deep all show hydrogen sulphide to be present.

B. Automatic Registrations

During the two anchor stations in the Gotland Deep continuous registrations were made of temperature and salinity (in situ membrane salinometer), and of temperature and oxygen (oxygen probe). Conditions in September were quite stable and no interesting changes were found, that are not represented by our analysis of the hydrographic data from the classical Nansen casts. Also the registrations of the partial pressure of the dissolved oxygen did not reveal any significiant changes other than those that shall be discussed under the chemical data.

In May 1968, however, very large fluctuations were observed both in the salinity temperature registrations and those of oxygen and temperature. We shall first discuss the former of these.

1. Salinity temperature registrations
May 1968

In Figure 16 (Plate 8) some typical registrations of the temperature and salinity are presented. The salinity profiles, which are represented by the lower set of curves, are given in scale divisions as they were recorded. This is justified, because the calibration

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Plate 8

Figure 14: Registrations of temperature at Station 597 May 1968 at three hourly intervals

Figure 15: Calibration curve for temperature salinity sensor May 1968

Figure 16: Temperature and salinity registrations in May 1968 at Station 597

curve is essentially linear – at least within the limit of error. The calibration was carried out by the method described by GIESKES (1967, loc.cit.). In Figure 15 (Plate 8) the calibration curve, that is representative for this set of curves, is presented. We can see that the accuracy is within 0.1 $^{o}/oo$ in salinity.

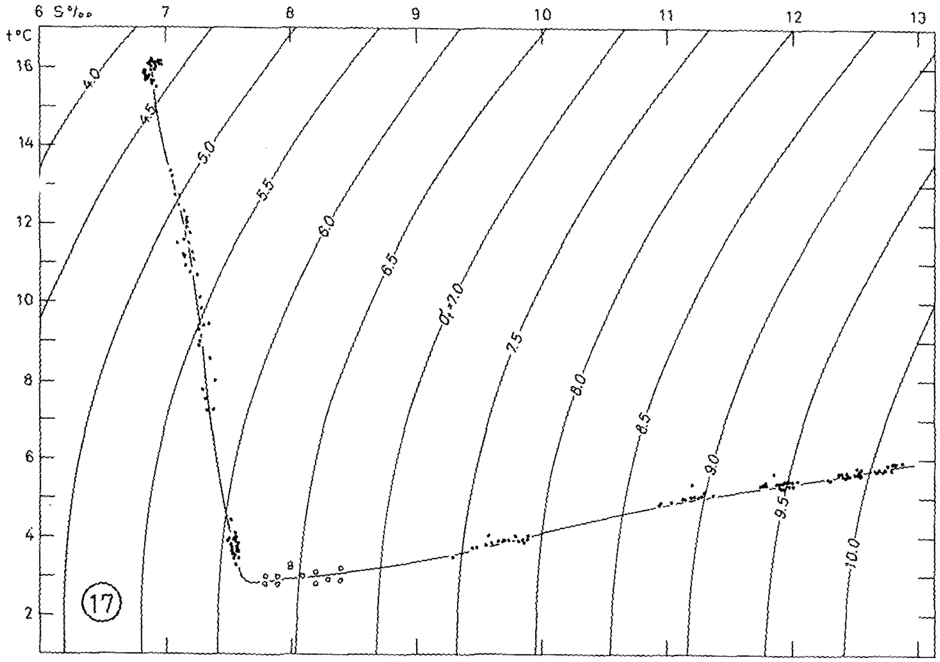
From the data on the salinity we observe again the slightly higher salinities in the winter layer. The changes in the temperature profiles, however, are particularly interesting. Between the depths of 0 m and 80 m enormous changes do occur. Therefore, we thought it would be useful to plot all temperature registrations, that were obtained with the temperature salinity sensor. In Figure 14 (Plate 8) these registrations are represented for depths between 0 m and 80 m. For reference, horizontal dashed lines are drawn to indicate the depths of 30 m and 70 m. The first registration was made on May 8, 04.00 h and the last one on May 12, 07.00 h.

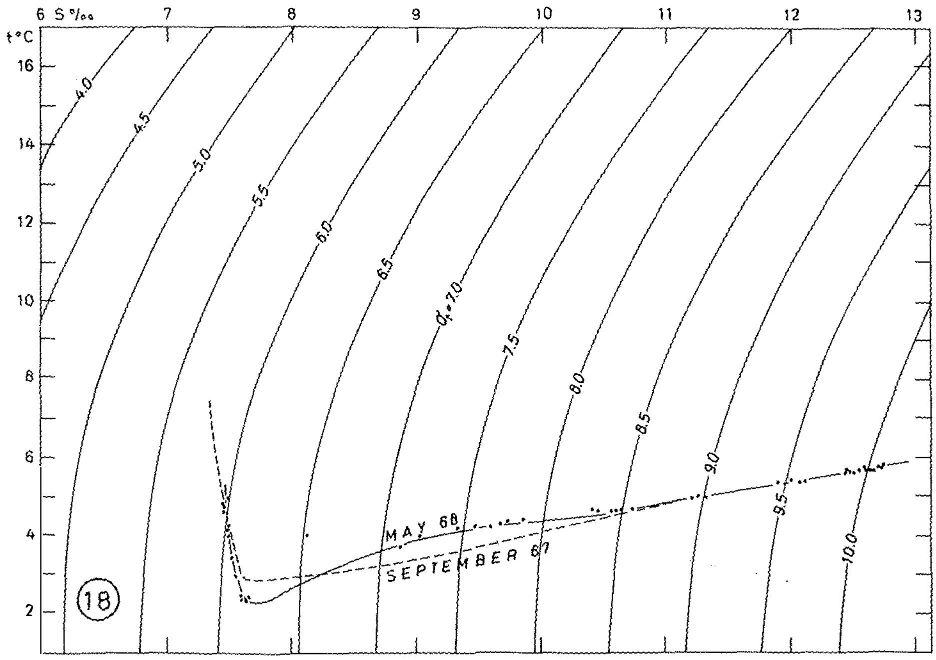
We can observe some characteristic features from these registrations. First of all we see the establishment of secondary thermoclines in depths of 20 m or less. These will partly be due to the advection through surface currents. Also the normal daily change in temperature will cause a variation in the heat exchange with the atmosphere. On May 9th and May 10th we find profound maxima in the surface temperature at the hours between 20.00 h and 22.00 h. Especially the build up of secondary thermoclines is pronounced during these days. One should note, however, that the maxima are quite late in the day. This may, of course, partly be caused by advection of water through surface currents.

The second feature is the structure of the winter water layer. From the registrations we clearly note a pulsating nature in the thickness of this winter water layer. We thought it would be useful to make an analysis of this phenomenon. For this we define the winter water layer to be characterized by the isotherms of 3°C. The winter water is hence all water with a temperature below 3°C. In Figure 13 (Plate 7) we have drawn the two 3°C isopleths for the May anchor station. We note that the pulsations in the upper isopleth are much larger than those in the lower level. In addition we have plotted the thickness of the 3°C layer, i.e., the thickness of the winter water layer. The vertical lines represent the period of 13.3 hours, which was the period of the internal waves found to be predominant in September 1967. The variations seem very significant and at least a vague correlation with internal waves of a period of 13.3 hours seems not improbable. The variations in the upper layer are much larger because there the stability is much less than in the lower level, where the main halocline is situated. In Figure 13 we have also plotted the difference in σ_t between the levels of 10 m and 50 m. The latter level is representative of the winter water layer. It is clear that only a very small difference exists in the densities of these two levels. Hence stability cannot be very high, resulting in the fairly high amplitudes of the upper 3°C isotherm.

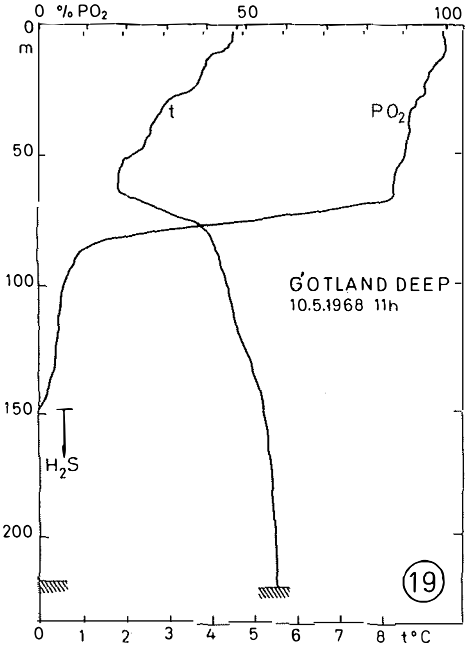
From these measurements again the presence of internal waves seem to be confirmed. It should be mentioned that just before both anchor stations strong winds did prevail in the area of investigation. HOLLAN (1969, loc.cit.) will discuss the origin and the development of internal waves due to such local weather disturbances. Internal waves, however, seem to play an important role in this area, especially because weather disturbances are not very uncommon over the Baltic Sea.

Plate 9
Figure 17: Temperature Salinity diagram for Station 2 September 1967
Figure 18: Temperature Salinity diagram for Station 597 May 1968





Tafel 9 (zu Gieskes/Graßhoff)



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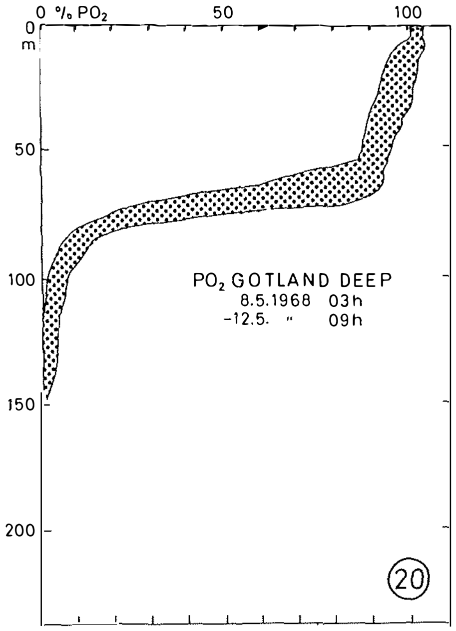

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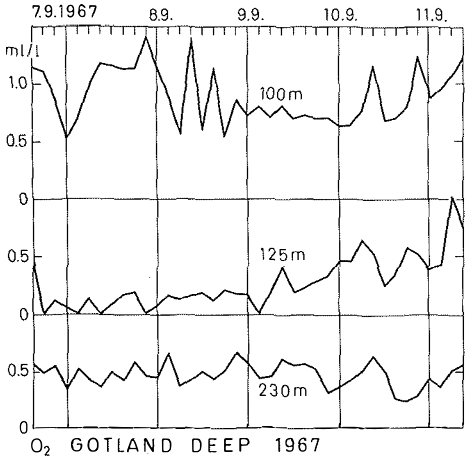

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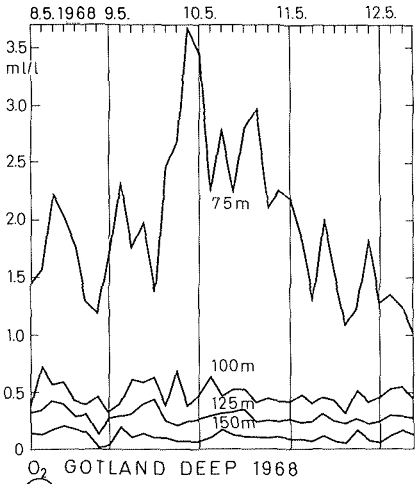

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Tafel 10 (zu Gieskes/Graßhoff)

2. Oxygen temperature registrations

The oxygen temperature registrations during the anchor station in May 1968 showed in general a saturation of oxygen in the surface layer, then about 90 % saturation in the winter water layer, after which a rapid decrease in oxygen followed below the main halocline. At about a depth of 150 m the oxygen disappeared and a negative signal in the instrument indicated the presence of hydrogen sulphide in the water. A typical registration is shown in Figure 19 (Plate 10).

The temperature profiles did confirm the observations as discussed in the preceding paragraphs.

In Figure 20 (Plate 10) all the registrations of the oxygen tension are superimposed upon each other, showing the degree of variability in the distribution of oxygen in the various levels. Especially in the thermo haline pycknocline this variability is quite large.

The significance of the variations of the dissolved oxygen will be discussed in the section on the chemical observations. It suffices here to state that the high variability in the dissolved oxygen will in part be due to the same phenomena that cause the pulsation of the winter water layer, i.e., to internal waves.

C. The chemical observations

In this section we shall restrict ourselves to the discussion of the changes in the following parameters: dissolved oxygen, dissolved inorganic phosphate, nitrate, and hydrogen sulphide. The significance of these parameters in regard to the chemical state of the water, and also the variability in the various levels shall be taken into consideration.

1. Dissolved oxygen

The regime of the dissolved oxygen in the Baltic Sea is discussed by FONSELIUS (1968 b) with particular reference to the oxygen deficit in the Baltic deep water. The oxygen deficit in the Gotland Deep has increased with the years since the beginning of the century. Presumably the amount of organic matter has increased also, thus causing the increasing deficit in oxygen in the lower layers of the Gotland Deep.

As has been mentioned in the section on the general hydrography of the area of investigation, the oxygen content in the summer surface layer usually is very high, showing more than 100 % saturation. In the winter water layer a slight drop in saturation occurs to 90 %. Unterneath the main halocline, however, the dissolved oxygen decreases rapidly. The values of the dissolved oxygen, which were measured in September 1967, are represented in Figure 23 (Plate 11). The variability of the data in the 75 m level can in general be traced back to the internal waves as discussed in section A.2. The changes in some of the deeper levels are also represented in Figure 21 (Plate 10). The changes in the 100 m level can only partly be due to the internal movement of the water mass, c.f. Figure 8 and 9. The gradient in the dissolved oxygen is very small in this depth. It should, however, be pointed out that just in the region between 100 m and 125 m depth a slight

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Plate 10

Figure 19: Oxygen Temperature registration Gotland Deep 1968
Figure 20: Composite curve of oxygen registrations Station 597 May 1968
Figure 21: Variations with time of the dissolved oxygen Station 2
Figure 22: Variations with time of the dissolved oxygen Station 597

maximum in the oxygen saturation can be observed. Although the fluctuations in the dissolved oxygen values can partly be ascribed to internal water movements, it seems that part of the fluctuations may be caused by other processes. The slight maximum in the value of the oxygen saturation may be caused by biological processes. The biomass in these levels is presumably not homogeneously distributed. If this is so, then it is conceivable that with the movements of patches of biomass, also fluctuations in the dissolved oxygen ought to be observed. One should note, that HOLLAN (1969, loc.cit.) in a level of 94.5 m finds some variations in the current speed of periods shorter than 13.3 hours. The changes in the dissolved oxygen in the 125 m level also show very rapid fluctuations, as is shown in Figure 21. Also in the depth of 230 m quite regular changes in the dissolved oxygen content can be observed. The very small variations may be within the limit of error, which is about ±0.1 ml/l at this concentration of oxygen (FONSELIUS, 1968). Yet regular changes can be observed, which are again presumably due to the changes in the distribution of the biomass and of the organic matter in the sea water near the bottom. The variations in the salinity as shown in Figure 9 also indicate changes in the water mass.

The variability in the dissolved oxygen at the May anchor station has already been discussed for the depths above 75 m in the paragraph on the oxygen temperature registrations. In Figure 22 (Plate 10) the changes in the titrated values of the dissolved oxygen for the lower levels are represented. The large chages in the 75 m level can be expected because the position of the halocline changes quite irregularly as is demonstrated in Figure 16. Also the variations in salinity as reported in Figure 11 are very irregular in this level. No special significance, therefore, can be attached to these variations. The changes in the 100 m, 125 m, and 150 m levels again are quite irregular. The distribution of the salinity in these levels, however, is also variable, as can be seen from Figure 11. The inhomogeneous distribution of the organic matter, which is also evident from the results of EHRHARDT (1969, loc.cit.), seem, at least partially, a cause of these fluctuations.

2. Nitrate

The nitrate is a significant parameter for the indication of the state of a water mass. In areas, such as the Gotland Basin, it ist of importance because we are able to locate the layers in which nitrification is setting in, and those where denitrification becomes predominant. We have already discussed this topic in section.A.1. of this paper. The short time variations for the anchor station of May 1968 are presented in Figure 26 (Plate 12). The changes are rather irregular and no special significance can be attached to these.

3. Dissolved inorganic phosphate

The changes in the dissolved inorganic phosphate are presented in Figure 24 (Plate 11) for the September anchor station. The vertical distribution has already been discussed in section A.1. in connection with Figure 5. The variability in all levels is quite pronounced, but a regular periodic pattern in the changes can hardly be recognized. We think that again the inhomogeneous distribution of organic matter is partly the cause of this

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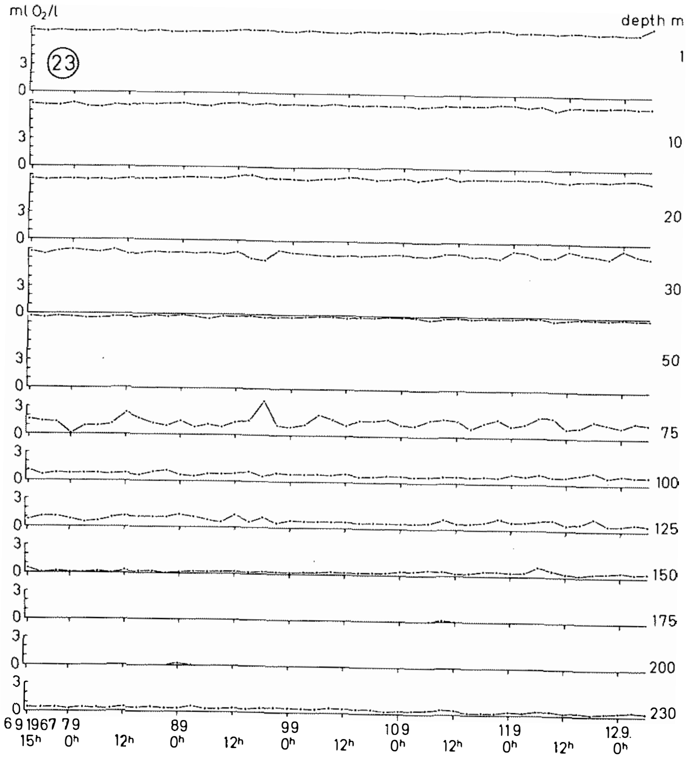
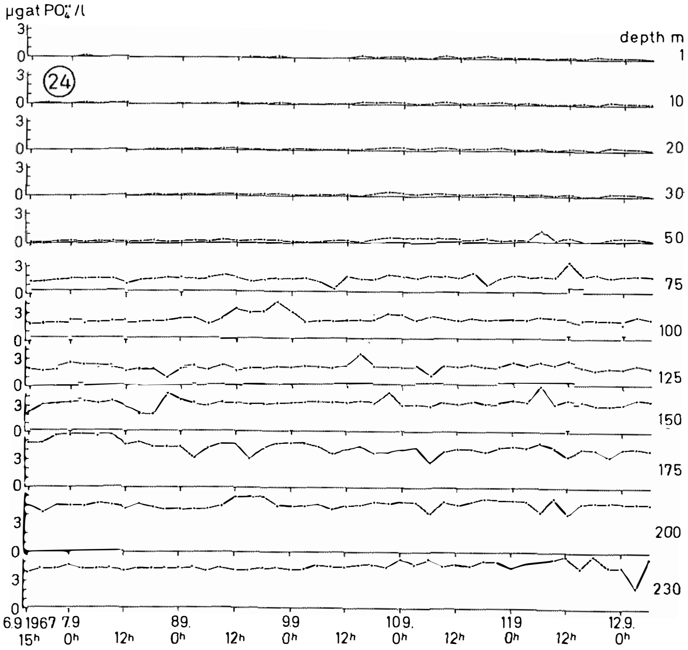
Plate 11

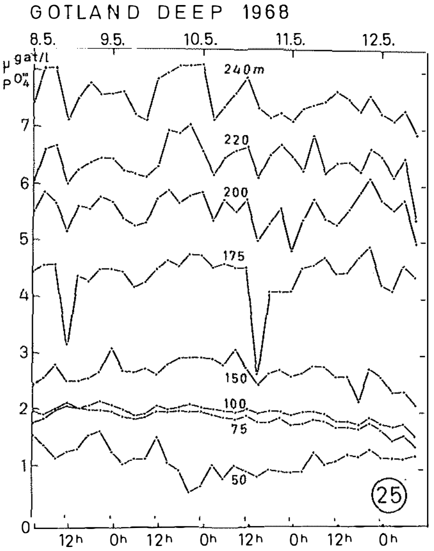
Figure 23: Variations with time of the dissolved oxygen Station 2

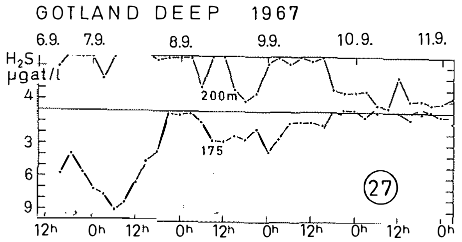
Figure 24: Variations with time of the dissolved inorganic phosphate Station 2

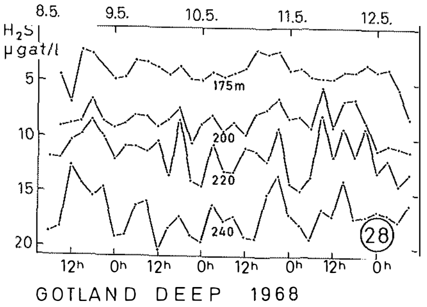


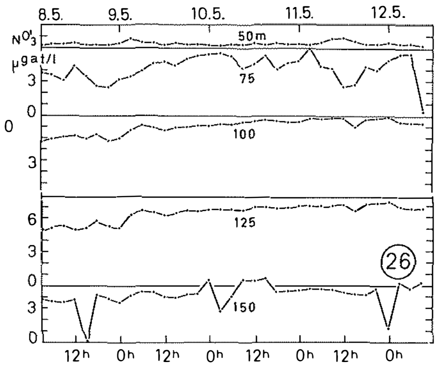


Tafel 11 (zu Gieskes/Graßhoff)









Tafel 12 (zu Gieskes/Graßhoff)

irregularity. The dissolved inorganic phosphate is often a product of the oxidation of organic matter as has been indicated by FONSELIUS (1967 a, loc.cit.) and by RICHARDS (1965, loc.cit.).

In May again a large variability in the values of the dissolved inorganic phosphate was observed. This is demonstrated in Figure 25 (Plate 12). The changes in the distribution of the concentrations in the lower levels, i.e., 175 m to 240 m, are particularly interesting. A definite correlation between the peaks and the throughs can be observed in Figure 25. Next to an irregular pattern due to the uneven distribution of the organic matter, the changes may very well be due to regular internal movements in the water masses. From Figure 7 we note that the gradients of this parameter are not very large in these layers. The changes of the phosphate content in one level are so large that „internal waves“ would have amplitudes of up to 10 meters just above the bottom. This is most unlikely. However, a periodic nature of the currents in the lower layers would conceivably cause the regular passage of biomass patches over the position of the sample bottles. Hence sometimes periods from peak to peak values of around 13.3 hours can be observed. The simultaneous changes in the levels from 175 m to 240 m seem to indicate that the „patches“ are extensive in the vertical direction. The continuous registration of the transparancy might be a useful tool in verifying the existance of these patches, because they may very well be associated with increased amounts of suspended matter, such as particulate organic carbon.

In addition to the above observations we would like to refer to the changes in the distribution of the hydrogen sulphide, which are shown in Figure 28 (Plate 12). Again regular changes can be observed, that are simultaneous with the changes in the phosphate content.

On the relation between the inorganic phosphate and the hydrogen sulphide we shall return in the next paragraphs.

4. Hydrogen sulphide

This particular compound is of utmost importance. Usually the appearance of hydrogen sulphide indicates a state of deterioration of the water mass under consideration. The formation of hydrogen sulphide coincides with a sharp change in the redox potential of the water (FONSELIUS, 1967 a, and RICHARDS, 1965, loc.cit., MANHEIM, 1961).

We shall first discuss the variability of this parameter with time for both anchor stations. In an additional section the relationship between the hydrogen sulphide and the phosphate contents will be investigated.

In September 1967 a situation was encountered that is characterized in Figure 2 and also in Figure 4. The hydrogen sulphide showed a tongue shaped distribution. In Figure 27 (Plate 12) we have plotted the changes in the concentrations in the depths of 175 m and 200 m. Immediately we note that the shape of the layer containing hydrogen sulphide is most variable. Sometimes no hydrogen sulphide is found in the level of 200 m, and at other times it is lacking in the 175 m level. This strongly suggests that indeed the

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Plate 12

Figure 25: Variations with time of the dissolved inorganic phosphate Station 597

Figure 26: Variations with time of the nitrate Station 597

Figure 27: Variations with time of the hydrogen sulphide Station 2

Figure 28: Variations with time of the hydrogen sulphide Station 597

hydrogen sulphide tongue as shown in Figure 2 is of a highly variable nature, and that it may have the appearance of patches. This presumably is due to the gradual mixing with the inflowing, slightly oxygenated bottom water. The fairly high concentrations of hydrogen sulphide at 175 m on September 7th are corroborated by the likewise higher concentrations of phosphate, as is demonstrated in Figure 24. This phenomenon shows that the analysis of chemical data is of great importance in these areas, because from the hydrographic data alone such structures can hardly be derived. We believe that these patches do not necessarily occur only because of clouds of organic matter and of sulpho bacteria, but that the patchlike structure is influenced by the mixing processes with the bottom water as well. Of course, both processes do play a role, and we have no means of indicating how much each does contribute to this phenomenon.

In May 1968 no tongue shaped distribution of the hydrogen sulphide was found, but a sharp rise in concentration occurred towards the bottom. This, for instance, is demonstrated in the Figures 6 and 7. The variability of this parameter is also large. In Figure 28 (Plate 12) we have plotted the changes with time of the hydrogen sulphide content in the various layers of the Gotland Deep. A certain correlation can be observed between the changes in the various levels, as was already pointed out in the paragraphs that dealt with the phosphate distribution. The gradient of the hydrogen sulphide towards the bottom is very pronounced, so that internal movements again will be very noticible.

5. Relation between hydrogen sulphide and dissolved inorganic phosphate

FONSELIUS (1967 a, loc.cit.) reports on the relation between changes in the apparent oxygen utilization (AOU) and the changes in the content of dissolved inorganic phosphate in the Baltic Sea. The relation differs very much from that predicted on the stoichiometric model of RICHARDS (1965, loc.cit.). The latter author based his model on the graduel oxidation by oxygen, nitrate, and sulphate of planktonic detritus, with a C:N:P ratio of 106:16:1. In the process, where sulphate reduction is involved, a ratio of the change in the content of hydrogen sulphide and of phosphate of $\Delta S^{--}/\Delta PO_4^{3-}(P) = 53$ is calculated. Fonselius data for the Baltic Sea, however, deviate considerably from this predicted ratio. We thought, therefore, that it might be worthwhile to plot the data for the dissolved inorganic phosphate as a function of the hydrogen sulphide content. In this manner we obtain Figure 29 (Plate 13) for the September station, and Figure 30 (Plate 13) for the anchor station of May 1968. In May 1968 there seems to exist a very definite relation between these two parameters. The scatter is only to be expected, but this does not conceal the functional dependance of the two factors. The straight line in Figure 30, however, has a slope of 0.23μgat $PO_4^{3-}(P)$/μgat H_2S (S), or a ratio of 4.35 in lieu of 53 as reported by Richards. In September 1967 the relationship is not very clear as can be seen from Figure 29. This may well be due to the gradual mixing of the layers, that contain hydrogen sulphide, with the slightly oxygenated bottom water.

FONSELIUS (1967 a, b, loc.cit.) points out that with the appearance of hydrogen sulphide a marked change in the redox potential of the water is associated. Under these reducing circumstances it will be possible for some substances, that are deposited in the

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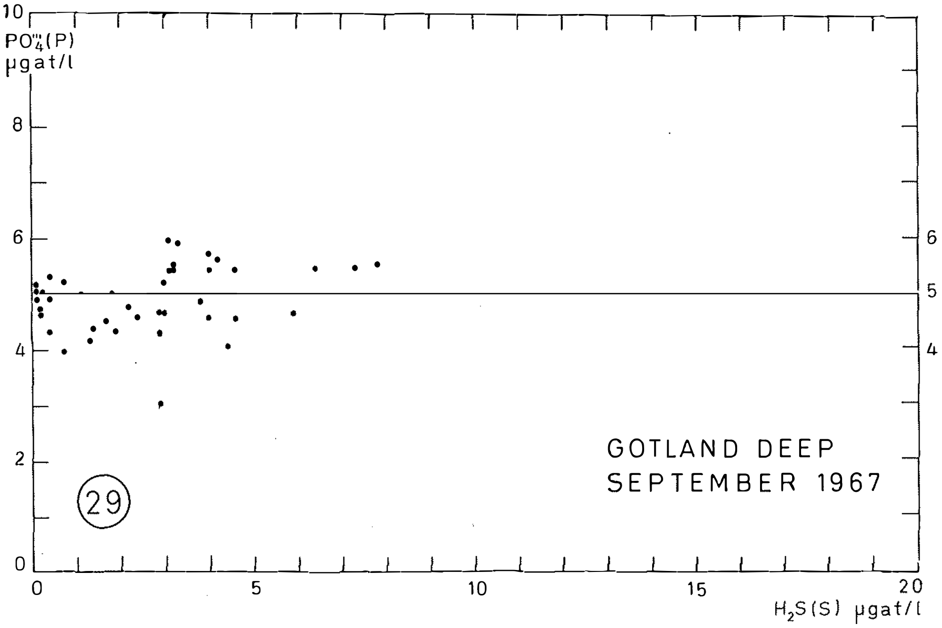
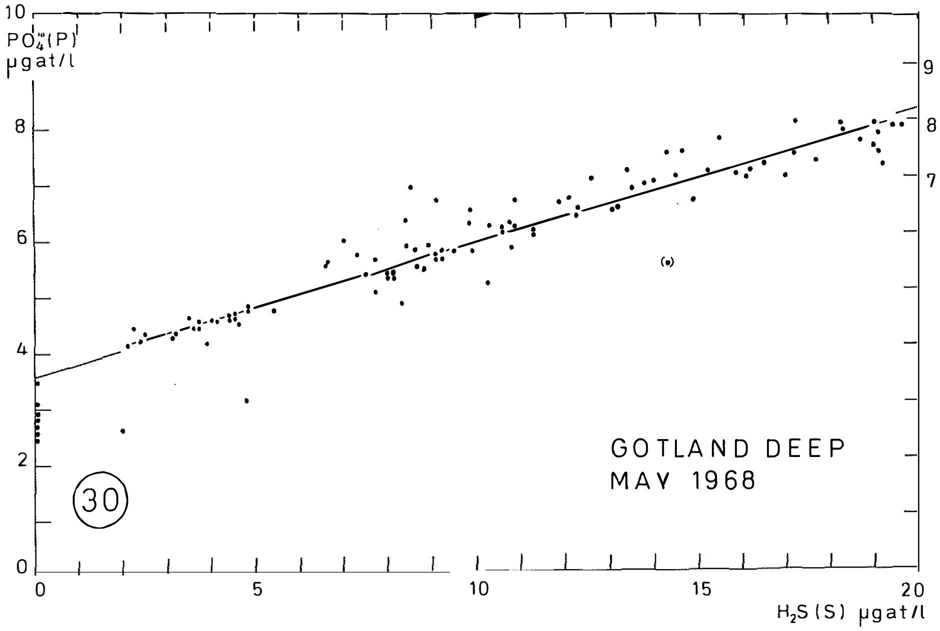
Plate 13

Figure 29: Relation between hydrogen sulphide and dissolved inorganic phosphate September 1967

Figure 30: Relation between hydrogen sulphide and dissolved inorganic phosphate May 1968





Tafel 13 (zu Gieskes/Graßhoff)

sediment, to go into solution. HUTCHINSON (1957, p. 738) indicates that tank experiments led to the observation of a simultaneous rise in phosphate and of ferrous iron under anoxic conditions. Also EINSELE (1938) discusses the solution and precipitation of iron and phosphate in oxidized and reduced conditions. Presumably some form of ferrous phosphate will go into solution. KESTER and PYTKOWICZ (1967) studied the apparent dissociation constants of phosphoric acid in sea water and found that at a pH = 7.6 the bulk of the phosphate appears in the ionic form HPO_4^{-}. It should be noted that these authors only made measurements at high salinites, but we feel that the above conclusion is still valid at salinities of about 12 $^{0}/oo$. FONSELIUS (1968, loc.cit.) finds that iron makes its appearance in the layers with hydrogen sulphide. We shall make an attempt to predict the amount of iron that would be liberated due to the dissolution of ferrous phosphate.

EHRHARDT (1969, loc.cit.) determined for the particulate organic matter in the Gotland Deep bottom water layers a nitrogen/carbon ratio of about 0.10. We shall assume that the composition of the organic matter can be described by the follwing atomic ratios C:N:P = 100:10:1. The sulphate reduction reaction would then lead to a ratio of $\Delta S/\Delta PO_4^{3-}$(P) = 50. From our measurements we know that for every increase of 10μgat S there will be a corresponding increase of 2.3μgat PO_4^{3-}(P). From the C:N:P ratio we would estimate, that the increase in phosphate would only be 0.2μgat PO_4^{3-}(P). The remaining phosphate should, therefore, originate from a dissolution of, e.g., ferrous phosphate, with a bruto formula of $Fe_3(PO_4)_2$. This means, that for every 1μgat PO_4^{3-}(P) that goes into solutions a corresponding 1.5μgions Fe^{++} will make their appearance. For every increase of 10μgat H_2S (S) we should find an increase of 3.15μgat Fe. FONSELIUS (1968, loc.cit.) shows an increase of 7μgat H_2S (S) in the Gotland Deep with a corresponding amount of 2.2μgat Fe. Similarly in the Farö Deep an amount of 1.5μgat Fe occurs with an increase of 5μgat H_2S (S).

However it seems that the ratio $\Delta S/\Delta PO_4^{3-}$ (P) in this case is about 3.1, whereas we found 2.3. On the other hand, if our results of Figure 30 are representative, a quantitative agreement between the amounts calculated and those reported by Fonselius is apparent.

KOROLEFF (1968) studied the iron contend of Baltic waters. He suggests, that indeed in stagnant waters both iron and phosphate will dissolve. From a calculation of the ionic product of Fe^{++} and S^{--} ions Koroleff shows near saturation of the stagnant water in ferrous sulphide. Unfortunately no reliable data are available for the ionic product of Fe^{++} and HPO_4^{--} ions, and also the solubility product of this compound is not very well known. We think calculations of these constants would have too speculative a nature. The above, however, emphasizes the need of a study of the state of iron and of phosphate in reducing and oxidizing environments, both in the free water zone and in the underlying sediments. Hence the determination of iron should be carried out on a routine basis in anoxic basins such as the Gotland Deep.

General conclusions

From the studies presented in this paper we may deduce that anchor stations in the Baltic Sea serve as most useful tools not only for the detection and the study of internal water movements, but also to gain insight in the variability of the chemical parameters.

From our studies of the variations of the physical parameters, and also from our continuous measurements we see that internal waves do play an important role in the Gotland Deep basin. HOLLAN (1969, loc.cit.) estimates that these internal waves are caused by weather conditions, e.g., by large storms. These bad weather conditions, however, occur very often in the area of the Baltic Sea, so that the presence of internal inertial movements can be assumed to be more or less permanent.

The data obtained from hydrographic stations with only one hydrographic cast will at best provide values, that fall within the deviation from some stastical average. The analysis of our chemical data seems to point in the same direction. Even at greater dephts the variations in these parameters are quite large, as is, e.g., demonstrated in the Figures 25, 27, and 28. In the case of the hydrogen sulphide values during September 1967, as presented in Figure 27, this variability becomes dramatic, showing the most extreme example.

We suggest that from permanent stations, such as the ones described in this paper, one can obtain a large amount of information on the significance of the data that are collected in the area, where such a station is made. Cooperation with biologists would still increase the usefulness of such stations, and it is suggested that additional data such as transparancy, data on dissolved and total inorganic iron, and analysis of the underlying sediment would help to gain a better understanding of the problem under investigation.

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The very helpful cooperation of captains and crews of R.V. „Alkor“ and of F.R.V. „Anton Dohrn“ is gratefully acknowledged. Also the good team spirit of the chemistry group of the Institut für Meereskunde an der Universität Kiel was a major contributor to the success of these two anchor stations. Mr. B. Higelke made the careful drawings, for which many thanks. The help of the Workshop of the Institut für Meereskunde an der Universität Kiel made possible, that all apparatus was in such fine working order. The financial assistance of the „Deutsche Forschungsgemeinschaft“ is also gratefully acknowledged.

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