FISHERY BOARD OF SWEDEN

Series Hydrography, Report No. 23

HYDROGRAPHY OF THE BALTIC DEEP BASINS III

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STIG H. FONSELIUS

LUND 1969
CARL BLOMS BOKTRYCKERI A.-B.

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Abstract

The major theme of this paper is the trend towards stagnation of the deep water basins of the Baltic proper.

Samples of Baltic water were taken from established stations periodically from the beginning of the century and these measurements constitute the data for this study.

Certain peculiarities of the Baltic's topography are shown to produce two water layers which are separated by a permanent halocline which impedes the mixing of the water layers.

Data from measurements at various Baltic stations illustrate a salinity increase in the Baltic in the present century. This salinity increase is considered to be the most significant factor contributing to the oxygen deficit of the Baltic's deep water. It is shown that the salinity increase raises the halocline's stability. The existence of a halocline implies that very little oxygen from the aerated surface water can penetrate through the halocline to the deep water. Oxygen in the deep water is exhausted through oxidation processes. Increased salinity is shown to make the halocline even less permeable to the mixing down of oxygen from the surface.

An analysis of phosphorus data in Baltic sea water for the present century shows a phosphate increase in the deep and surface waters. This increase is shown to have increased primary production and through this to have increased oxygen consumption in the deep water because greater amounts of decaying matter sink down into the deep water.

It is shown that once a body of water becomes stagnant the condition tends to perpetuate itself and worsen. This is because inflowing water of a lower density than the stagnant water passes over the stagnant water and because when new water does penetrate, its oxygen quickly reacts with the H_2S present in the stagnant water and is consumed.

The reasons for the increace in salinity and phosphorus (the causes of the stagnation development) are discussed. The salinity increase is influenced by meteorological factors and the reasons why it occurred are: the decreased runoff to the Baltic from the rivers which discharge into it, the decreased water exchange through the Danish sounds and the increased intensity of the

bottom current in the Belts and Kattegat. The reasons for the increase in phosphorus are that the increased H_2S in the Baltic creates reducing conditions which cause phosphorus to be released from the bottom sediments and from inorganic particulate matter and that there is a great amount of phosphorus in the sewage water which is emptied into the Baltic.

The implication of the findings is that if there is a continuation of the trends toward increased salinity and phosphorus concentration in the Baltic, the sea's deep water shall soon become devoid of organic life.

I. Introduction

Summary of earlier chemical work in the Baltic

(A map of the Baltic with all stations mentioned in the present paper is shown in fig. 1).

Systematic chemical investigations were started in the Baltic area in the beginning of the 20th century. For the most part separate analyses of only a few elements, mainly dissolved oxygen, carbon dioxide and nitrogen, had been done earlier. O. PETTERSSON (1898) carried out such work in Sweden. According to SIMONOV (1965) there were also some independently performed complete chemical analyses of sea water samples from the Baltic proper and the Gulf of Finland.

The International Council for the Exploration of the Sea (ICES) was formed during an oceanographic conference in 1902 in Copenhagen (EKMAN et al. 1907). The participants were mainly from the countries in northern Europe and for this reason the conference dealt extensively with the Baltic. A network of international stations and sections were established there. Regular hydrographic and chemical measurements were planned to be carried out and the Baltic was divided into investigation areas. Sweden was charged with the responsibility for the area west of Gotland and the important Landsort Deep. Probably because of a lack of ships and funds, this work was done only sporadically.

Except for the periods of the two World Wars there exists a nearly complete series of observations for the Finnish area. These observations had already begun in the beginning of the century in the Gulf of Bothnia, the Gulf of Finland and the northern Baltic proper. The work was soon extended to the central Baltic proper. Ordinarily the expeditions took place yearly with the research ship "Nautilus" and in 1939 with the "Aranda". First there were only chlorinity and oxygen analyses. In 1908 other chemical observations, mainly pH and alkalinity, were started. In 1928 the analysis of nutrient salts began. The Finnish observations were carried out on 81 standard stations including the Gotland Deep. The results are published in "Havsforskningsinstitutets Skrifter" in Helsinki.

There have been many Russian investigations of the Baltic but unfortunately the results are rather inaccessible. The "Kompass" worked in the Gulf of Finland, the central Baltic and the Gulf of Riga in 1908. A great deal of dissolved oxygen data was collected (LEBEDINTSEV 1910). DERYUGIN (1923,

1947) initiated many hydrochemical analyses in the eastern part of the Gulf of Finland and the Neva estuary in the years between 1920 and 1937.

During 1931 to 1938 the research ship "Sexstant" from Estonia did oxygen analyses in the Gulf of Finland, the Gulf of Riga and the northern Baltic proper.

All of the above analyses were usually carried out during the summer period.

In the Danish sounds in 1923 fairly regular oxygen analyses and pH measurements began. Measurements were taken even in the winter months. Nutrient salts began to be analyzed during the 1930's. The Danish ships "Dana" and "Biologen" and the Swedish "Skagerak" worked in this area.

German oceanographers began in 1926 to collect extensive chemical material. Oxygen and pH were measured and after 1930 nutrient salts were also included in the program. These expeditions with the "Poseidon" did not occur yearly but they included different seasons (SCHULZ 1956).

The "Hidrografs" from Latvia during 1934—1938 conducted extensive hydrochemical analyses in the Gulf of Riga and the central Baltic. This work often covered the autumn-winter period and usually complete chemical analyses were done (MIEZIS and OZOLIŅŠ 1940).

Before World War II regular hydrochemical work covering all seasons was not in effect in the Baltic. The results that were obtained from the few early investigations that did occur, were extensively used by Finnish, Russian and German scientists and became the bases for later work in the Baltic. The material for these early studies was usually collected on large cruises such as the "Kompass" expedition in 1908, the "Poseidon", "Nautilus" and "Skagerak" expeditions in 1922 and the "Aranda" and "Triton" expeditions in 1939. (The German "Triton" expedition is noteworthy because its program included analyses of phosphate, silicate and nitrate and because it covered almost the entire Baltic proper). All of these results have been published in the "Bulletin Hydrographique" of the ICES.

The situation today is that chemical conditions in the northern and southern parts of the Baltic have been somewhat well described due to the work of Finnish and German oceanographers. In contrast conditions in the central and especially in the western Baltic have not been well known.

The oxygen conditions of the Baltic have been extensively investigated. The first oxygen analyses were carried out by O. PETTERSSON during the 1890's. He used his own volumetric method (PETTERSSON 1898). Although most of these results have never been published the original notes are still available at the Bornö laboratory of our institute. The results show considerably great variations when double analyses have been made, but are correct within an order of magnitude. The method was laborious and slow. Only few analyses could be carried out at every station. The WINKLER method (WINKLER 1888) which was introduced around 1903 is a technique which oceanographers use even today. Small improvements and changes have been introduced but the primary analyses may still be regarded as valid. Works concerning the oxygen distribution which are relevant are papers by LEBEDINTSEV (1910), SCHULZ (1923), DERYUGIN (1923, 1947), BUCH (1931, 1954), BUCH and GRIPENBERG (1938), WATTENBERG (1940) and a monography by SCHULZ (1932).

Several works concerning the carbon dioxide distribution have been published. Some of the papers cited above include discussions of carbon dioxide problems and several other works can be indicated such as BUCH (1917, 1933, 1945), GRIPENBERG (1937, 1960), SCHULZ (1922), WITTIG (1940), CHERNOVSKYA (1962) etc. Special attention must be given to BUCH's work of 1945 which deals with extensive material from the northern and central parts of the Baltic proper and from the Gulf of Bothnia and the Gulf of Finland during 1927 to 1938. It forms a basis for the understanding of the whole carbon dioxide system and explains the relation between different hydrographic and biological factors.

All these works have contributed to the understanding of the gas state in the Baltic. They clarify for instance the development of the stagnation phenomena which is caused by conditions in the bottom topography and the limited water exchange through the sounds.

It was mentioned earlier that regular collection of nutrient salt data began during the 1930's. Mainly phosphate data were obtained but some silicate and nitrate analyses were made also. Results from the years before World War II have been published by BANSE (1947), BUCH (1932, 1934), KALLE (1932, 1943), MEYER and KALLE (1950), WATTENBERG (1940), WATTENBERG and MEYER (1936) and GESSNER (1933, 1940). Most of the papers deal only with phosphate. In spite of the fact that nutrients were the least investigated components in the Baltic these scientists could establish the basic facts in the distribution of nutrients and connect this to the hydrographic conditions.

The lack of regular observations during all the seasons was a serious shortcoming of data which were obtained before World War II. This was especially true of nutrient salts data. There were few existing complete series and they were of only regional importance.

After World War II the hydrochemical observations were again started. They resumed at the end of the 1940's and the beginning of the 1950's. In 1951 the Soviet Union instituted regular measurements. The hydrographic institute in Leningrad carried out expeditions to the permanent international stations in the Gulf of Finland and in the northern and central parts of the Baltic proper. At first only oxygen, salinity and temperature were measured. Soon pH and alkalinity were included. From 1957 nutrients have been assayed too. Sometimes the expeditions were extended to the southern Baltic. In 1957 the hydrographical institute in Riga began hydrochemical work in the Gulf of Riga and the central Baltic proper. Several other Soviet institutes work in the Baltic. The data are available through the international data centers. The work during the IGY 1957—1958 and the International Geophysical Cooperation 1959 has been very extensive.

Regular hydrochemical investigations began again in 1954 at the Finnish Institute of Marine Research in Helsinki with the new "Aranda". The material is collected annually during the summer period in the Gulf of Bothnia, the Gulf of Finland and the northern and central Baltic proper. Occasionally winter expeditions have been carried out in the Gulf of Bothnia aboard icebreakers (PALOSUO 1964 a).

Poland conducts hydrochemical work in the Bay of Gdansk and the southern Baltic proper during all seasons. The German oceanographic institutes in Kiel and Warnemünde also perform quite extensive hydrochemical programs but these are not as regular as the Soviet and Finnish programs. Several expeditions covering great parts of the Baltic have, however, been reported.

In the Danish sounds and the western parts of the Baltic proper fairly regular observations of oxygen and sometimes of the phosphate content have been done by Danish and Swedish ships. This work began in 1948.

The Swedish "Eystrasalt" worked during World War II in the Gulf of Bothnia. After the war it continued there and also occasionally in the Landsort area. The "Orion" from the Hydrographic office of the Swedish Navy worked after the war in the western and central parts of the Baltic proper including the Gotland Deep. All these observations have not been published but have been made available to the author.

From 1957 the "Skagerak" from the Fishery Board of Sweden began regular hydrographic studies in the Baltic including the main international stations. Occasionally the expeditions have been extended to the Gulf of Bothnia. From 1959 four expeditions have been carried out annually covering all four seasons. The work has included oxygen, pH, alkalinity and phosphate measurements. The results have been published in ICES data lists and from 1967 in "Meddelanden från Havsfiskelaboratoriet".

ICES has had a "Baltic Committee" for cooperation in the Baltic area until 1966. Unfortunately not all Baltic countries are members of ICES. Therefore a working group called the "Baltic Oceanographers" has been established outside the ICES but it communicates with the ICES through the "Subcommittee for Cooperation in the Baltic" in the Hydrography Committee. The "Baltic Oceanographers" met for the first time in Helsinki in 1957 and an international working program and certain standard sections and stations were agreed upon. The "Baltic Oceanographers" have since then met in Kiel 1960, Göteborg 1962, Warnemünde 1964, Leningrad 1966 and Sopot 1968. A cooperative program with 11 participating ships was conducted in the Baltic proper in August 1964. A new cooperative program called the "Baltic Year" has been planned for 1969 with all Baltic countries participating. The work will be concentrated on the chemical parameters. Another program in 1970 will probably mainly deal with water level and current measurements in the Gulf of Bothnia.

During the last years four intercalibration tests of chemical methods used in the Baltic area have been carried out. In 1965 the "Aranda" from Helsinki, the "Hermann Wattenberg" from Kiel and the "Skagerak" from Göteborg met at Copenhagen (FONSELIUS 1965), (GRASSHOFF 1965), (KOROLEFF 1965 a, b, c). The "Okeanograf" from Leningrad, the "Professor Otto Krümmel" from Warnemünde, the "Alkor" from Kiel and the "Skagerak" met at Leningrad in June 1966 (FONSELIUS 1966 a), (GRASSHOFF 1966 a), (NEHRING 1966). In September 1966 HMS "Hydra", the "Johan Hjort" from Bergen, the "Alkor", the "Aranda" and the "Skagerak" met again at Copenhagen (FONSELIUS 1966 b), (GRASSHOFF 1966 b), (KOROLEFF 1966), (BUTLER 1967), (COX 1966), (JONES et al. 1966), (PALMORK 1966). In 1968 an intercalibration was carried out at Gdynia with the "Alkor", the "Aranda" and the "Professor Otto Krümmel". Danish and Polish shore laboratories have participated in the intercalibration tests. It was found that the analysis results tend to be in general agreement to a surprising extent and that the results of analyses from different laboratories in the area are generally comparable.

II. On the chemical conditions in the Baltic

The Baltic is directly connected to the world ocean through the Belts and the Öresund. Therefore its water is brackish which means the water is a mixture of ocean, river and rain water. Because of its connection with the ocean the Baltic has to be considered as a sea and not a great salt lake. Characteristic for the Baltic is that the water mass is divided into two layers, a surface layer with a very low salinity and below that a deep water body with considerably higher salinity. This is caused partly by the great fresh water supply from runoff and precipitation and partly by the inflow of salt water from the Kattegat.

The water balance of the Baltic is positive, i.e. the sum of the annual fresh water supply is greater than the annual evaporation. The evaporation happens to be almost exactly as great as the precipitation during the year (BROGMUS 1952). Therefore the surface of the Baltic normally lies higher than the surface of the ocean outside in the North Sea. The excess of fresh water mixed with salt water streams out to the Kattegat. The salinity of the Baltic remains relatively constant. If there was no transport of salt water into the Baltic, its salinity would decrease continuously and it would be transformed into a fresh water lake. The surface layer has a lower density than the deep water body. Between the two layers a halocline or pycnocline is formed called the primary halocline. At this depth the salinity and consequently also the density of the water suddenly increases downward inside some 10 m.

This halocline separates the two water layers throughout the whole Baltic were the depth is great enough, i.e. more than about 60 m. The inflowing water sinks at the salt front in the Danish sounds below the outflowing surface water and streams as a slow bottom current over the sill at Darss into the Baltic following the deepest parts along the bottom. The Baltic consists of a system of different basins connected to each other over sills. The inflowing water fills these basins one after the other causing continuous dilution (EKMAN 1893). Therefore the salinity of this water decreases more and more on its way east and north. The halocline is an impediment to the mixing or exchange between the deep water and the surface water. There occurs a slow mixing through the halocline giving the surface water a low salinity. In the central Baltic the salinity of the surface water is about 1/5 of the salinity of the ocean water while the salinity of the deep water is about 1/3 of the ocean water salinity. The concentration of oxygen throughout the water is not at a constant level because of the slow mixing through the halocline. The surface water is well aerated but the oxygen contents of the lower waters are continously decreasing from top to bottom. The reason is that there is almost no supply of oxygen to the deep water from the moment it sinks down below the surface water at the entrances to the Baltic. The original oxygen in this water is partly consumed by oxidation processes and only insufficient amounts of oxygen can be added through the slow mixing through the halocline.

Because the salt water which is mixed into the Baltic water is real ocean water it has ocean water properties. Also all the main constituents of ocean water are found in almost the same constant proportions as in the original ocean water in the Baltic. Fresh water from rivers, streams and precipitation is not equal to the "Aqua Destillata" of the chemist. It contains dissolved and suspended material. The water quality depends on many factors. The chemical composition of the precipitation depends on the origin and the route of the air mass involved in the precipitation (Eriksson 1959) and the composition of the river and stream water depends on the properties of the ground in the area which discharges its water through the water system. The Swedish and Finnish rivers originate mainly in granite areas which are rich in silicon but poor in limestone. The water of the Neva river is a mixture of granite rock soil water and limestone soil water. The Narva river and the rivers at the east and south coast of the Baltic proper contain water from limestone soil areas (Buch 1945). This influences the ion content of the Baltic water. The surface water is most influenced since it contains higher amounts of river water than the lower waters. The high limestone and silicon content of the water is notable in the Baltic. The limestone content is the most important factor. The silica exists dissolved in water in concentrations 20 below ~~0.2~~ μg-at/l and it is only slightly dissociated in silicate ions. Calcium exists in the sea water in high concentrations because it is one of the major elements of the ocean water. It is probably brought out into the Baltic as dissolved carbonate, mainly together with hydrogen carbonate and possibly also as sulfate ions. This increases the alkalinity of the Baltic water (Buch 1945). The alkalinity is defined as:

$$A = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

The influence of other ions is negligible except in stagnant water where HS^-, $H_2PO_4^-$, HPO_2^{2-} and NH_4^+ may have some influence (Richards et al. 1965). The hydrogen carbonate ion has the greatest influence on the alkalinity and because large amounts of calcium carbonate are brought to the Baltic with the river water, the alkalinity will to a certain degree be an indicator of the limestone content of the river water (Buch 1945). The reason why the calcium content is not quite proportional to the alkalinity is that the river waters also contain magnesium carbonate and sulfate ions.

The relation between the calcium content and the alkalinity of the Baltic water has been investigated by **Gripenberg** (1937) and **Wittig** (1940) and the magnesium anomalies by **Nehring** and **Rohde** (1967) and **Rohde** (1966). **Kwiecinski** (1965 a) has investigated the SO_4^{2-}/Cl^- relation. He found generally an excess of sulfate ions with respect to ocean water. The surface water always showed an excess of SO_4^{2-}, especially in the eastern an southern parts of the Baltic. During stagnant conditions when H_2S had been formed in the deep water he found a deficit of SO_4^{2-} compared to what is found in ocean water. **Baars** (1930) has shown that the sulfide ions in stagnant water are formed from sulfate ions and not as one easily would believe from organic sulfur compounds. **Skopintsev** (1957) has demonstrated that this is true also for the H_2S in the deep water of the Black Sea. **Kwiecinski** (1965 b) also found a clear relation between the excess of Ca ions and Δ-S, i.e. the difference between the salinity determinations through conductivity measurements and through chlorinity titrations. Conductivity determinations with a "salinometer" measures the electrical conductivity of the water sample. This depends on the sum of ions dissolved per volume unit of water. It is influenced by all ions present in the water, also by those originating from dissolved gases. Chlorinity titrations determine only the sum of the halogen ions. The assumption of this technique is that major ions are present in constant proportions to the chlorinity. The salinity is computed from the chlorinity using an experimentally determined formula (**Knudsen** 1901). Because there are anomalies in the content of calcium, magnesium, carbonate (specifically hydrogen carbonate) and sulfate in relation to the chlorinity of Baltic water, the two salinity methods give different results. The salinometer gives the sum of all the ions; the chlorinity titration gives only the ions which are in a determined relation to the chlorinity. The latter method gives the "conservative ions" in the water. Unfortunately it has hitherto not been possible to find a distinct relation between the methods. The salinometer may give up to 0.1 ‰ higher salinities (**Kwiecinski** 1965 b), (**Grasshoff** 1966 a, b), (**Cox** 1966). The variations are considerable in different parts of the Baltic, on different depths and during different seasons.

Because all the salinities from the beginning of the century until present time in the Baltic have been determined through chlorinity titrations, the Hydrographic Department of the Fishery Board has continued to use the chlorinity titration on Baltic water in spite of the fact that the salinometer is a much faster and more convenient instrument. In this way the long measurement series in the Baltic is continued.

III. General information

a. Station list, maps, topography

Fig. 1 shows a map of the Baltic with all the stations mentioned in the present paper marked. Table I shows the coordinates and depths of these stations. The depth given does not necessarily indicate the maximum depth of the deep basin. In some cases the station has been moved from the original place (FONSELIUS 1962).

The Baltic consists of a series of deep basins separated by sills. The system of basins has been described by the author earlier (FONSELIUS 1962). In the present paper the Baltic proper has been divided in main basins and these in sub-basins. The main basins are: The Arkona Basin, the Bornholm Basin and the Central Basin. The Central Basin consists of several smaller basins and can be divided in three large basins: the Eastern Gotland Basin (generally called the Gotland Basin in literature), the Northern Central Basin and the Western Gotland Basin. These again are divided in smaller sub-basins (see table II). The topography of the main parts of the Central Basin are shown in figures 2, 3, 4 and 5. The Landsort Deep has here been included in Fig. 5 which shows the Western Gotland Basin. Fig. 4 shows a separate map of the Landsort Deep.

b. On the volumes of the deep basins

No information on the volumes of the deep basins is available in the literature. An attempt has therefore been made here to compute the volume of each basin. Depth lines for 60 m and 100 m have been drawn on Swedish sea charts, scale 1:500,000, printed by Kungl. Sjöfartsverket (edition 1962). For each deep basin the depth lines for every 50 m has been drawn. For the Northern Central Basin the 125 m line has also been drawn. The volumes have been computed with the formula:

$$V=\frac{(a_1+a_2)}{2}\cdot h$$

where V is the volume, a_1 the upper surface, a_2 the under surface and h the depth in meters between the surfaces. The surfaces have been determined

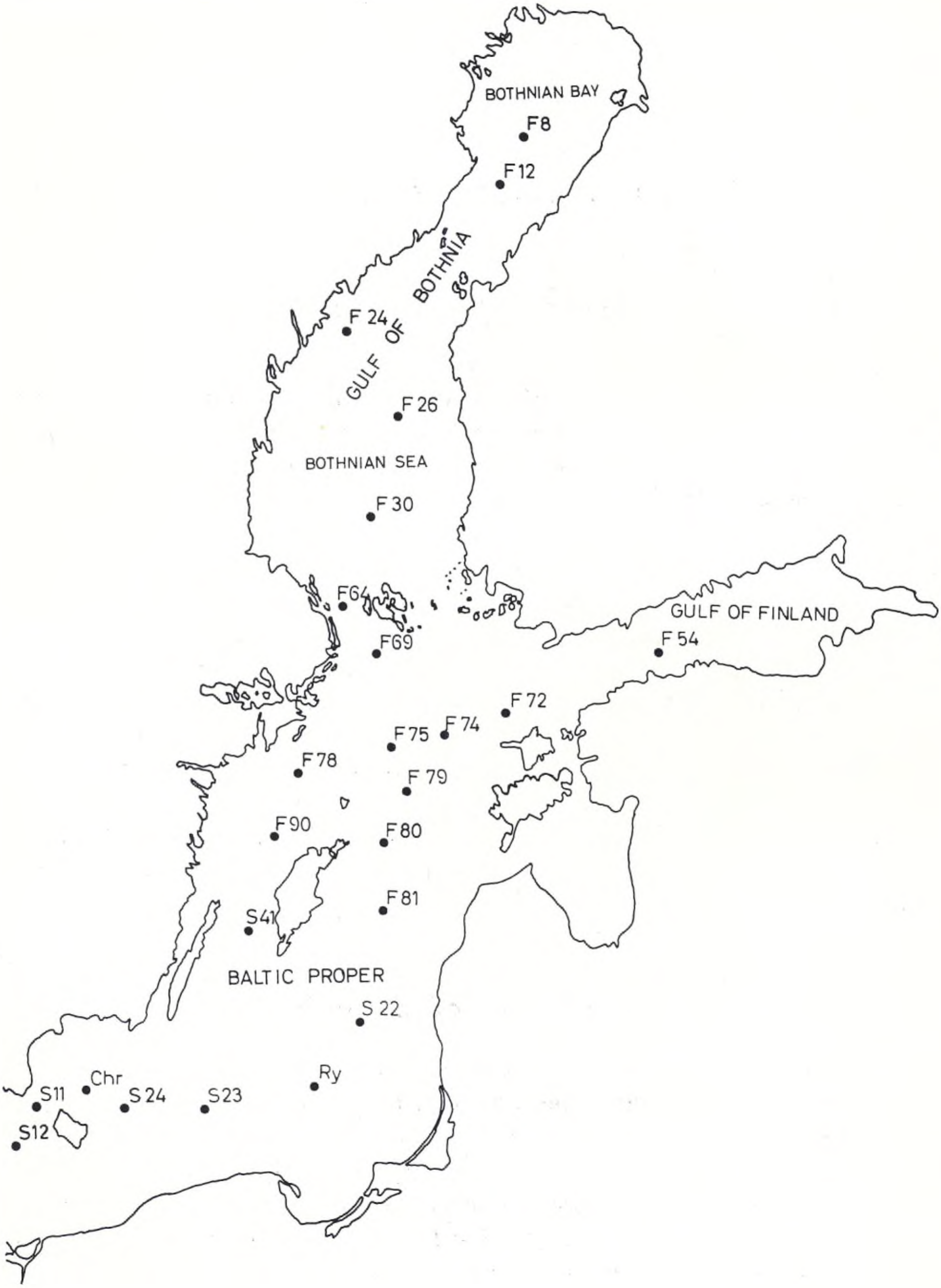

Fig. 1. Map of the Baltic showing the stations mentioned in this work and the main parts of the Baltic.

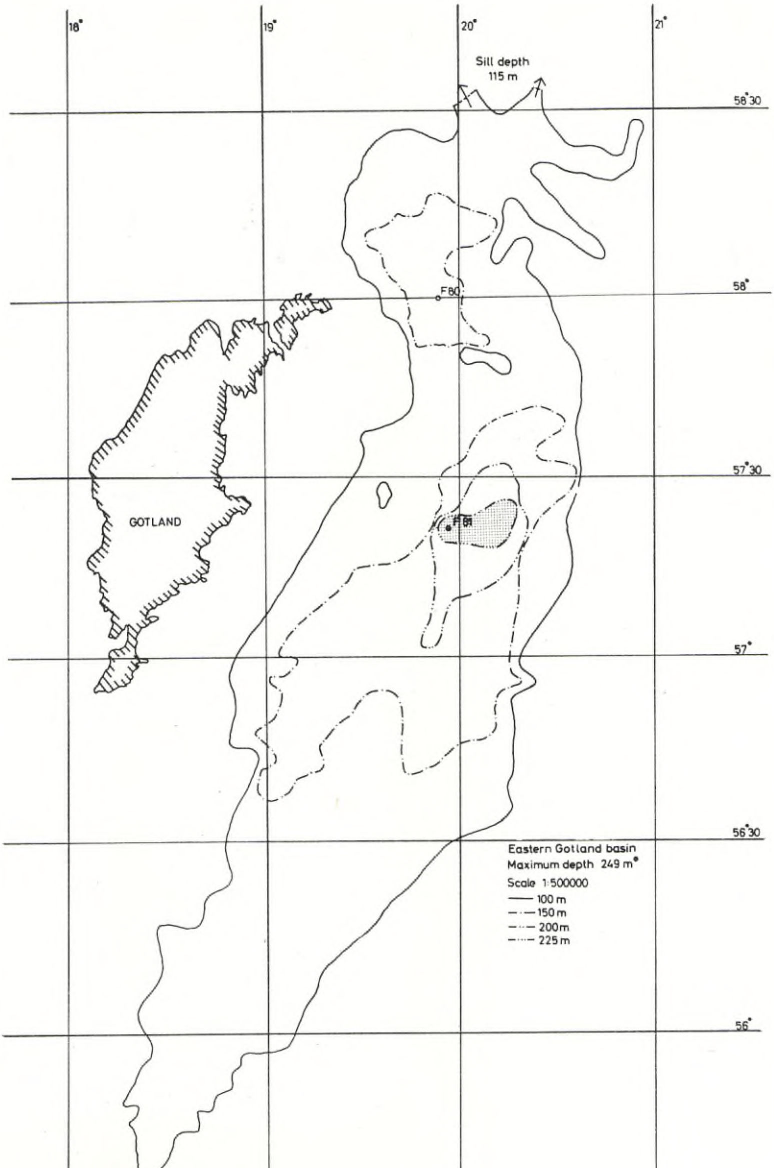

Fig. 2. The Eastern Gotland Basin. Depth lines for 100, 150 and 200 m are drawn. The depth below 225 m is shaded.

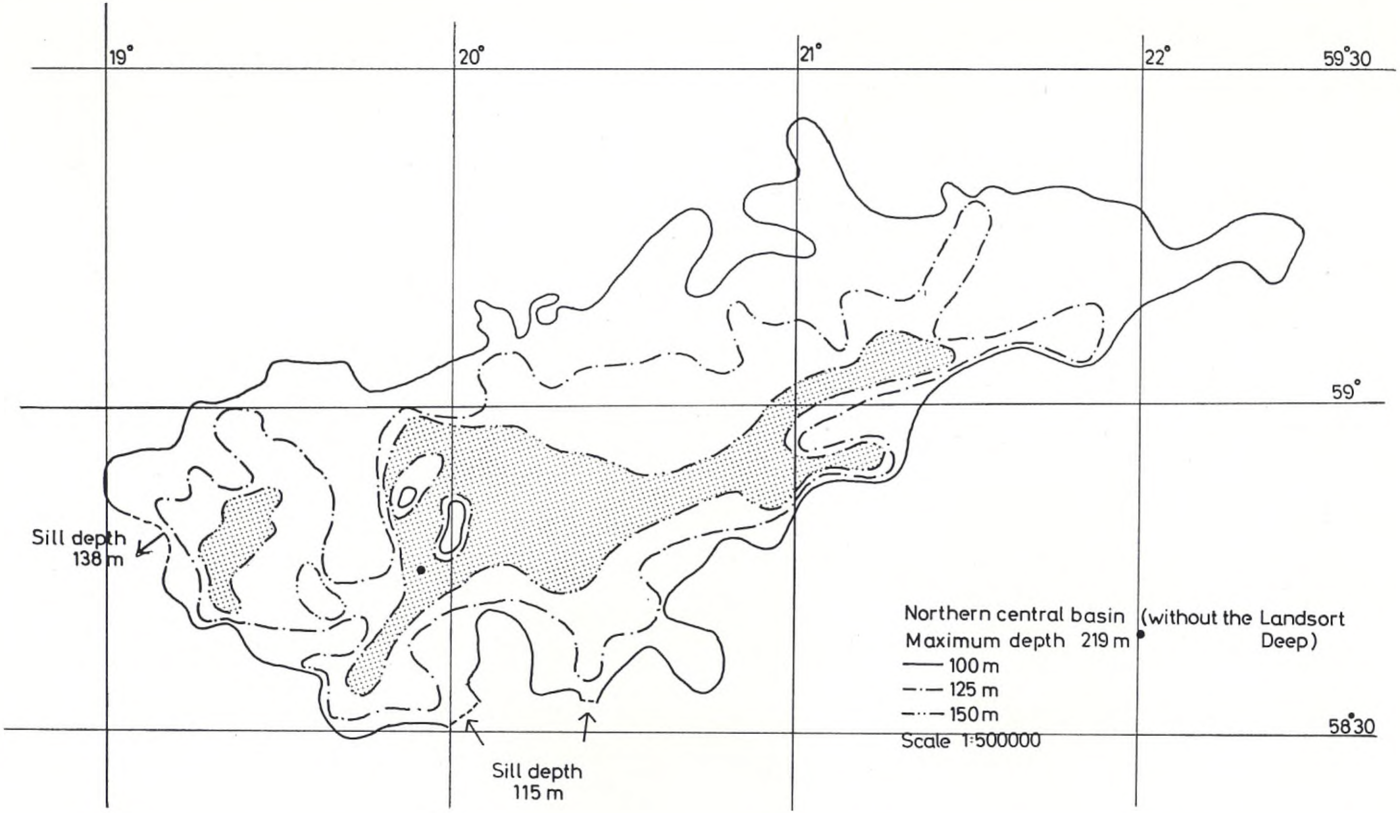

Fig. 3. The Northern Central Basin (without the Landsort Deep). Also called the Northern Basin in this paper. Depth lines for 100 and 150 m are drawn. The depth below 150 m is shaded.

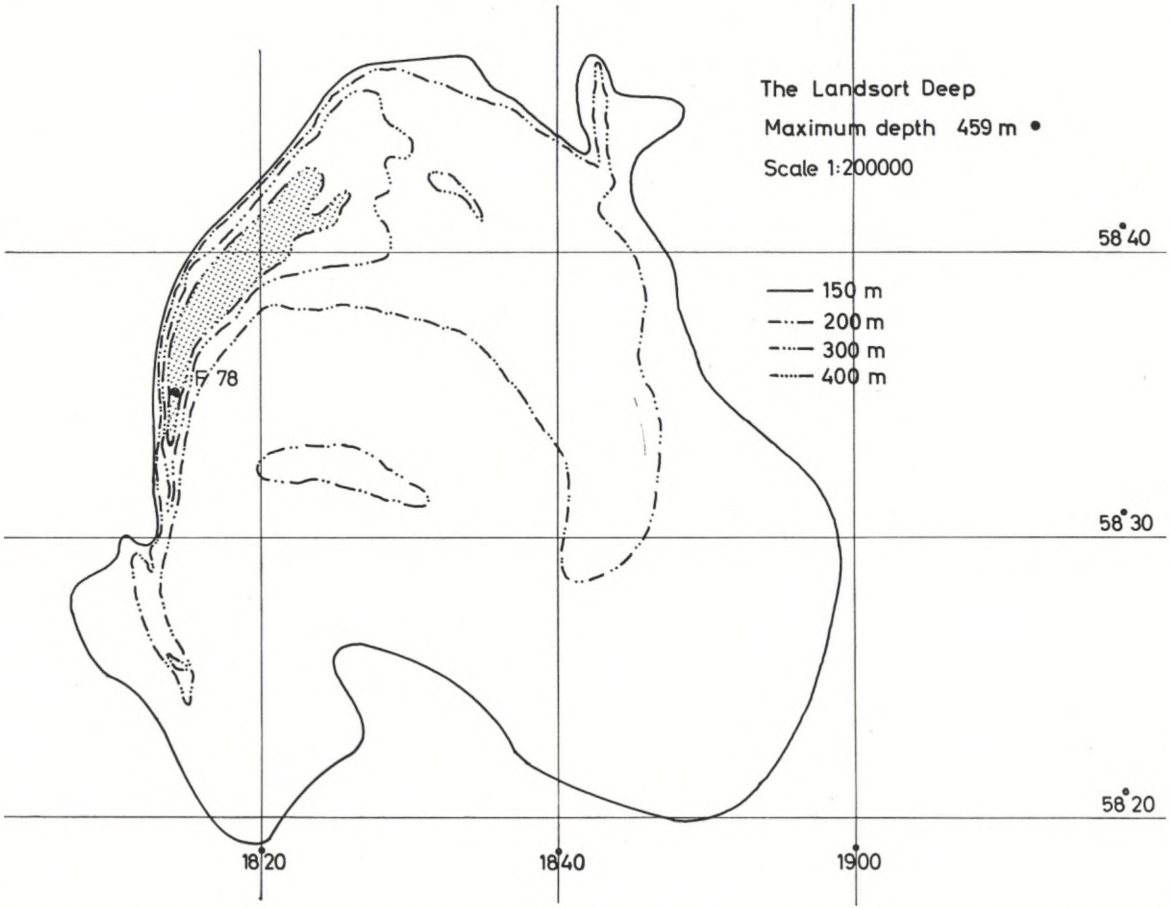

Fig. 4. The Landsort Deep. Depth lines for 150, 200, 300 and 400 m are drawn. The depth below 400 m is shaded.

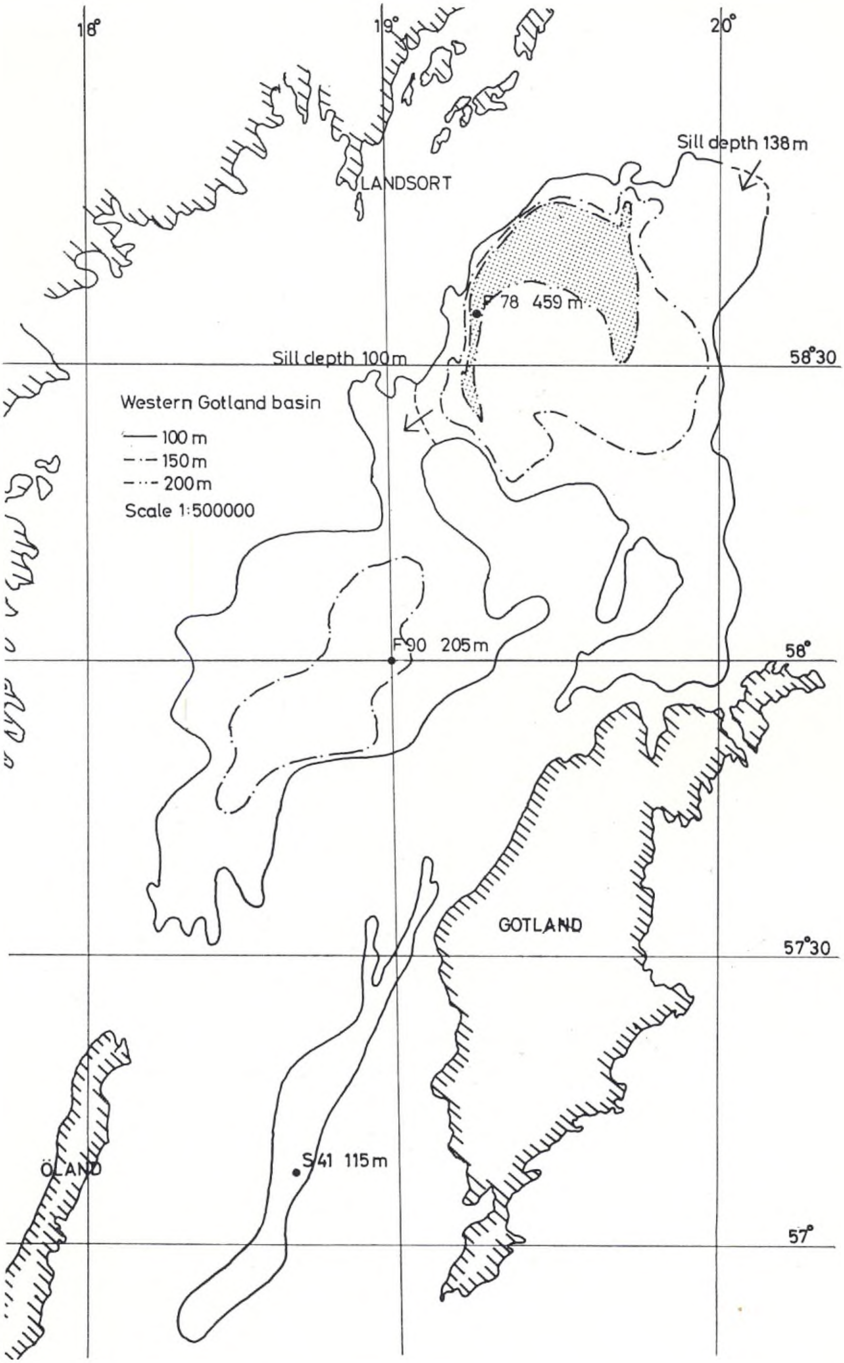

Fig. 5. The Western Gotland Basin (including the Landsort Deep). The depth lines for 100, 150 and 200 m are drawn. The Landsort Deep is shaded.

Table I. Hydrographic stations in the Baltic, the Kattegat and the Skagerack.

Station number and name	Latitude N	Longitude E	Depth m.
S 12 Arkona Deep	55°00′	14°05′	55
[S 11	55°17.5′	14°24′	51]
Chr Christiansö Deep	55°23.5′	15°17′	94
S 24 Bornholm Deep	55°15′	15°59′	95
S 23 Stolpe Deep	55°13′	17°04′	95
R (Ry)	55°38′	18°36′	102
S 22	56°07′	19°19′	115
F 81 Gotland Deep	57°20′	19°59′	249
F 80 Fårö Deep	58°00′	19°54′	205
F 79	58°26.5′	20°20′	140
F 75	58°53′	20°19′	170
F 74	59°02′	21°05′	178
F 72	59°17′48″	21°34′	176
F 78 Landsort Deep	58°35′	18°14′	459
F 90 Norrköping Deep	58°00′	18°00′	205
S 41 Karlsö Deep	57°07′	17°40′	112
F 69 Lågskär Deep	59°46′	19°47′	195
F 64 Åland Sea Deep	60°12.5′	19°07′	301
F 33	60°33′	18°55′	137
F 30	61°05′	19°35′	129
F 26	61°59′	20°04′	110
F 24 Ulvö Deep	62°50.5′	18°56′	293
F 12	64°13′	22°04′	110
F 8	64°40.5′	22°44′	94
F 54	59°43′	25°01′	101
Kullen	56°14′	12°22.2′	25
Fladen	57°11.5′	11°40′	75
M 6 Skagerack Deep	58°10′	09°30′	700

with a planimeter. The volumes, sill depths and maximum depths of the basins are shown in table II. The sill depths have in some cases been taken from SCHULZ (1956) but generally they have been estimated from the charts.

The volumes of the Arkona basin and the Bornholm basin are from KULLENBERG's work (1968).

KULLENBERG has computed the volume of the Central basin to be 3500 km^3. The volumes of the different sub-basins have, however, not yet been published. The method used for the computation was much more accurate than the method used by the author (KULLENBERG pers. comm.). This may explain the difference of 600 km^3 in the volume of the Central basin obtained by KULLENBERG and the author. KULLENBERG's work is at present not completed and may need to be controlled and revised in the details.

Therefore the author has used his own crude values in the present work. The method used may probably give around 10—15 % too high values. These discrepancies will, however, not influence the rather crude calculations made in this paper very much.

c. Units and expressions

The unit "microgram-atom" is generally used in chemical oceanography. It is here shortened to µg-at.

When the expression PO_4-P (phosphate-phosphorus) is used it always means the total amount of P in H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} present in the water.

Hydrogen sulfide or H_2S includes, when used below, also the ions HS^- and S^{2-}. It is here usually expressed in µg-at/l. It is inconvenient to use H_2S in ml/l when O_2 values are also included in figures which show the distribution of the two gases because of the great differences in the concentration of them in the Baltic water. In some cases H_2S has been given in both units. Occasionally it is convenient to express H_2S as "negative oxygen", but this unit does not give the real amount of H_2S present in the water and should therefore only be used as an oxidation equivalent for comparison purposes. "Negative oxygen" is the amount of oxygen equal to the amount of H_2S produced through reduction of SO_4^{2-}. The sulfate ion contains 4 atoms of oxygen which are used for the bacterial oxidation of organic matter and 1 atom of sulfur which is reduced from S^{6+} to S^{2-}. Multiplication of the H_2S value expressed in ml/l with 2 gives the "Negative O_2".

When oxygen saturation values have been used, they have been calculated according to FOX (1907) because the tables computed during the last years have not been internationally agreed upon.

d. A practical modification of the phosphate analysis method and the fast routine work with a spectrophotometer aboard ships

Experience has shown that the "single solution" method by MURPHY and RILEY (1962) is the best and most suitable phosphate analysis method for routine work at sea.

There are some modifications of the technique which can be introduced. Intercalibration tests (KOROLEFF 1965 c), (FONSELIUS 1966 a), JONES et al. 1966) have shown that filtering of the sample is not necessary in the Baltic and North Sea areas if sample water is used as reference solution instead of distilled water. An even better method is to use sample water acified with acid and molybdate because the absorbance of the sample may change when reagents are added. Also this corrects the turbidity of the sample water.

The single solution recommended by MURPHY and RILEY is stable for only 12 hours and a new solution has to be prepared every day. If the ascorbic acid solution, however, is stored separately, as suggested by KOROLEFF (pers. comm.), the solutions have been found to be stable for several weeks. The analysis method used at the Fishery Board of Sweden is carried out as described below:

The reagents recommended by MURPHY and RILEY are used in the original concentrations. All reagents except the ascorbic acid solution are mixed together and stored in a brown glass bottle. The ascorbic acid solution is stored separately in a dark glass bottle in the refrigerator. From each water sample 2 glass stoppered 50 ml test tubes are filled with 25 ml of sample

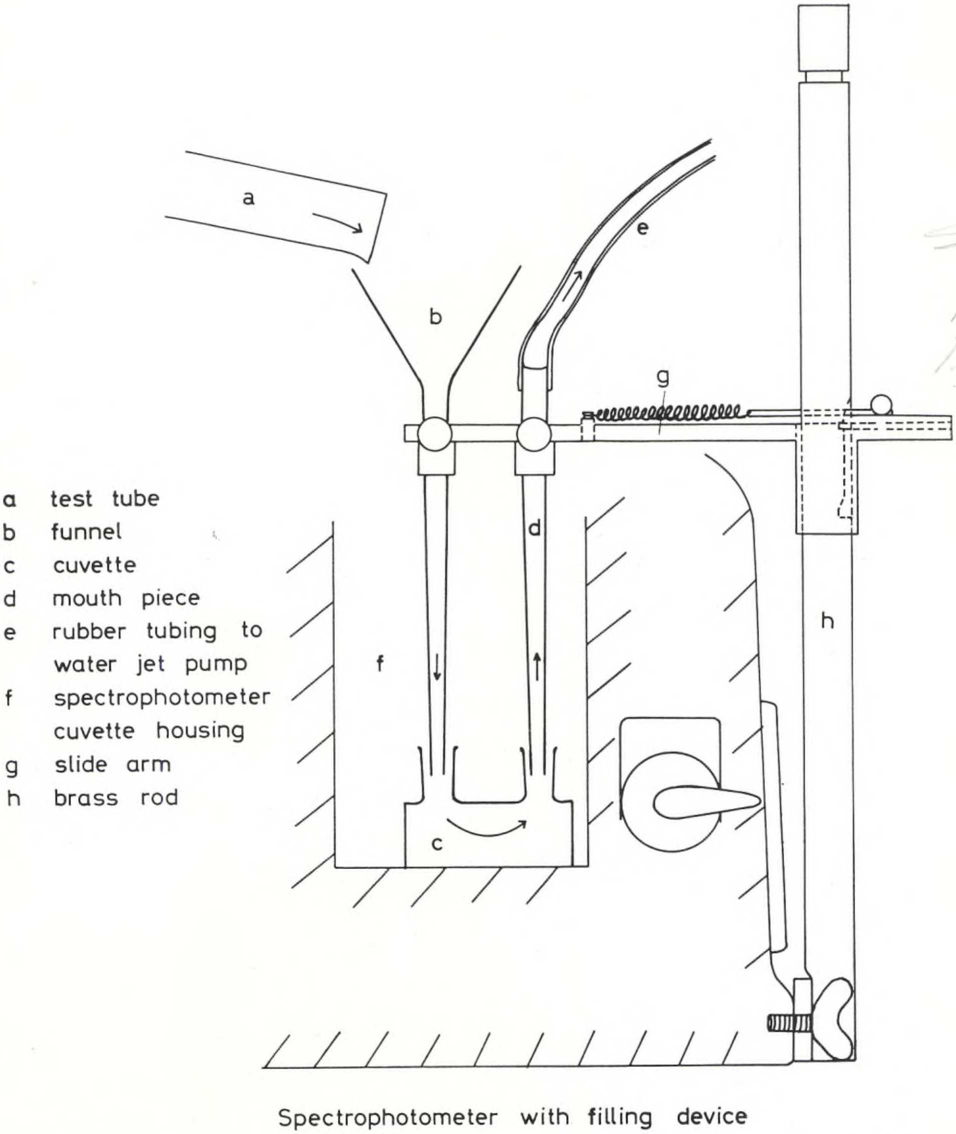

Fig. 6. Apparatus for fast filling and draining of cuvettes in a spectrophotometer.

Skulle ha
flyttats
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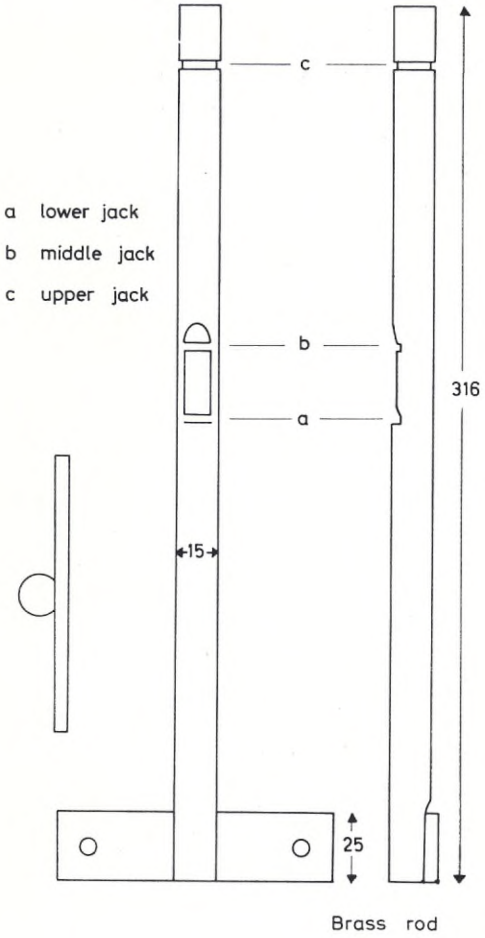


Fig. 7. Stand made of brass to the apparatus in Fig. 6.

using a Vogel pipette. To both test tubes 3.5 ml of the mixed reagent is added with an automatic 5 ml DL syringe pipette (manufactured by Dansk Laboratorieudstyr A/S, Ryesgade 3, Copenhagen N, Denmark). To the second test tube 1.5 ml of ascorbic acid solution is added with a similar 2 ml syringe pipette. The test tubes are stoppered and shaken and allowed to stand for a minimum of 10 minutes and a maximum of 12 hours. The absorbance of the samples is measured in a Beckman B spectrophotometer at 882 mμ using 5 cm cuvettes. The water of the first ascorbic acid free test tube is used in the reference cuvette. The results are evaluated by comparison with a curve which is constructed by means of a standard series of phosphate solutions.

For the routine work at sea the spectrophotometer has been furnished with an arrangement for fast filling and draining of sample water without removing the cuvettes from the cuvette housing. The method is applicable to

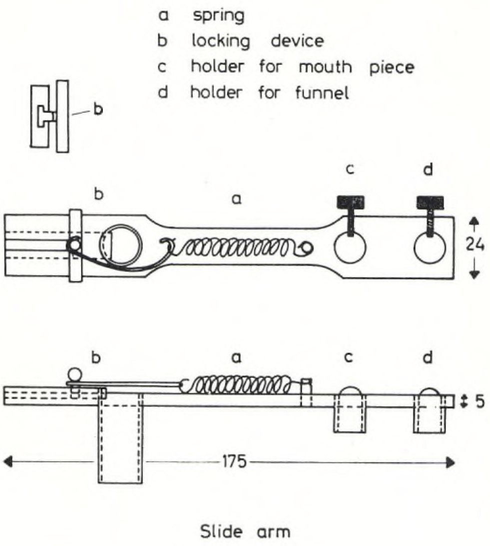


Fig. 8. Details of the slide arm belonging to the apparatus in Fig. 6.

most models of spectrophotometers and photometers and may be used in most kinds of routine measurements aboard. The construction of the device is described in detail below:

A stand made of brass (Fig. 6 h) is clamped to the base of the spectrophotometer with two screws. A sliding arm (Fig. 6 g) can be moved up and down the rod. The arm can be locked in three positions (Fig. 7 a, b, c) by means of a spring locking device (Fig. 8 b) and jacks in the rod. The sliding arm extends over the cuvette housing (Fig. 6 f) and is fitted with two holes (Fig. 8 c, d) corresponding to the two necks of the cuvette (Fig. 6 c) when it is in the light path. A small glass funnel and a mouth piece of glass tube (Fig. 6 b, d) are fastened through the two holes with the under ends at the same height. The mouth piece is connected to a water jet pump by means of a rubber tubing (Fig. 6 e). When the slide arm is locked in its lowest position, the funnel and the mouth piece extend through the necks exactly to the bottom of the cuvette. In the second position the ends extend half way into the necks (Fig. 6). In its highest position the slide arm can be turned away from the cuvette housing and the cover of the housing can be closed.

When the work begins, the cover is opened, the water jet pump is put to work and the two cuvettes are placed in position in the cuvette housing of the photometer. They are stored filled with distilled water. The stoppers are removed and the slide arm is carefully lowered into its lowest position. The water is now automatically sucked out from the cuvette. By filling sample water through the funnel the cuvette is washed (Fig. 6 a). Then the arm is lifted into the middle position. The main part of the sample is now

Table II. Volumes, sill depths and maximum depths of the Baltic deep basins.

Name of basin or deep	Volume km^3	Sill depth m	Max. depth m
Arkona basin (below 30 m)	70	17	55
Bornholm basin (below 60 m)	160	45	105
Central basin (below 60 m)	4100	60	459
1. Eastern Gotland basin (below 100 m)	921	60	249
a. Gdansk basin (below 100 m)	10	88	116
b. Gotland Deep (below 150 m)	196	60	249
c. Fårö Deep (below 150 m)	25	140	205
2. Northern Central basin (below 100 m)	558	115	459
a. Northern basin (below 100 m)	228	115	219
b. Landsort Deep (below 100 m)	270	138	459
3. Western Gotland basin (below 100 m)	101	100	205
a. Norrköping Deep	—	100	205
b. Karlsö Deep	—	101	112
Baltic proper+Gulf of Finland (0—60 m)	9500	—	—
Baltic proper+Gulf of Finland (totally)	13600	—	—

drained into the funnel and flushed through the cuvette. The jet pump prevents the cuvette from overflowing. The arm is then lifted in the uppermost position and the second cuvette is moved in position. The same procedure is repeated with the second test tube. The slide arm is turned away and the cover is closed and the sample is measured. The procedure is repeated with next set of samples. The water jet pump is connected to the salt water system of the ship and is kept going during the whole analysis procedure. The method allows a fast and safe handling of the samples even in bad weather.

IV. A new stagnation period in the central Baltic

Stagnation periods caused by salt water inflows are well known in some of the Baltic deep basins. Only one such stagnation period has been described in the literature before World War II (KALLE 1943). After the war the frequency of the stagnation periods seems to have increased. Two such periods have been described in previous papers by the present author (FONSELIUS 1962, 1967).

During the spring of 1965 there was a new inflow of high saline water with a high density into the bottom area of the Gotland basin. The salinity of the bottom water increased from 12.90 ‰ in January to 13.10 ‰ in April. Fig. 9 shows how during the summer and autumn the bottom water was slowly diluted by diffusion and turbulence through the boundary layer. During the spring of 1967 the bottom water was renewed by an increase of the salinity close to the bottom. During the inflow of 1965 the oxygen values below 200 m increased to nearly 2 ml/l. This can be seen in Fig. 10. Oxygen-poor water, however, remained in the layers above the new water. Oxygen concentrations as low as around 0.9 ml/l were found there. During the autumn of 1965 the oxygen values of the deep water decreased leaving a small

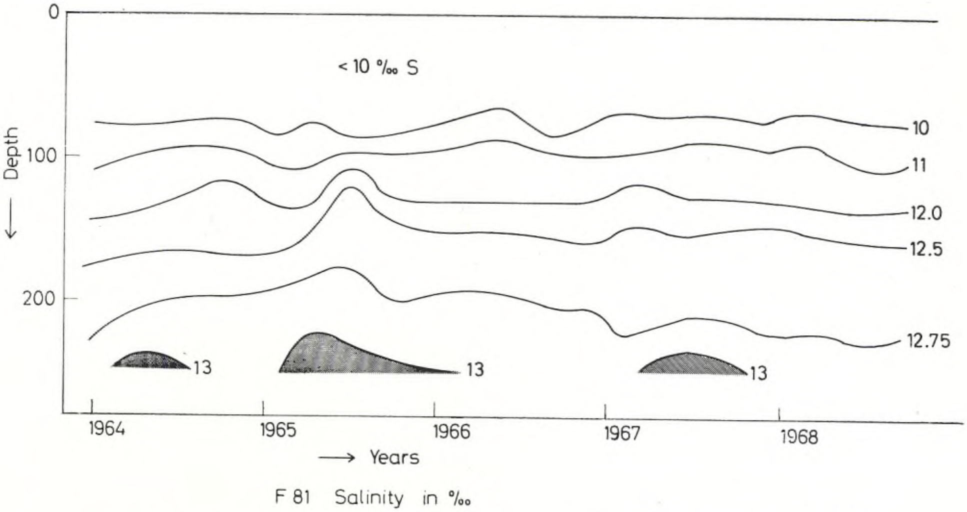


Fig. 9. The salinity changes in the Gotland Deep between 1964 and 1968.

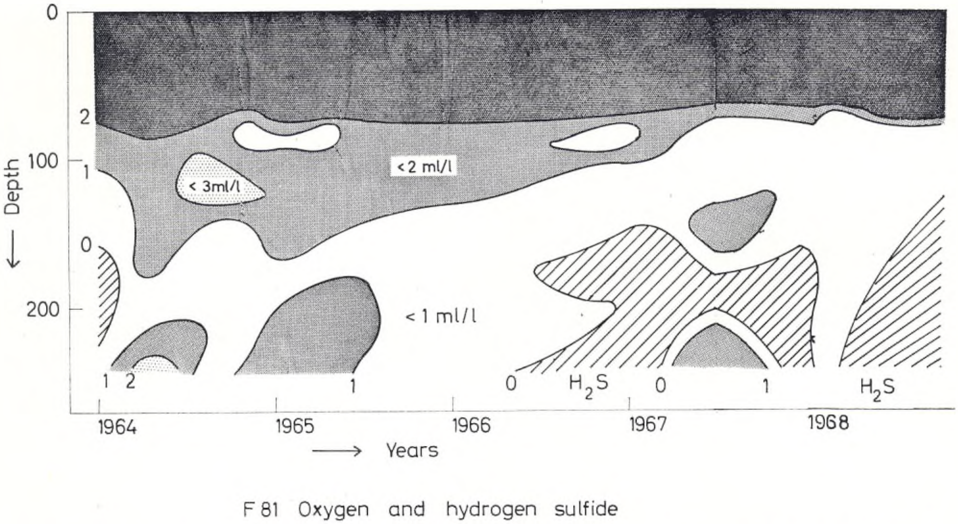


Fig. 10. Oxygen and hydrogen sulfide in the Gotland Deep between 1964 and 1968.

maximum at 200 m. During 1966 this development continued and two well pronounced oxygen minima, one at 175 m and the second close to the bottom below the 200 m maximum could be seen. During the summer H_2S was formed in the two minima areas leaving an oxic zone between them. In November there was still traces of oxygen left at the 200 m level but in February 1967 total stagnation had developed in the deep water and H_2S was found from 150 m down to the bottom of the basin. In June it was found that oxygen-rich water had replaced the stagnant water close to the bottom. There was, however, still stagnant water containing H_2S remaining between 175 m and 200 m.

The new water had such a high density that it remained in the deepest part of the Gotland basin and lost its oxygen. During the winter there again appeared H_2S in the bottom water. A very weak renewal of the whole water mass occurred in the beginning of 1968 but very soon the oxygen disappeared again and the H_2S layer began to grow. At present (November 1968) the H_2S extends up above 150 m.

When the oxygen in the deep water decreases, there is always a corresponding increase of the phosphate values. Fig. 11 shows the phosphate concentrations during the same period as the previous figures. The phosphate distribution tends to be a negative picture of the oxygen distribution with maxima where the oxygen has minima. The phosphate concentration is always relatively low in the inflowing oxygen-rich water. However, in stagnant water it increases rapidly because of the accumulation of phosphate set free from decaying organic matter and possibly partly because of the

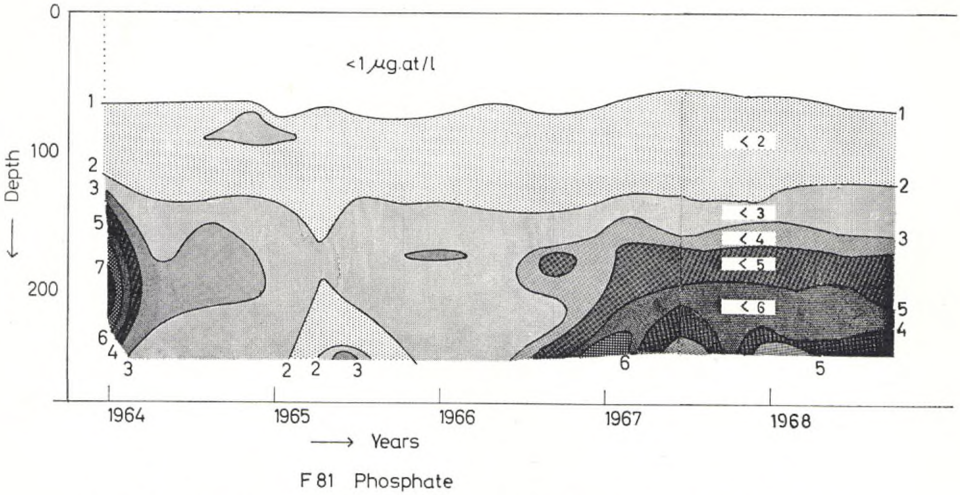


Fig. 11. Phosphate changes in the Gotland Deep between 1964 and 1968.

dissolution of phosphate from the sediments or sedimenting inorganic matter. The phosphate in the intermediate stagnant layer can, however, hardly originate from the bottom sediments.

Fig. 12 shows in detail the distribution of the hydrographic factors in the Gotland Deep and the Fårö Deep in May 1966. The oxygen minima at 175 m and 240 m in the Gotland Deep can be seen here. No traces of H_2S were found in the two deeps. Fig. 13 shows the conditions in August 1966. H_2S had been formed in great amounts in the Fårö Deep. In the Gotland Deep the H_2S formation had just begun close to the bottom and around 175 m. The phosphate values show corresponding maxima in the H_2S zones. Fig. 14 shows the situation in November 1966. At the time the H_2S increased to very high concentrations in the bottom layers in the Gotland Deep. There was still an isolated layer of H_2S containing water at 175 m. The water between these layers was almost anoxic and showed a high phosphate concentration. No H_2S had yet developed there. Fig. 15 shows the development of the stagnation in February 1967. Then the H_2S layer extended up to 150 m. The remains of the oxic zone at 200 m can be recognized as a small minimum in the distributions of both H_2S and PO_4-P. Surprisingly the water of the Fårö Deep had been renewed and all H_2S had disappeared there. Fig. 16 shows the beginning of the inflow of new water into the Gotland basin. Oxygen was again found in the bottom water but stagnant H_2S containing water still remained at the 200 m level. H_2S was again found in the Fårö Deep. This may have possibly been stagnant water from the Gotland Deep which had been forced down into the Fårö Deep over the sill between the two deeps.

Fig. 17 shows two longitudinal sections through the Baltic proper along

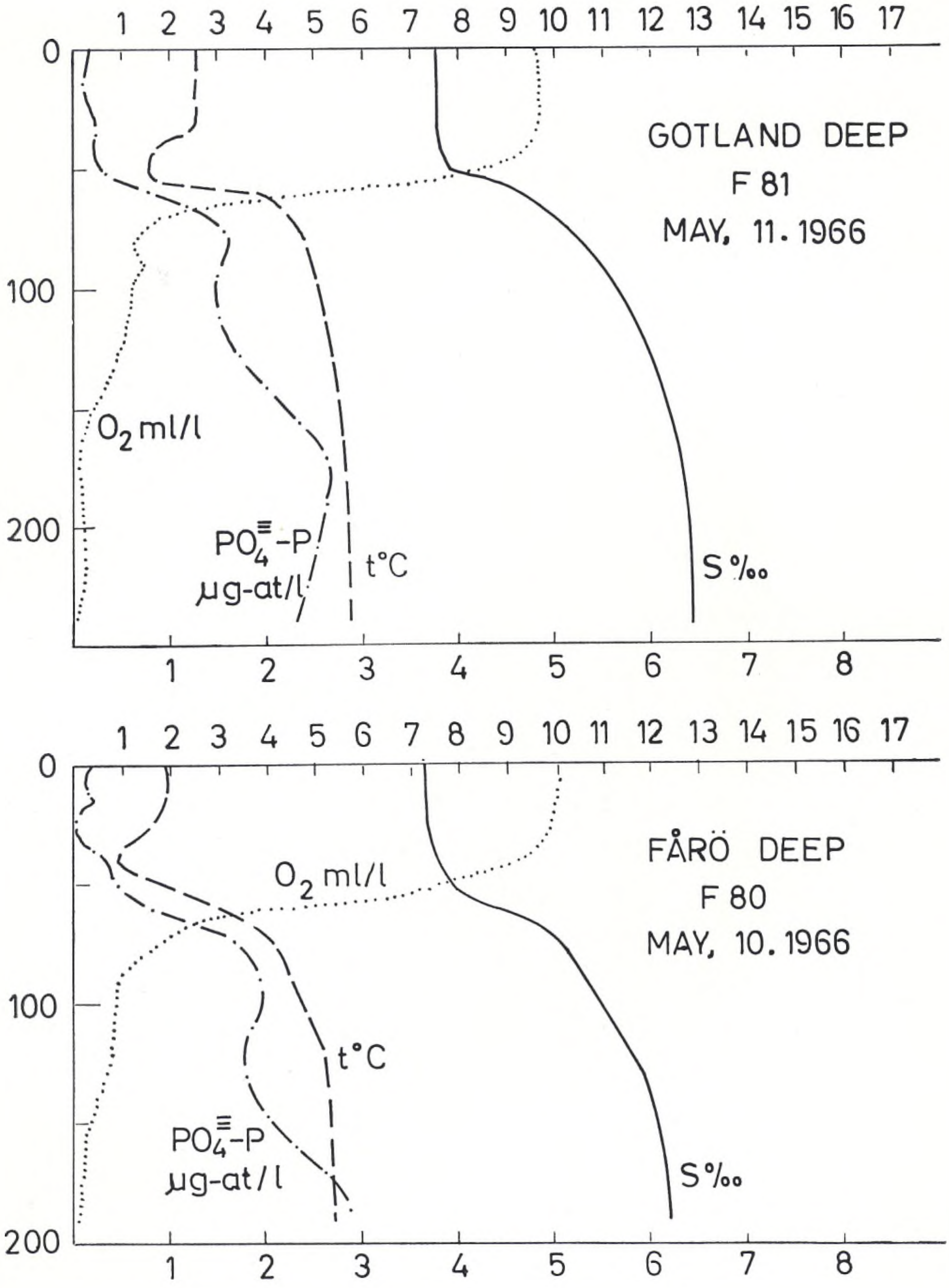


Fig. 12. Vertical distribution of hydrographical factors in the Gotland Deep and the Fårö Deep in May, 1966. The upper scale shows salinity, temperature and oxygen. The under scale shows phosphate.

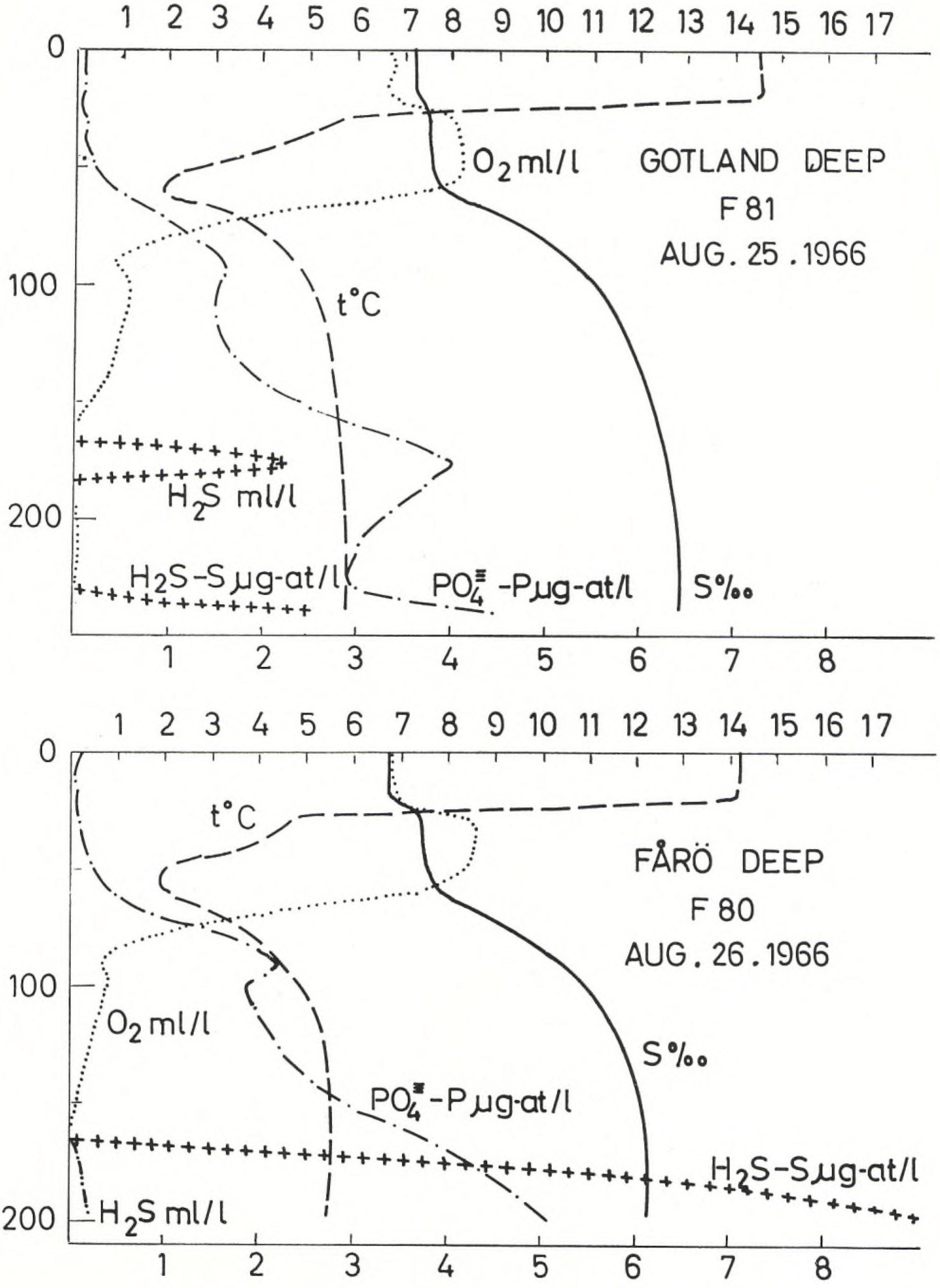
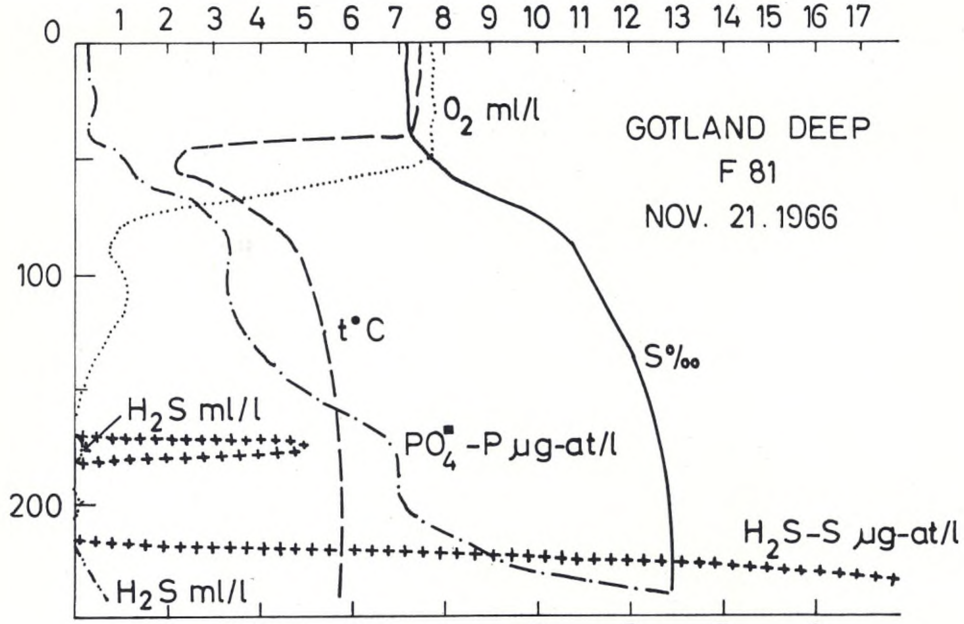


Fig. 13. Vertical distribution of hydrographical factors in the Gotland Deep and the Fårö Deep in August, 1966. The upper scale shows salinity, temperature, oxygen and hydrogen sulfide. H_2S is expressed both in ml/l and µg-at/l. The under scale shows phosphate.



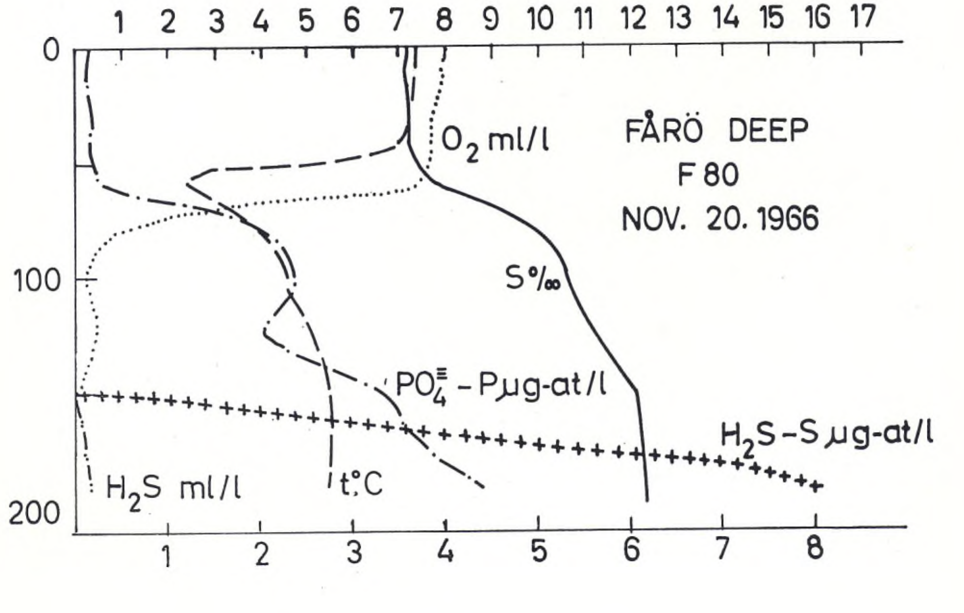


Fig. 14. Vertical distribution of hydrographical factors in the Gotland Deep and the Fårö Deep in November, 1966. The upper scale shows salinity, temperature, oxygen and hydrogen sulfide. H_2S is expressed both in ml/l and µg-at/l. The under scale shows phosphate.

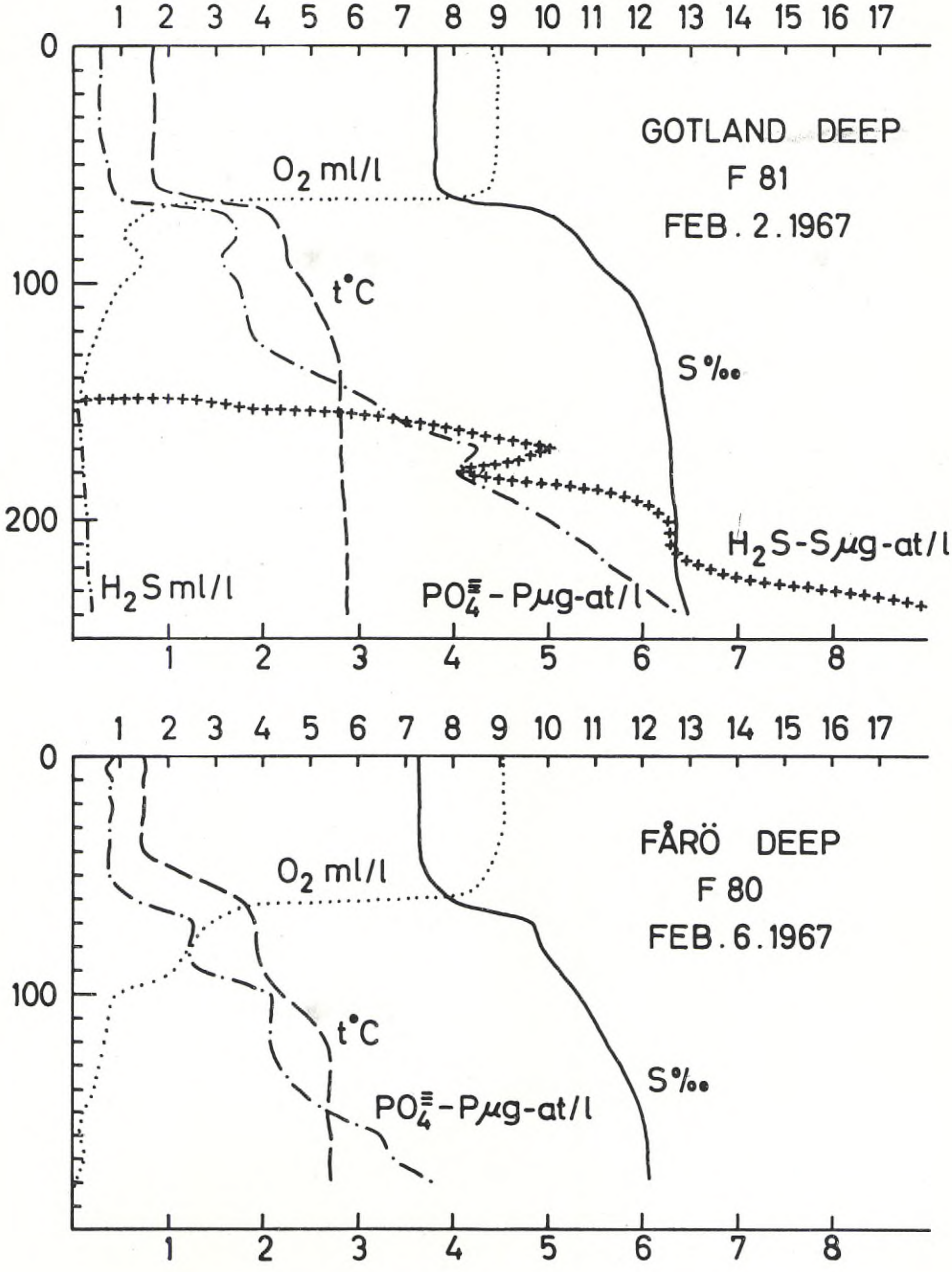


Fig. 15. Vertical distribution of hydrographical factors in the Gotland Deep and the Fårö Deep in February, 1967. The upper scale shows salinity, temperature, oxygen and hydrogen sulfide. H_2S is expressed both in ml/l and µg-at/l. The under scale shows phosphate.

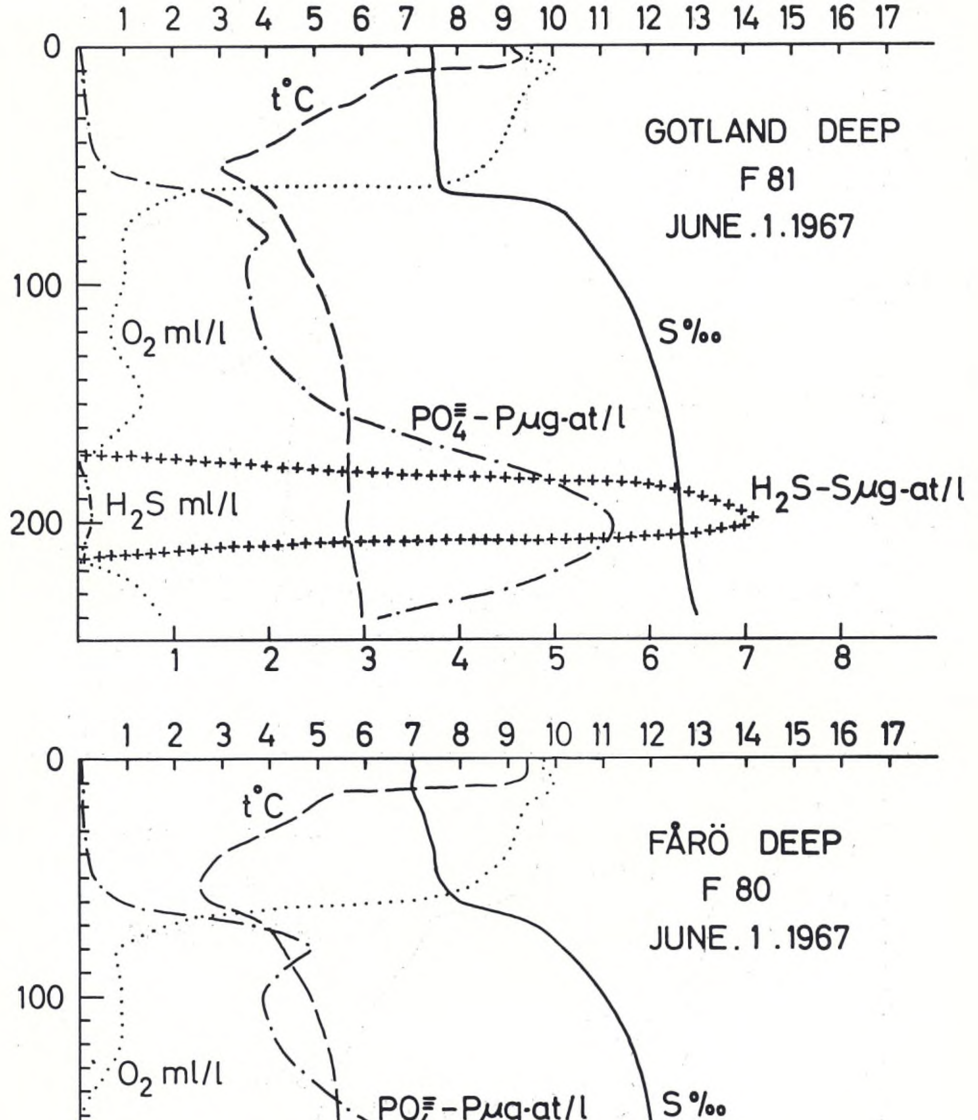


Fig. 16. Vertical distribution of hydrographical factors in the Gotland Deep and the Fårö Deep in June, 1967. The upper scale shows salinity, temperature, oxygen and hydrogen sulfide. H_2S is expressed both in ml/l and µg-at/l. The under scale shows phosphate.

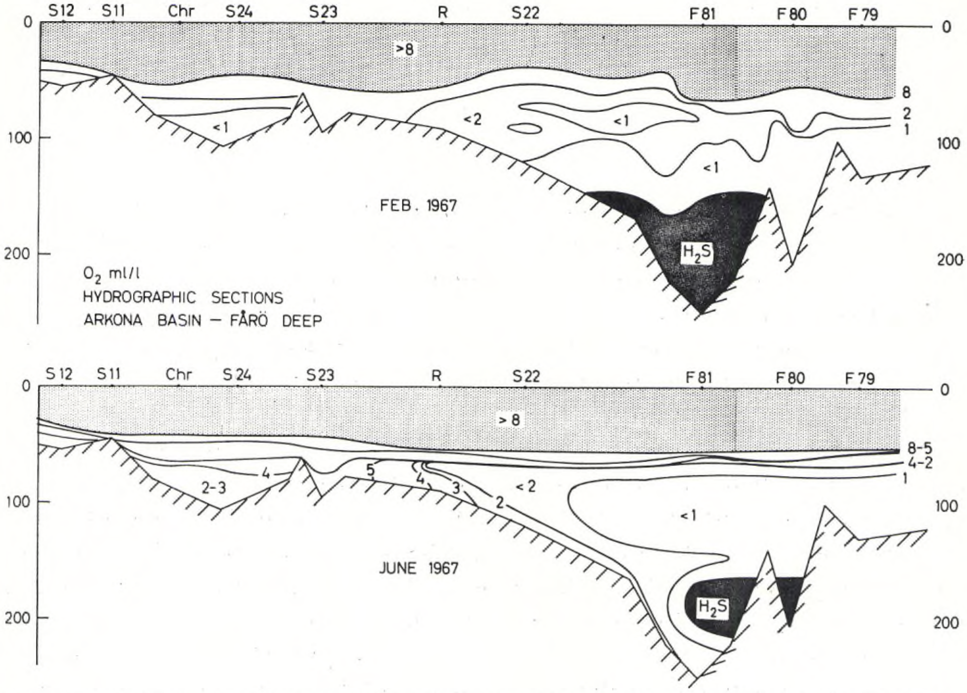


Fig. 17. Longitudinal sections of the Baltic proper through the stations S 12, S 11, Chr, S 24, S 23, R, S 22, F 81, F 80 and F 79, showing the distribution of oxygen and hydrogen sulfide in February and June, 1967.

the route of the "Skagerak" from the Arkona basin to the station F 79 north of the Fårö Deep. The sections show the oxygen distribution in ml/l and the H_2S contaminated areas in February and June 1967. The section above shows the conditions in February. The Gotland Deep is filled with H_2S containing water almost up to the sill of the Fårö Deep. The Fårö Deep does not contain any H_2S but the oxygen values are very low. The conditions below the halocline which is situated close under the isoline for 8 ml O_2/l in the figure are quite disturbed. A large area with oxygen values below 1 ml/l can be found in the water around 75 m. During the February 1967 expedition 18 stations were worked in the Gotland basin including the Fårö Deep. The figure therefore gives a very detailed and representative picture of the conditions in this area. The figure indicates that water from the layers above the H_2S zone would be forced over into the Fårö Deep. This may be the reason why the H_2S had disappeared there.

The section below in the figure shows the conditions in June 1967. Oxygen-rich water is shown to be streaming down into the Gotland basin expelling the stagnant water. A part of the H_2S containing water seems to have been forced over into the Fårö Deep.

When the stagnant water is mixed with oxygen-containing water the oxygen reacts with the H_2S oxidizing the sulfide to molecular sulfur or possibly into sulfate. This reaction consumes free oxygen from the water:

1) $$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

2) $$H_2S + 2O_2 \rightarrow H_2SO_4$$

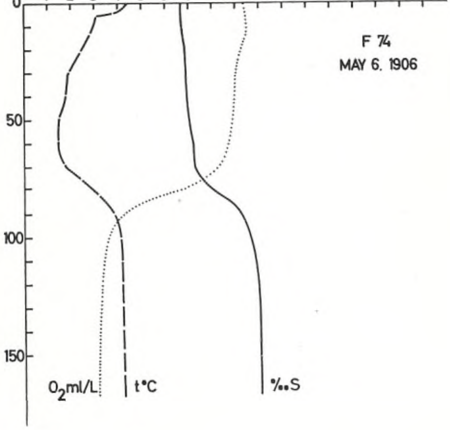
Probably the second reaction occurs in sea water (DYRSSEN pers. comm.). This relation requires 2 molecules of oxygen for every molecule of sulfide oxidized. The mixing occurs mainly in the deep water area north of the eastern Gotland basin and the water has there a very low oxygen content. The only supplies of oxygen are inflows of new deep water over the sills along the bottom of the Baltic proper from Kattegat and a little mixing in the boundary layer at the halocline. The renewal of the water in the Gotland basin forces almost oxygen free water over into the deep areas north of Gotland. This then impairs the oxygen conditions there. As has been shown earlier by the author (FONSELIUS 1967) the accumulated phosphate is released from the Gotland basin through the new inflow. It is mixed into the deep water of the northern Baltic proper and eventually, mainly during the winter, it is brought up to the surface layers. One may therefore expect a "fertilization" of the Baltic surface water again. The results from the "Skagerak"-expeditions in the Baltic during 1968 show that the new water in the Gotland basin lost its oxygen very quickly again. The stagnation continues and there are no signs of a new great inflow. On the contrary, the stagnant conditions grow worse and worse in the whole Baltic proper. Hydrogen sulfide was found even in the Bornholm basin during the autumn and winter.

V. On the oxygen deficit in the Baltic deep water

Oceanographers with some experience of the hydrographic conditions in the Baltic certainly have observed that the oxygen values in the deep water below the halocline have been extremely low during the last decade. They must also occasionally have experienced the smell of hydrogen sulfide in the bottom water of the Gotland basin. One may easily get the impression that these conditions are normal in the Baltic deep water since for at least 80 years it has been known that there is an oxygen deficit in the deep water. This water can only be renewed through inflows of Kattegat water through the Danish sounds (Ekman 1893).

Station profiles from different decades of this century show remarkable differences in the oxygen concentration of the deep water, especially in the northern part of the central basin. Fig. 18 shows the salinity, temperature and dissolved oxygen distribution at station F 74 in the northern Baltic proper in May, 1906. The depth there is more than 150 m and the station may well represent the conditions in the deep water of the whole of this area. The deep water there has a relatively homogenous composition from the halocline down to the bottom. This indicates good mixing. The temperature of the deep water was in May, 1906 about 4.2°C and the salinity at 150 m was 10.1 ‰. At the same depth there was 3.15 ml dissolved oxygen per liter. Fig. 19 shows the same station in July, 1939. The temperature of

Fig. 18. Vertical distribution of hydrographical factors at station F 74 in the Northern Central Basin in May, 1906.



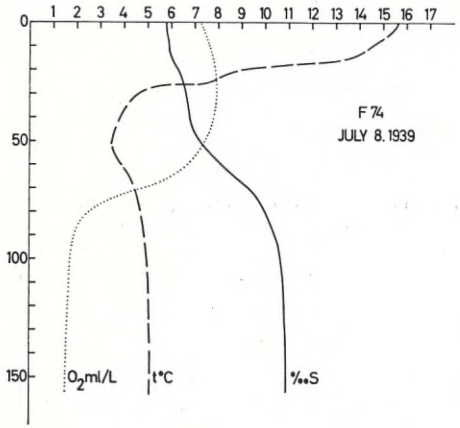


Fig. 19. Vertical distribution of hydrographical factors at station F 74 in the Northern Central Basin in July, 1939.

the deep water was now nearly 1°C higher than 1906, i.e. 5.2°C. The salinity at 150 m was 11.0 ‰ and there was only 1.5 ml O_2/l. It can be seen that the oxygen was half of the value it was 30 years earlier in spite of the fact that temperature and salinity had undergone only slight changes. Fig. 20 shows the conditions at the same station in June, 1967. The temperature has decreased slightly to 4.9°C but the salinity has increased a little to 11.15 ‰ at 150 m. There has, however, been an alarming decrease in the dissolved oxygen and it is now only 0.4 ml/l. The same conditions exist at other deep stations in this area.

In the following figures every available oxygen value from the literature and the ICES data lists for each particular station was used in order to test the continuity of the decreases in dissolved oxygen. At station F 74 the oxygen saturation values at 150—170 m from 1900 to 1967 have been

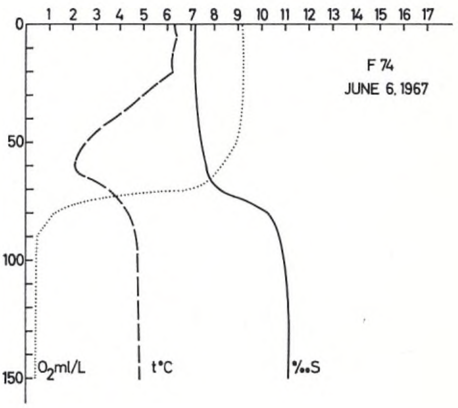


Fig. 20. Vertical distribution of hydrographical factors at station F 74 in the Northern Central Basin in June, 1967.

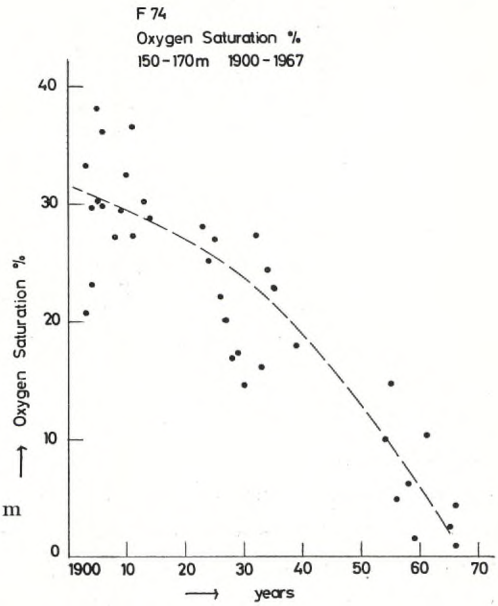


Fig. 21. The oxygen saturation at 150—170 m depth at station F 74 from 1900 to 1967.

computed. Fig. 21 shows how these values form a steeply falling curve. One may extrapolate that all dissolved oxygen will be used up in a very short time. Fig. 22 shows the absolute values for dissolved oxygen in ml/l at 100 m depth on station F 75 during the same period. This station is located almost

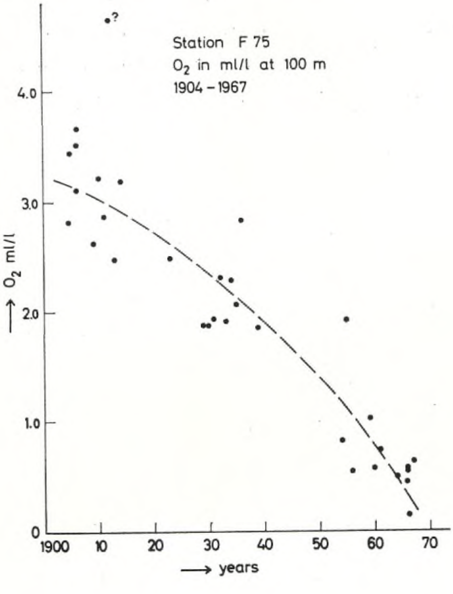


Fig. 22. Oxygen in ml/l at 100 m depth at station F 75 from 1900 to 1967.

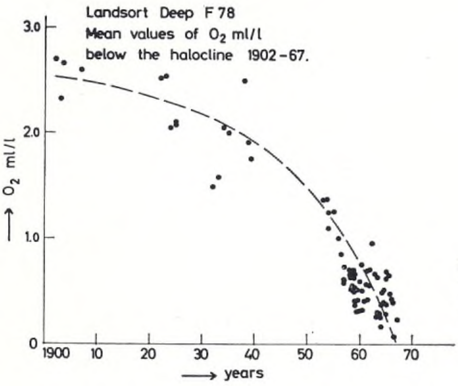


Fig. 23. Mean values of dissolved oxygen in ml/l below the halocline at station F 78 (Landsort Deep) from 1900 to 1967.

in the middle of the northern central basin. It is in the same vicinity as station F 74 and the oxygen curve for this station shows the same trend as at F 74. Fig. 23 shows the mean values for dissolved oxygen below the halocline at station F 78 and it is plotted in the same manner as the curves for the above stations. This station is the Landsort Deep, the deepest spot of the Baltic. Here one observes again the same pattern for the oxygen curve. If this trend continues for some years, the oxygen will disappear completely from the deep water. Then the formation of hydrogen sulfide through sulfate reducing bacteria will begin in the oxygen free water and soon it will spread to the higher layers just below the halocline.

There are no deep stations west of Gotland with a long record of oxygen measurements, but at present the conditions are just as bad there as north of Gotland and there is no reason to believe that the development has been different in this area. Hydrogen sulfide (H_2S) has been found there on several occasions. This is supported by measurements taken from the Norrköping Deep (F 90) at 150 m (Fig. 24) and from the Karlsö Deep (S 41) at 100 m

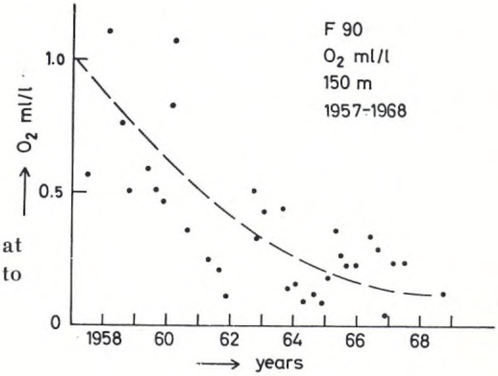


Fig. 24. Oxygen in ml/l at 150 m depth at station F 90 (Norrköping Deep) from 1957 to 1968.

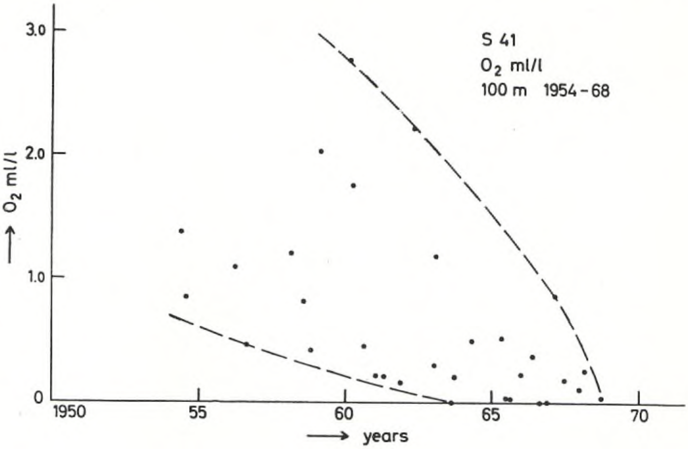


Fig. 25. Oxygen in ml/l at 100 m depth at station S 41 (Karlsö Deep) from 1954 to 1968.

during the period 1954 to 1968 (Fig. 25). At both stations the oxygen values decreased from the time the measurements began and are now close to O.

The Gulf of Finland is not separated from the Baltic proper by any sills and for this reason it may be regarded as a part of the central basin. There are no stations in the Gulf of Finland with a sufficient depth to be of significance, where continuous oxygen measurements have been taken from the

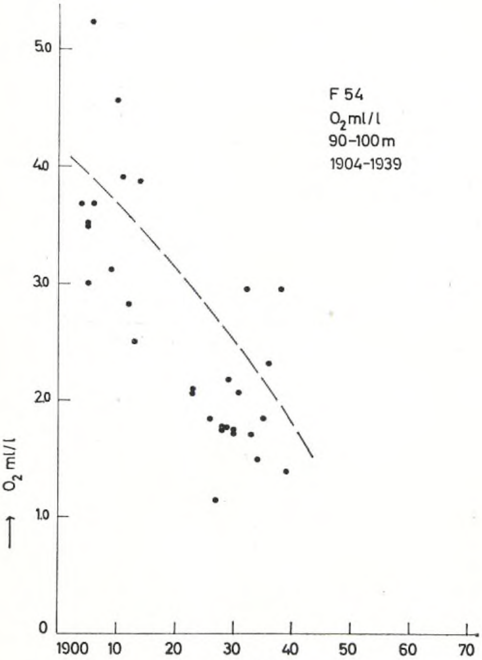


Fig. 26. Oxygen in ml/l at 90—100 m depth at station F 54 in the Gulf of Finland from 1904 to 1939.

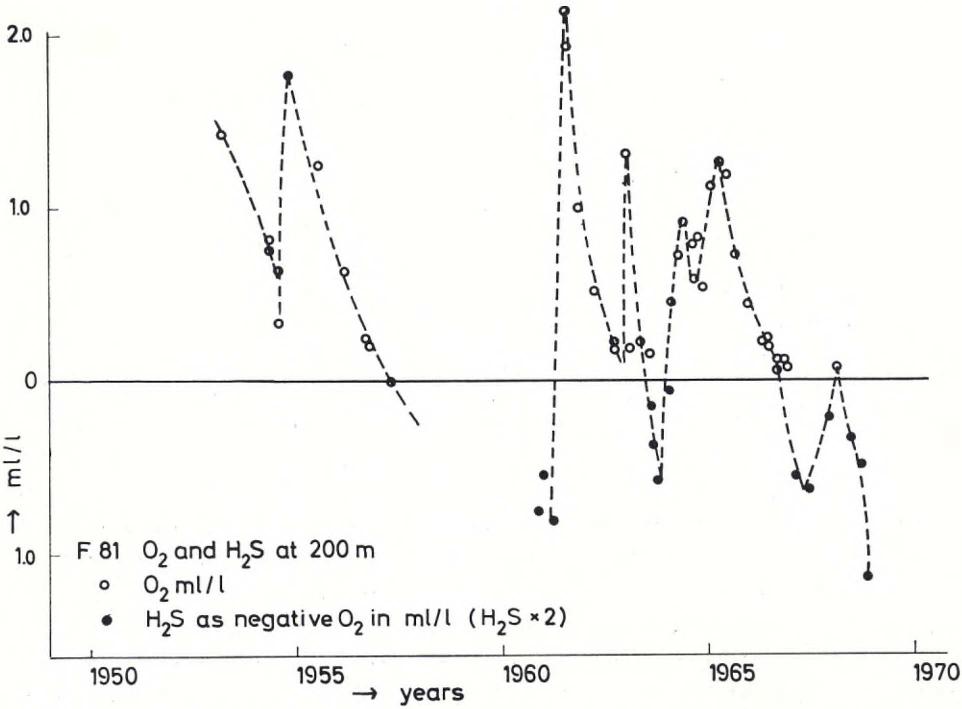


Fig. 27. Oxygen and hydrogen sulfide at 200 m depth in the Gotland Deep between 1953 and 1968. O_2 is expressed in ml/l, H_2S as "negative oxygen" in ml/l.

beginning of the century to present time. Fig. 26 indicates the oxygen values at station F 54 in the deepest part of the Gulf of Finland on the line Tallinn—Helsinki. The values are from 90—100 m depth. The measurements ended in 1939. After World War II the station was no longer located on international waters. Therefore it has not been possible to visit the station and no data have been published in the ICES data lists. The pattern of the oxygen values which have been collected is similar to patterns elsewhere in the central Baltic for the same period. It is quite possible that developments in terms of oxygen values at station F 54 have continued to parallel developments in the central Baltic.

The oxygen deficit in the Gotland basin has been described in earlier works (Fonselius 1962, 1967) and also chapter IV of this paper. Fig. 27 shows the oxygen variations and the forming of H_2S in the Gotland basin at station F 81 from 1953 to 1968. The oxygen values are given in ml/l and the H_2S values as "negative oxygen" ($H_2S \times 2$) in ml/l (the definition of negative oxygen is given in chapter III). The figure illustrates in detail how the oxygen continuously decreases after every inflow of new salt water. It can also be seen that the development of anoxic conditions after a salt inflow takes about 1 to 2 years and that the anoxic conditions at present seem to be worse than ever before. It is interesting to note that the great stagnation 1951 to 1961 actually can be divided in two parts. There occurred a new inflow of heavy oxygen-rich water in 1955 (Fonselius 1962). After this inflow the real anoxic conditions with development of H_2S began.

It has been shown by the author (Fonselius 1962) that the oxygen values in the deep water of the Bornholm basin show fast and great variations because the inflow area is quite near. For the above reasons the following discussion will not deal with the Bornholm basin.

The Gulf of Bothnia is separated from the Baltic proper by a sill with a sill depth of approximately 45 m. According to Hela (1958) and Palosuo (1964 b) a narrow 70 m passage exists through this sill to the Åland Sea. Because the halocline in the Baltic proper at present is located at around 60 m depth (see chapter VI) one expects that there will be only a small supply of Baltic deep water to the Åland basin. This has been confirmed through salinity observations at station F 69 in the Åland Sea (Palosuo 1964 b). Oxygen conditions in the central basin north of Gotland are poor. For this reason the oxygen values would be expected to decrease slightly in the deep water of the Åland Sea over a period of time. Fig. 28 shows the oxygen values in ml/l at 150—170 m on station F 69 from 1899 to 1961. A decrease of the oxygen values is indicated in the figure. The oxygen saturation values for F 69 on the same occasions were computed and are indicated in Fig. 29.

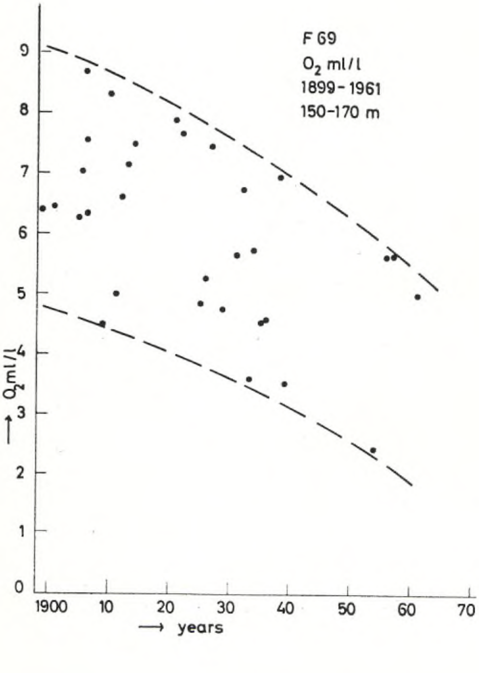


Fig. 28. Oxygen in ml/l at 150—170 m depth at station F 69 in the Southern Åland Sea from 1899 to 1961.

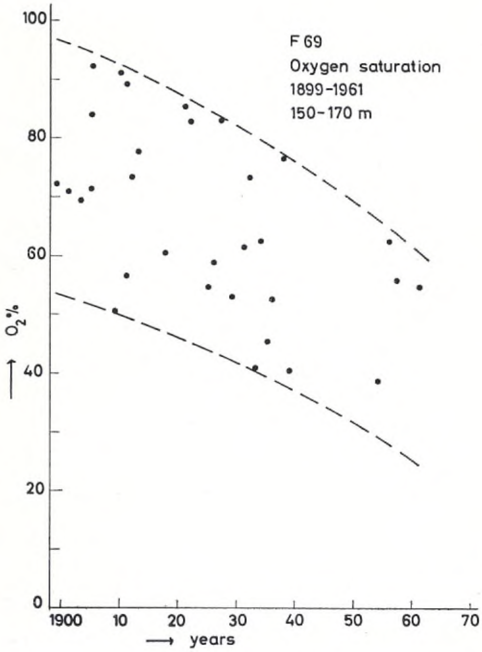
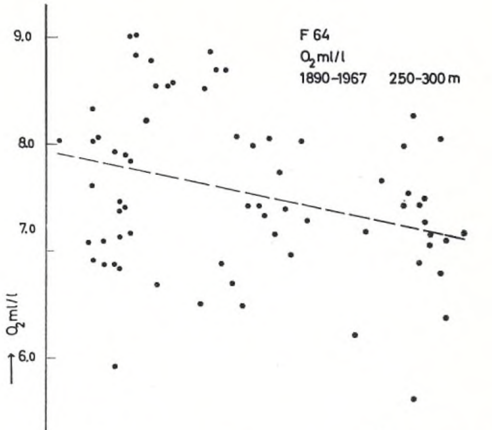


Fig. 29. Oxygen saturation values at 150—170 m depth at station F 69 in the Southern Åland Sea from 1899 to 1961.

Fig. 30. Oxygen in ml/l at 250—300 m depth at station F 64 in the Northern Åland Sea between 1890 and 1968.



The Åland Sea is divided into two basins by an approximately 80 m deep sill. The deepest station in the northern Åland basin is F 64. Fig. 30 shows the oxygen values at 250—300 m depth at this station. Only a slight influence of the Baltic deep water is detected here. The values were recorded from 1890 to 1968.

The Gulf of Bothnia has generally been regarded as a sea with a very good yearly aeration because of the thermohaline convection during the winter. This is not quite true. From GRANQVIST's work (1938) it is obvious that the southern part, the Bothnian Sea, renews its bottom water through horizontal exchange. During the winter, cold surface water from the northern Baltic proper sinks into the Åland Sea and streams along the bottom channel to the Bothnian Sea following the deepest parts. It circulates counterclockwise along the bottom. The winter convection does not reach through this water (PALOSUO 1964 b). Therefore the oxygen values in the far western deep part of the Bothnian Sea are lower than in the southern and eastern parts. If the amount of oxidizable organic matter were to be increased in the water, as for instance through waste disposal from the cellulose industry, then the oxidation of this matter could decrease the oxygen values of the deep water. Fig. 31 shows the oxygen values from 175—200 m depth between 1900 and 1968 at station F 24. This station is the Ulvö Deep, the deepest spot of the Bothnian Sea. The figure illustrates a steady decrease in oxygen values. Perhaps the

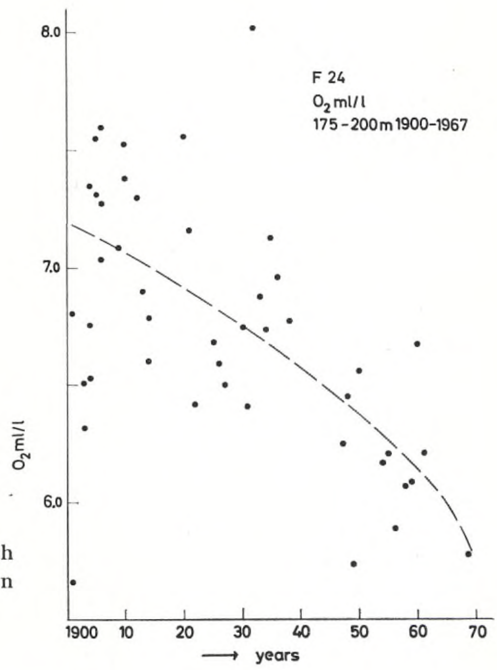


Fig. 31. Oxygen in ml/l at 175—200 m depth at station F 24 (Ulvö Deep) in the Bothnian Sea between 1900 and 1968.

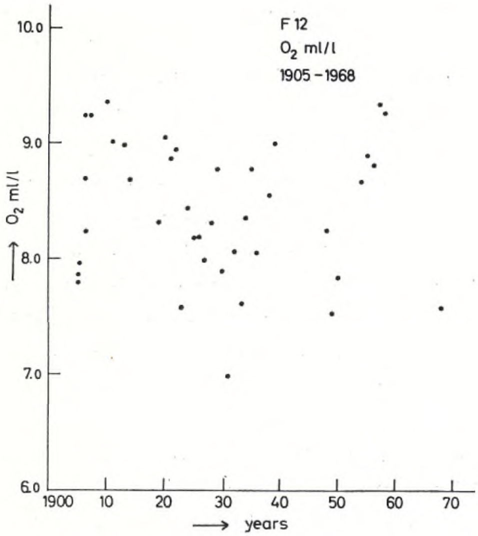


Fig. 32. Oxygen in ml/l at 100 m depth at station F 12 in the Bothnian Bay between 1900 and 1968.

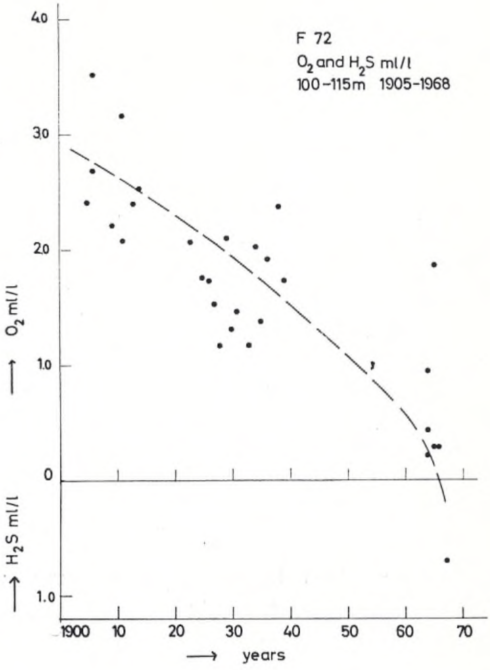


Fig. 33. Oxygen and hydrogen sulfide at 100—115 m depth at station F 72 in the Northern Central Basin at the mouth of the Gulf of Finland between 1905 and 1968. H_2S is shown in ml/l as negative values.

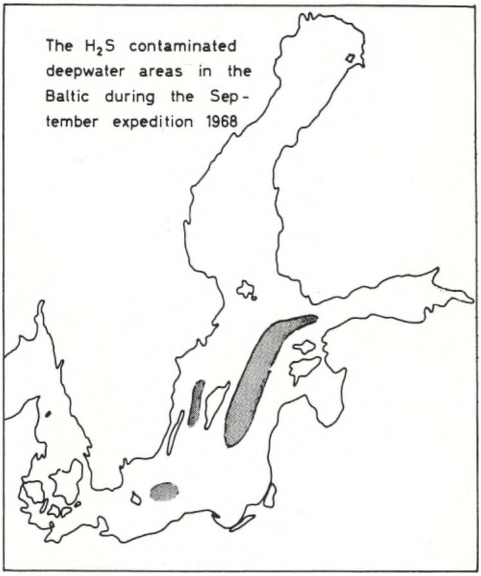


Fig. 34. The H_2S contaminated deep water areas in the Baltic proper in September, 1968. The areas are only approximately marked; the bottom topography is disregarded.

above mentioned oxidation process which involves waste disposal is responsible for this. It is also possible that the continuous decrease of oxygen values is caused by the increased salinity of the deep water (see chapter VI).

No such effect could be detected in the shallow northern part of the Gulf of Bothnia, the Bothnian Bay. Fig. 32 shows the oxygen values at 100 m depth at station F 12 from the beginning of the century to the present time. The great variations of the oxygen values indicate that the winter convection extends down to the bottom in this part of the sea and renews the bottom water every year.

During the "Skagerak" cruise in September, 1968 the chemical parameters were determined in the Baltic proper and the Gulf of Bothnia. It was observed that the oxygen conditions in the Baltic proper were extremely bad. H_2S was found in the deep water of the Bornholm basin, the Gotland Deep, the Fårö Deep, the Norrköping Deep and the Karlsö Deep. Surprisingly H_2S was also observed at stations F 74, F 75 and F 72 in the Northern Central basin. H_2S has never been observed at these stations earlier. It was indeed astonishing to find H_2S at 100 m depth at F 72 which is located at the mouth of the Gulf of Finland. Fig. 33 shows the oxygen values at this station from the beginning of the century to September, 1968 at 100 m. The curve is extended below zero and shows H_2S as a negative value in ml/l. The map in Fig. 34 shows the H_2S contaminated deep water areas of the Baltic in September, 1968. There still was no H_2S in the Landsort Deep. A brief discussion can clarify the reasons for this.

The Landsort Deep is a crescent formed depression with very steep sides.

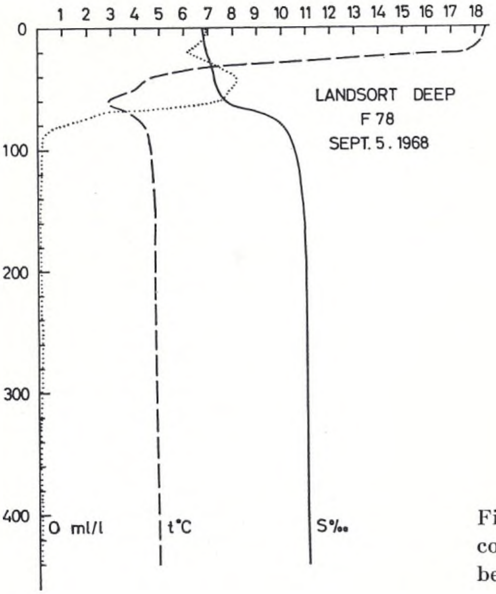


Fig. 35. Vertical section of the hydrographic conditions in the Landsort Deep in September, 1968.

The deepest part (maximum depth 459 m) is a very narrow canyon (Fig. 4). In the northern part the canyon opens to the east. The bottom currents must be relatively fast because the water is quickly exchanged. The very homogeneous conditions in the water below 100 m indicate that the mixing in the deep water is quite good (Fig. 35). Thus the Landsort Deep has withstood contamination until recently. If H_2S does appear there it will be because the Northern Central basin contains enough H_2S to penetrate over the sill between the Northern basin and the Landsort Deep. (The Landsort Deep can be viewed as a sort of indicator of the conditions in the whole deep water body north of Gotland; the absence of H_2S does not permit us to deduce anything about the conditions in neighboring water, but its presence in the Landsort Deep implies that H_2S exists in the Northern basin). Observations taken in September, 1968 indicate that H_2S will penetrate over the sill between the Northern basin and the Landsort Deep very soon.

In November, 1968 in the Landsort Deep H_2S was found from 300 m down to the bottom. This is the first time H_2S has been recorded in the Landsort Deep.

A more detailed picture of the increasing oxygen deficit in the deep water of the Landsort Deep is given in Fig. 36. Here the development from 1890 to the present time is shown in a time diagram. Only the isolines for each ml/l oxygen have been drawn. The curves have been smoothed and the conditions during the World Wars have been interpolated. It can be seen how the oxygen deficit continuously increases. The isoline for 4 ml/l O_2 was close to

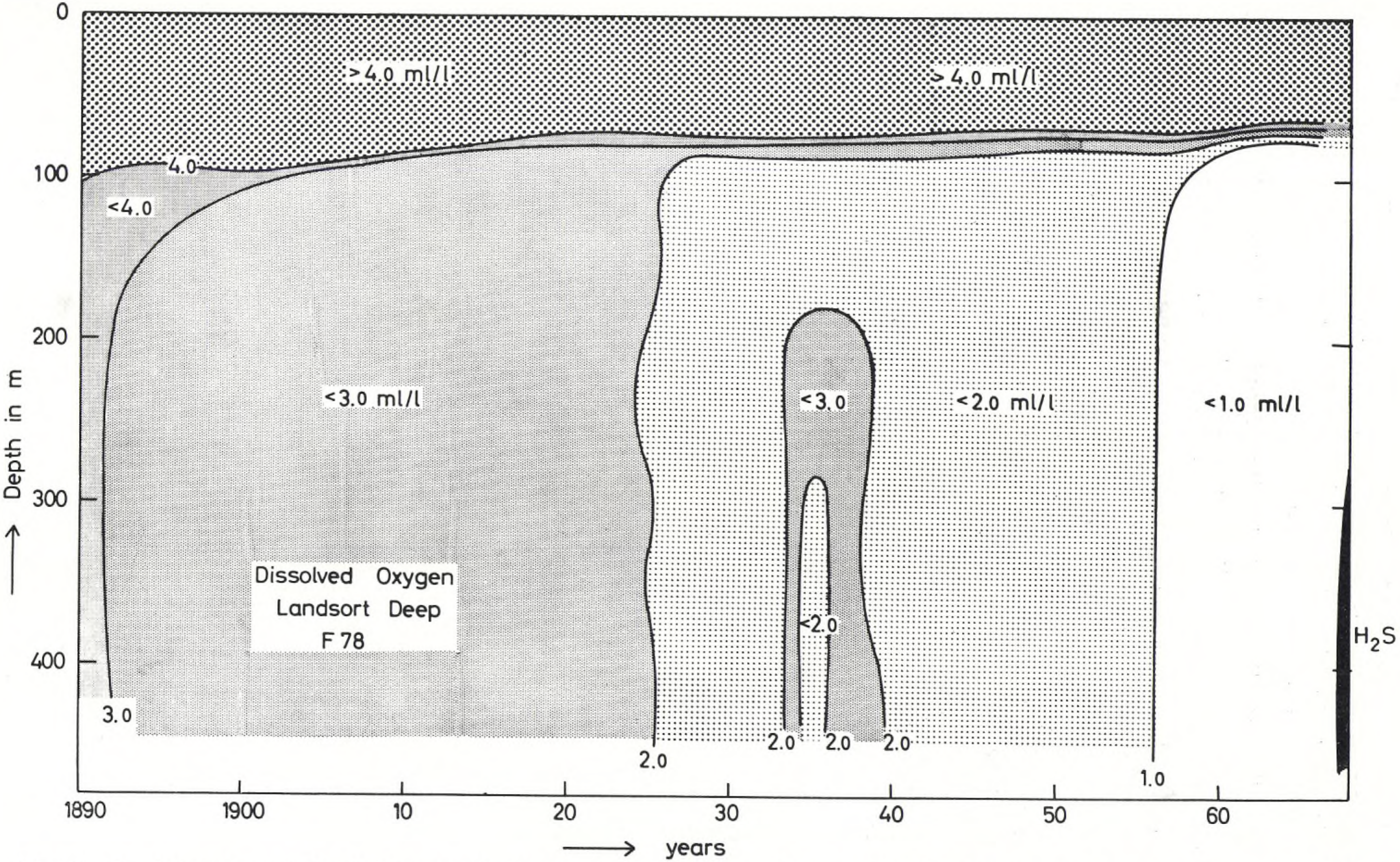


Fig. 36. The distribution of dissolved oxygen in the Landsort Deep from 1890 to 1968, showing the appearence of hydrogen sulfide in November, 1968. (Smoothed figures).

100 m in the beginning of the century and is now almost at 60 m. The improved conditions during the 1930's can also be viewed as an increase of the oxygen values in the deep water during that period (see chapter VI). The very last results from the November expedition 1968 are included in the figure. H_2S was now observed in the Landsort Deep from 300 m down to the bottom. It was mentioned above that this contaminated water originates from the deep areas of the northern Central basin. The H_2S has now reached the sill level to the Landsort Deep there and the anoxic water streams over the sill down into the Landsort Deep.

If this development continues in the Baltic deep water, the whole water mass below the halocline will soon turn into a lifeless "oceanic desert" such as is found in the Black Sea. The present stagnation will probably lead to a catastrophe for the bottom fauna in the deep areas of the whole Baltic proper.

VI. On long-time variations of salinity, temperature and density

It is a well established fact that the salinity of the Baltic water has increased since the beginning of the 20th century. This increase has been described by several authors: GRANQVIST (1952), SEGERSTRÅLE (1953), LINDQUIST (1959), AHLNÄS (1962), SOSKIN (1963), HELA (1966). This increase has occured both in the surface water and in the deep water. It is more easily followed in the deep water where the annual variations of the river water discharge will not cause direct and fast fluctuations of the salinity.

The salinity increase at the station F 81 in the Gotland basin from 1900 to 1968 is shown in Fig. 37. The values up until 1960 are taken from the work of SOSKIN (1963). The later values are yearly mean values of the measurements carried out by the Fishery Board of Sweden. There do not exist any data from the time of the two World Wars, but judging from the conditions before and after the wars, one may draw the conclusion that no important changes have occured in the Gotland basin during these periods. It should be noted that although SOSKIN's data are claimed to be annual mean values, there exist only one single series of measurements for most of the years. These measurements can not be assumed to always be representative for a year.

From the figure one can see the decrease of the salinity during the 1930's described by SOSKIN (1963) and others. This decrease occurred both in the surface water and the deep water. During 1938—1939 a new inflow of more saline water began in the bottom layers. This process most probably continued during World War II. From the figure it can be concluded that the surface salinity has remained above 7 ‰ since 1947 and that the salinity below 150 m has not decreased below 12 ‰ during the same period. The great salt inflow during 1951—1952 (FONSELIUS 1962) raised the salinity above 13 ‰ at 150 m. During the following stagnation period, which began in 1955, the salinity decreased continuously and reached the isohaline for 13 ‰ at 225 m depth in 1959. There are no direct signs of a beginning general decrease of the salinity in the Baltic as claimed by SOSKIN (1963). On the contrary, the salinity may well continue to increase.

The isohaline for 8 ‰ can be considered to be the upper limit for the halocline in the Baltic proper (HELA 1966). From the previous figure it can be seen that the increased salinity of the deep water has forced the halocline

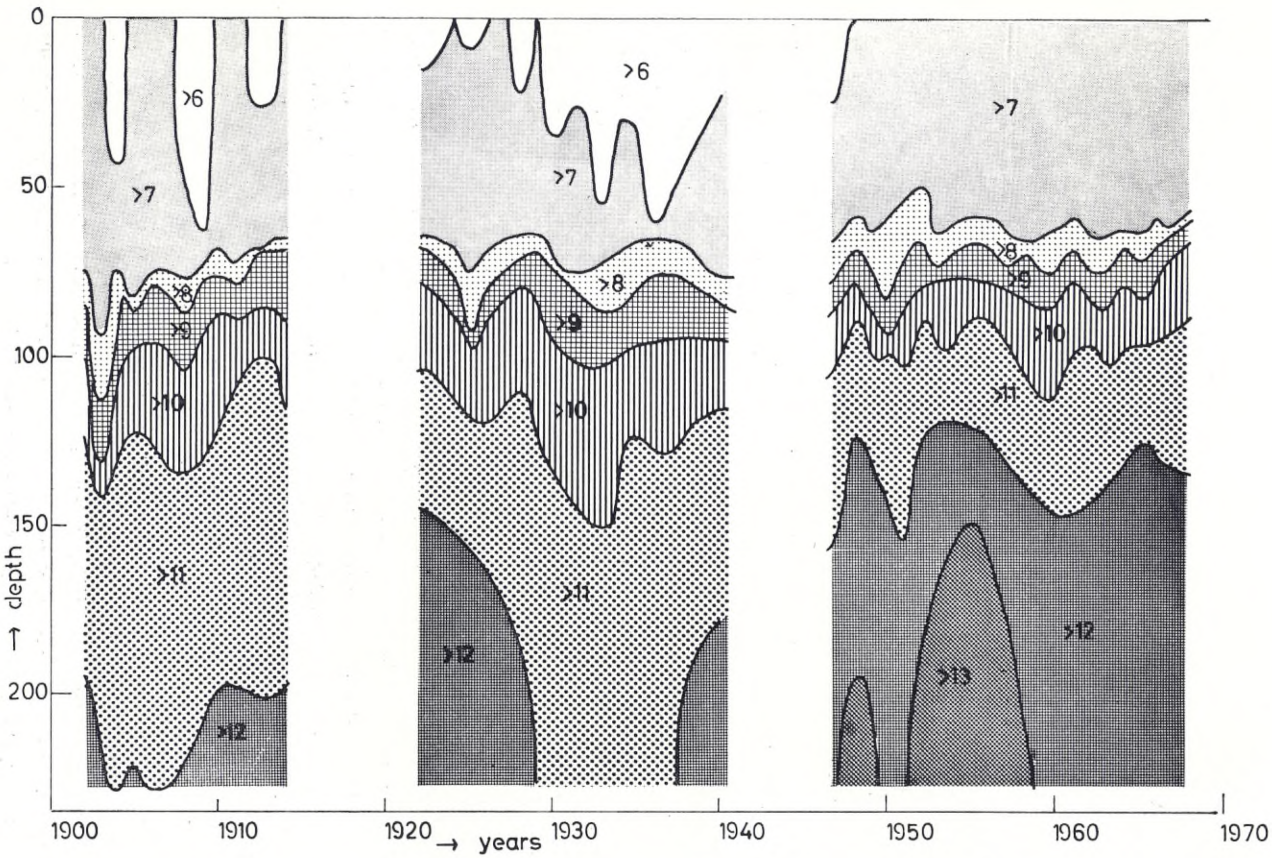


Fig. 37. Salinity variations in the Gotland Deep as yearly mean values from 1900 to 1968.

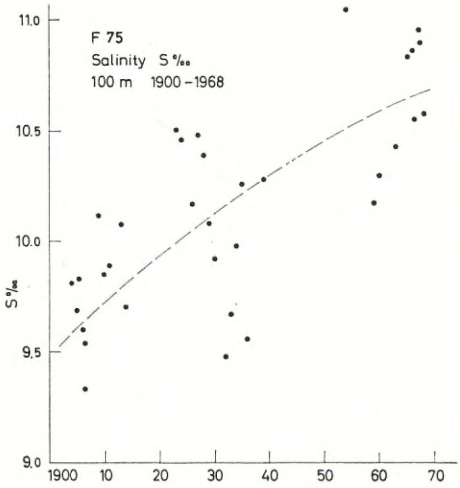


Fig. 38. Salinity variations at 100 m depth at station F 75 in the Northern Central Basin from 1900 to 1968.

upwards. During the first years of the century the halocline began at a depth of 80 m. Now in 1968 it begins at about 60 m. The deep water body of the Baltic proper has therefore increased about 200 km³.

This salinity increase is also demonstrated in fig. 38 where the salinities on station F 75 at 100 m depth between 1900 and 1968 are marked. There is a considerable scattering of the values, but it can be seen that the salinity increased during the 1920's and decreased in the beginning of the 1930's.

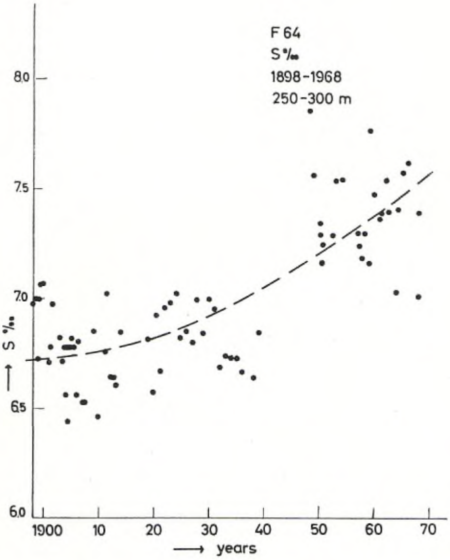


Fig. 39. Salinity variations at 250—300 m depth at station F 64 in the Åland Sea from 1898 to 1968.

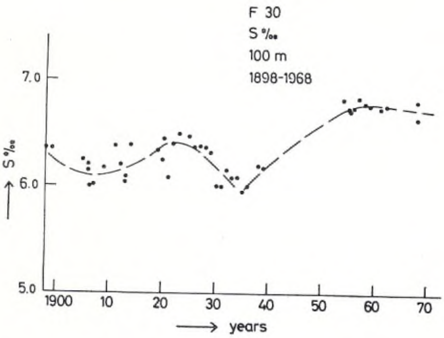


Fig. 40. Salinity variations at 100 m depth at station F 30 in the Bothnian Sea from 1898 to 1968.

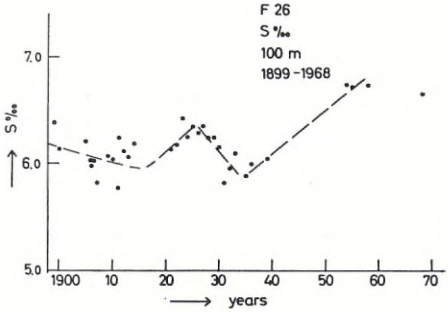


Fig. 41. Salinity variations at 100 m depth at station F 26 in the Bothnian Sea from 1899 to 1968.

After World War II the salinity as an average was about 1 ‰ higher than before. The reasons for these fluctuations shall be discussed below.

The increased salinity of the deep water may also be seen in the Åland Sea. The salinity change in the 250—300 m layer at station F 64 in the Åland Sea is shown in Fig. 39. Over a period of 70 years the salinity has changed from about 6.75 ‰ to 7.5 ‰. When the halocline in the Baltic proper raised higher and higher, the sill to the Åland Sea was left below it. (It will be recalled that it was mentioned in chapter V that there is a narrow channel with a sill depth of 70 m between the Baltic proper and the Åland Sea). The raising of the halocline in the Baltic proper made it possible for high saline deep water to flow down into the Åland Sea and the Gulf of Bothnia and consequently raise the salinity there. This can explain the decreasing oxygen values in the deep water of the Åland Sea and the Bothnian Sea.

Figures 40, 41 and 42 show examples of the salinity changes in the deep water of the Bothnian Sea at stations F 30, F 26 and F 24. All three stations show a decrease in salinity from the beginning of the century to about 1910. In 1910 the salinity began to rise and reached a maximum around 1925. After this a continuous decrease began and a new minimum was reached in 1935. From that time the salinity begins to rise again; this process seems to still be continuous, but at a slower tempo. The 1935 salinity minimum has been described and explained by Soskin (1963).

The salinities in the Bothnian Bay give a somewhat different picture. Fig. 43 and Fig. 44 show the salinity at station F 12 and F 8 in the deep water of the Bothnian Bay. There was not any decrease in salinity during the first decades of the century; on the contrary there seems to have been a small increase until 1920. After 1920 a decrease began and the lowest values were reached around 1936, or maybe later. Unfortunately there are no measurements from 1939 until 1954 because of the war. Therefore it is not possible

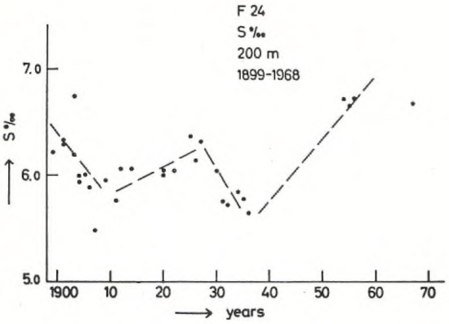


Fig. 42. Salinity variations at 200 m depth at station F 24 (Ulvö Deep) in the Bothnian Sea from 1899 to 1968.

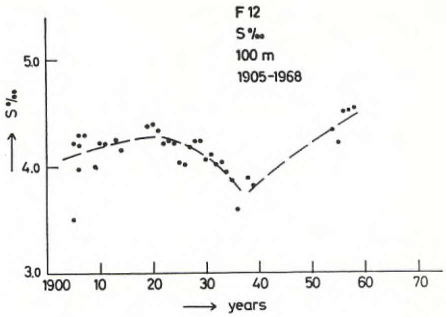


Fig. 43. Salinity variations at 100 m depth at station F 12 in the Bothnian Bay from 1905 to 1968.

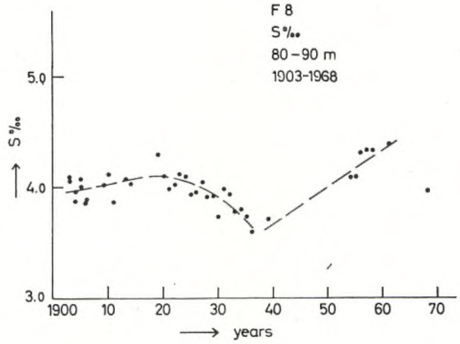


Fig. 44. Salinity variations at 80—90 m depth at station F 8 in the Bothnian Bay from 1903 to 1968.

to state when the increase of the salinity began again. The very last measurements in September, 1968 indicate a small decrease of the salinity. More information is needed from this area.

Soskin (1963) has thoroughly investigated the problem of the increased salinity of the water in the Baltic and in the following discussion of this subject the author will draw very heavily upon his work.

One factor responsible for the increased salinity of the water in the Baltic is a decreased river outflow to the Baltic basin. It seems useful to look closely at the outflow patterns for important rivers discharging into the Baltic during this century. From annual moving average outflow values it can be shown that the outflow decreased during the first decades but increased during the 1920's and the first years of the 1930's. During the second half of the 1930's and the beginning of the 1940's the outflow was extremely low but it increased again after World War II. It never again reached its long time mean value after the war. These observations can be connected with the extremely low salinities during the 1930's and the increased salinity after World War II. There is a correlation between the increasing river outflow and the decreasing salinity in the Gulf of Finland during the 1930's and the decreasing outflow and increasing salinity after World War II. (These conclusions are derived from data from Finnish coastal stations).

The following factors are according to SOSKIN (1963) responsible for the increased salinity of the water in the Baltic:

1) A decreased runoff to the Baltic basin will increase the salinity of the Baltic in spite of the fact that the part of the water exchange through the Danish sounds caused by runoff will decrease as a consequense.
2) An increased intensity of the deep current in the Kattegat and the Danish sounds.

The main reason for these processes are changes in the atmospheric circulation which have been observed over a long period. Cyclonic activity over Europe diminished and during the 1930's anticyclonic conditions developed. The latter atmospheric conditions cause a decrease in precipitation resulting in a corresponding decrease of runoff.

Another factor which has contributed to the increasing salinity of the Baltic must be mentioned. Through the influence of westerly storms over the North Sea, salt water has been forced over the sills into the Baltic. This happens only during special circumstances. The most important of these inflows happened during November—December 1951 when about 200 km^3 of salt water was forced into the Baltic. This occasion has been described and explained by WYRTKI (1954). The increased salinity and the following stagnation in the Gotland basin after 1951 has been described by the present author (FONSELIUS 1962). Several smaller inflows occured later (FONSELIUS 1967, chapter IV of this paper).

DICKSON (1968) has studied variations of the salinity in the Northern Atlantic and adjacent seas over long periods. He found a direct correlation between the mean salinity anomaly curve for the Irish Sea and the Lappegrund lightvessel in Öresund at 12.5—15 m depth. The Irish Sea data, according to DICKSON, mirror the hydrographic conditions in the shelf area as a whole. The fluctuations in the shelf area are thought to be caused by southerly-wind-induced variations in the oceanic inflow. DICKSON concludes that any acceleration of Atlantic water inflow to the shelf area is accompanied by an acceleration of the inflow to the Kattegat, the Belts and the Öresund. He explains further that special circumstances exist in the Transition Area and make it necessary that other factors be considered. For instance the volume of the Baltic compensation current may increase if there is a relative drought and such a drought can be caused by a persistent blocking anticyclone over Scandinavia. These observations support SOSKIN's theories.

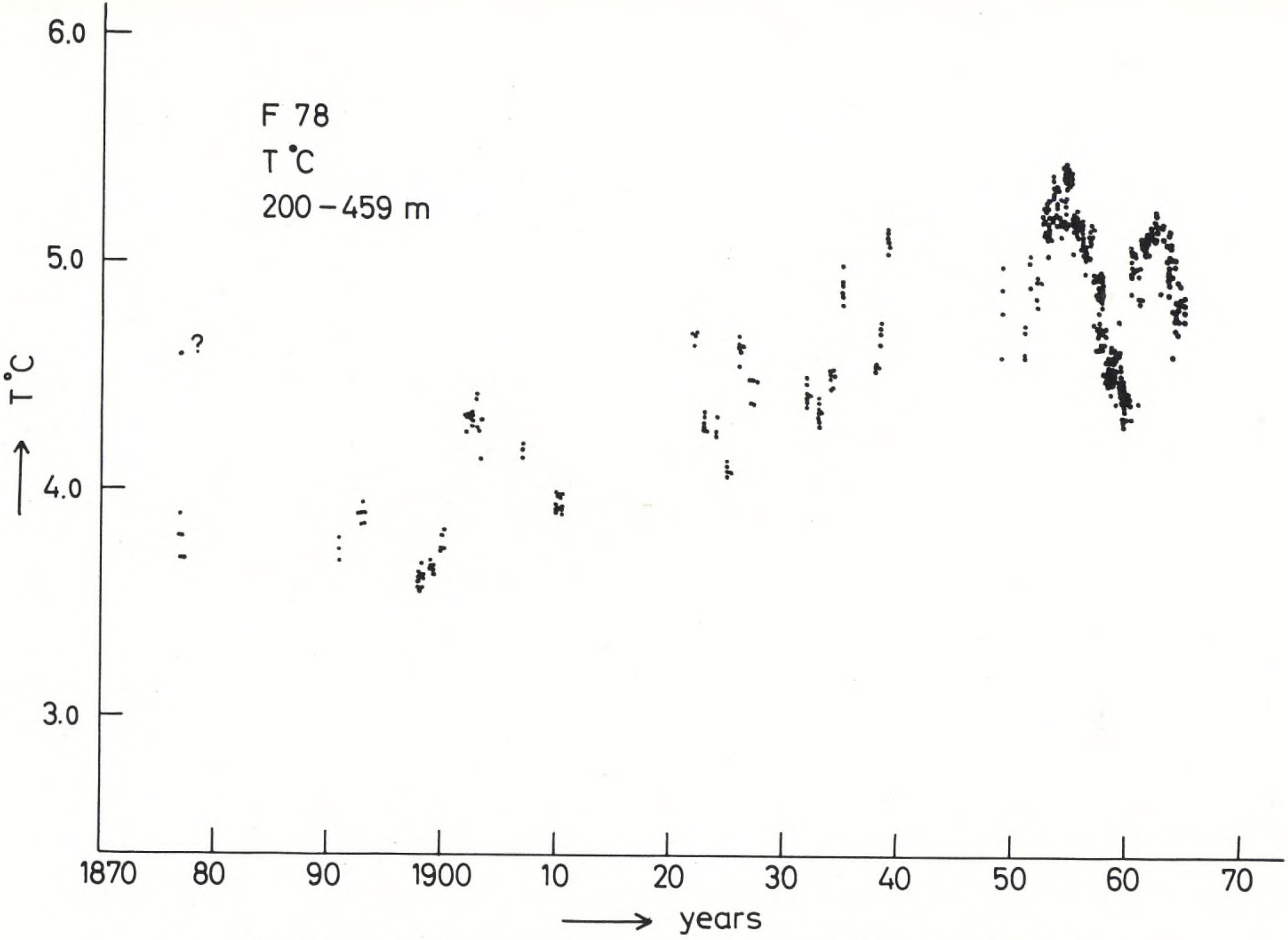


Fig. 45. Temperature variations in the deep water of the Landsort Deep from 1877 to 1966.

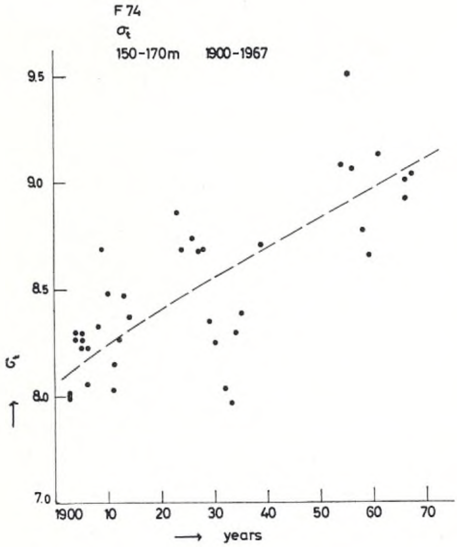


Fig. 46. Variations of σ_t at 150—170 m depth at station F 74 in the Northern Central Basin from 1900 to 1967.

KULLENBERG (1955) has theoretically shown that the salinity of a semienclosed basin like the Baltic, shall increase if the supply of fresh water to the basin decreases.

It has been established that the temperature of the oceans has increased during the 20th century and that this has influenced the temperature of the Baltic water (SOSKIN 1963). Fig. 45 shows this increase in the deep water of the Landsort Deep from 1877 to the present time. All temperature values between 200 and 459 m found in the literature are included in the figure. The great salt inflow during the 1950's increased the temperature of the deep water to around 5.5°C but during the following stagnation period the temperature decreased more than 1°C. A new inflow around 1960 again increased the temperature to almost 5.3°C. Then a new decrease began which still continues. The temperature values at present are about 0.8°C above the temperatures which were obtained when the measurements began in 1877.

The density of the water is a function of both temperature and salinity. An increase of 1 ‰ in the salinity will, however, increase the density of the water several times more than an increase of 1°C in temperature will decrease it. Because of the increased salinity of the water the density of the Baltic water has increased during the present century. The increase is greater in the deep water than in the surface water. The density increase of the deep water at station F 74 from 1900 to 1967 is shown in Fig. 46. The increase of the density is almost 1 unit of σ_t.

The change in vertical direction of the σ_t is nearly proportional to the vertical stability of the system (SVERDRUP et al. 1942). Therefore the stability E of the Baltic water is a convenient measure of the difference in density

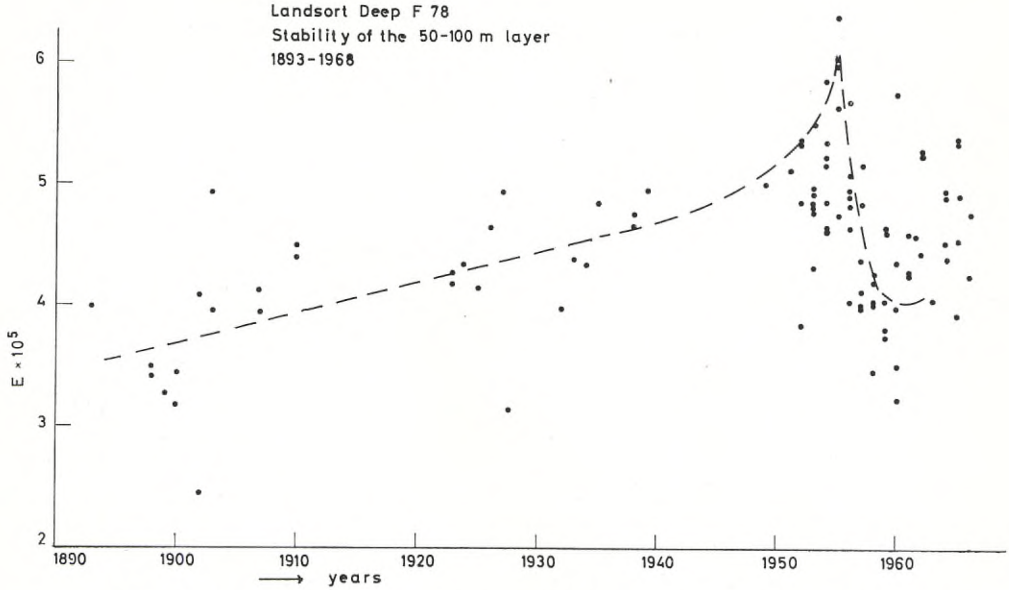


Fig. 47. Variations of stability (E) in the 50—100 m layer in the Landsort Deep from 1893 to 1968.

between the surface and the deep water. The salinity and temperature have ordinarily been determined at every 10 m in the Baltic down to 80 m. The depth of the halocline may vary due to internal waves and even if this factor is not considered the above mentioned measurements are not frequent enough to get the exact shape of the halocline. The standard depths in the Baltic do not include 90 m and therefore this depth is not always sampled. In order to be sure that the halocline is always included, the stability of the 50—100 m layer has been computed in this work. Fig. 47 shows the changes of the stability between 50 and 100 m in the Landsort deep from 1893 to 1968. The high stabilities caused by the great salt inflow in 1951 are followed by decreasing stability numbers until the new water inflows into the Baltic during 1959—1961. It is difficult to get a very clear picture of the development after 1961 but one can see that the stability numbers are higher at this time than during the beginning of the century. A much clearer picture is given when only the summer values are used. During the summer the stability reaches its maximum due to the formation of the thermocline. These conditions are shown in Fig. 48, where only the values for June, July and August from the previous figure have been used. It may be concluded that the summer stability has increased nearly one unit of $E \times 10^5$ during the 20th century. In the introduction another reason for using only summer values was noted and that is that there exist almost only summer values from the Baltic before World War II.

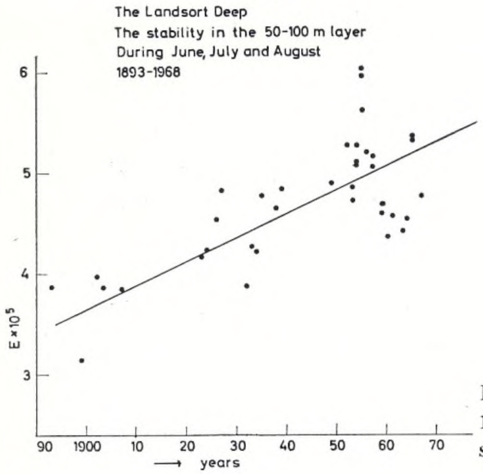


Fig. 48. Variations of stability (E) in the 50—100 m layer in the Landsort Deep during the summer months from 1893 to 1968.

A more detailed picture can be given when values from the Gotland Deep are examined. Here all existing values including the winter values have been used. Fig. 49 shows the stability in the 50—100 m layer at F 81 from 1893 to the present time. The different inflows and the stagnation periods can be identified. **Kalle** (1943) described the first stagnation period which was caused by an inflow of heavy water in 1928. This stagnation ended in 1932 or 1933. The great inflow of 1951 increased the stability to almost 7×10^5 E.

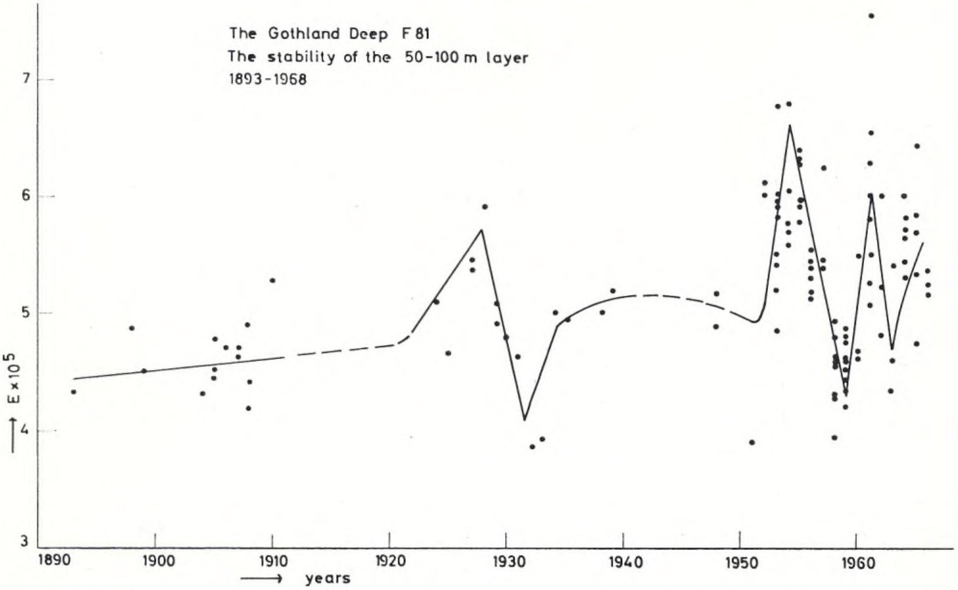


Fig. 49. Variations of stability (E) in the 50—100 m layer in the Gotland Deep from 1893 to 1968.

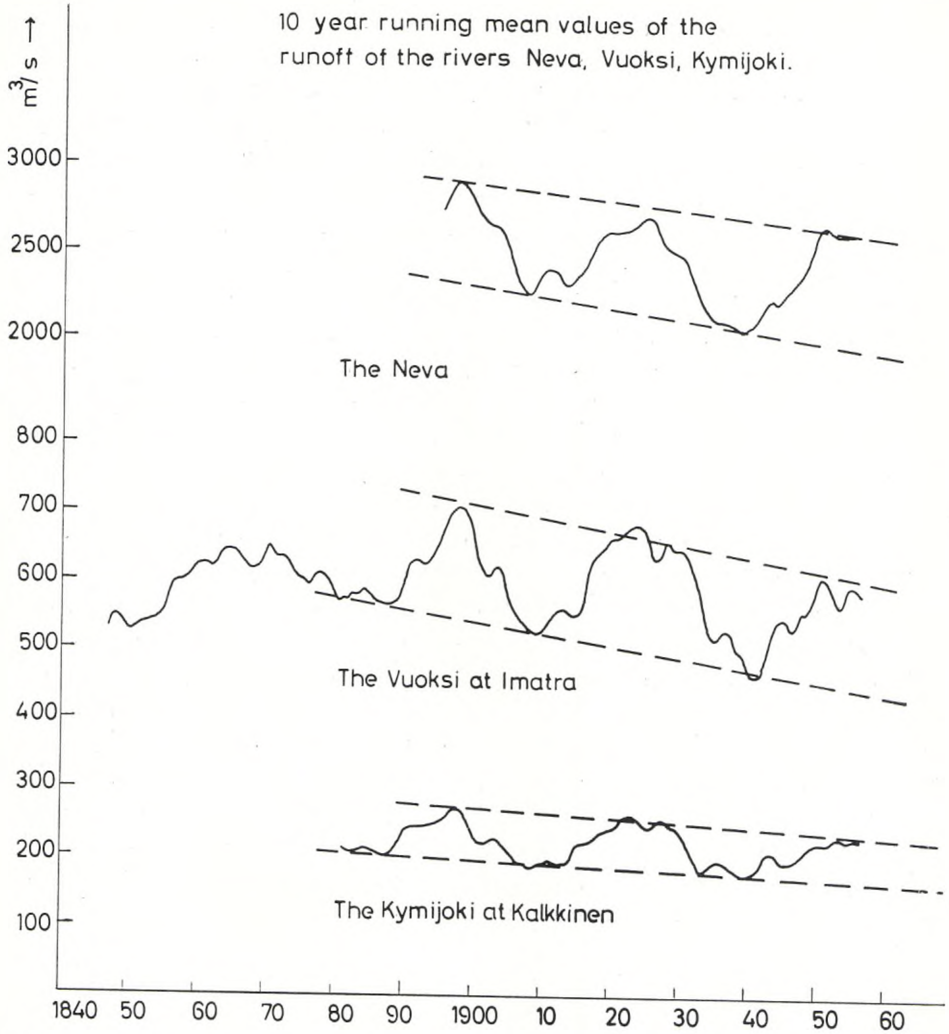


Fig. 50. Runoff values in m³/s from the Neva, Vuoksi and Kymijoki rivers computed as 10 years running mean values.

The following stagnation was broken by a new inflow, which reached its maximum in 1961. This inflow after a period caused a new stagnation which was broken in 1964 (FONSELIUS 1962, 1967). The figure also indicates that the stability slowly has increased during these inflows and that cycles of inflows with subsequent stagnation periods get more and more frequent.

Very few hydrographic observations were made in the Baltic area before 1900. Therefore it is almost impossible to draw any reliable conclusions about the conditions in the Baltic during the 19th century. There exists, however, an uninterrupted series of runoff measurements from the Finnish river

Vuoksi at Imatra which began in 1847 (SIRÉN 1958). The river Vuoksi does not flow into the Baltic but into Lake Ladoga which runs into the Gulf of Finland through the Neva river. There are uncertainties in these values from the 1800's because it is possible that changes in the river profile at the place where the observations were performed have occured. Still the series do give some indication of the changes in runoff. The Vuoksi river belongs to the Finnish inland water system; its runoff fluctuations have been compared to the fluctuations of rivers discharging in the Baltic. Fig. 50 shows 10 year running mean values for the Vuoksi from 1847 compared to similar mean values for the Kymijoki at Kalkkinen and the Neva. The values for the Neva are from ANTONOV's (1964) work. It can be seen from the figure that all the rivers show the same trend. SOSKIN (1963) has shown that the runoff from the Neva river is similar to the runoff of all rivers discharging into the eastern Baltic. Therefore it may be assumed that the runoff of these rivers also has been similar to the runoff of the Vuoksi during the 19th century. There seems to have been a period of low runoff around the middle of the century, a period of higher runoff around 1860—1870 and a new low period around 1880—1890. SOSKIN (1963) has shown the close correlation between runoff and salinity during the 20th century. Therefore it may also be assumed that the salinity in the Baltic was high during the middle of the 19th century, that it decreased during the 1860's and 1870's and that it again increased during the 1880's. In 1890 a new decrease began. The series is too short to identify any exact patterns but the little data that exist show a certain periodicity in the runoff variations. There seems to be a general decreasing trend of the runoff in all three rivers from the beginning of the 20th century. If this is a true trend and it does continue there is not much hope for improved oxygen conditions in the Baltic deep water.

VII. On the phosphorus in the Baltic

Phosphorus is a nutrient which is necessary for most living organisms. It is considered to be the limiting growth factor for the primary production in the Baltic (FONSELIUS 1967). Phosphorus occurs in sea water in organic and inorganic forms and for each of these forms soluble and particulate variations exist; soluble organic, particulate organic, soluble inorganic and particulate inorganic. The most important form is the inorganic soluble phosphorus which occurs as dissolved ortho-phosphate. It is directly available to the phytoplankton. A form of particulate inorganic phosphorus is suspended apatite grains. Organic phosphorus originates from living organisms; the particulate form may be living micro-organisms or dead parts of organisms; dissolved organic phosphorus occurs in the cell juice of organisms or may be formed through decay of dead organic matter and it is not directly available to the phyto-plankton before it has been transformed into inorganic form.

Inorganic soluble phosphorus is routinely determined aboard research vessels and so the ortho-phosphate is analyzed. These analyses were even carried out in the Baltic before the World War II (see Introduction). Unfortunately few results were published because of the technical and analytical difficulties encountered in the work. The scattering of the values was considerable. On some occasions also total phosphorus was analyzed by the laborious technique of boiling with sulfuric acid.

The analytical methods improved after World War II and phosphate is now analyzed aboard all research ships in the Baltic area. The single solution method by MURPHY and RILEY (1962) is used in all countries around the Baltic. Intercalibration tests have shown that the results of the different laboratories agree surprisingly well (FONSELIUS 1966), (JONES et al. 1967). Since different methods of preservation of the sample have failed (KOROLEFF 1968) it has been found that the analyses have to be carried out immediately after the sampling aboard the ship in order to avoid changes in the phosphate content of the sample through biological activity.

The results obtained before World War II showed that phosphate is the main constitutent of the total phosphorus in sea water. After the war better methods to routinely analyze total phosphorus were instituted. At the Fishery Board of Sweden KOROLEFF's (1968 a) method has been successfully used. Examples of such analyses are shown in Figures 51 and 52. Fig. 51 shows

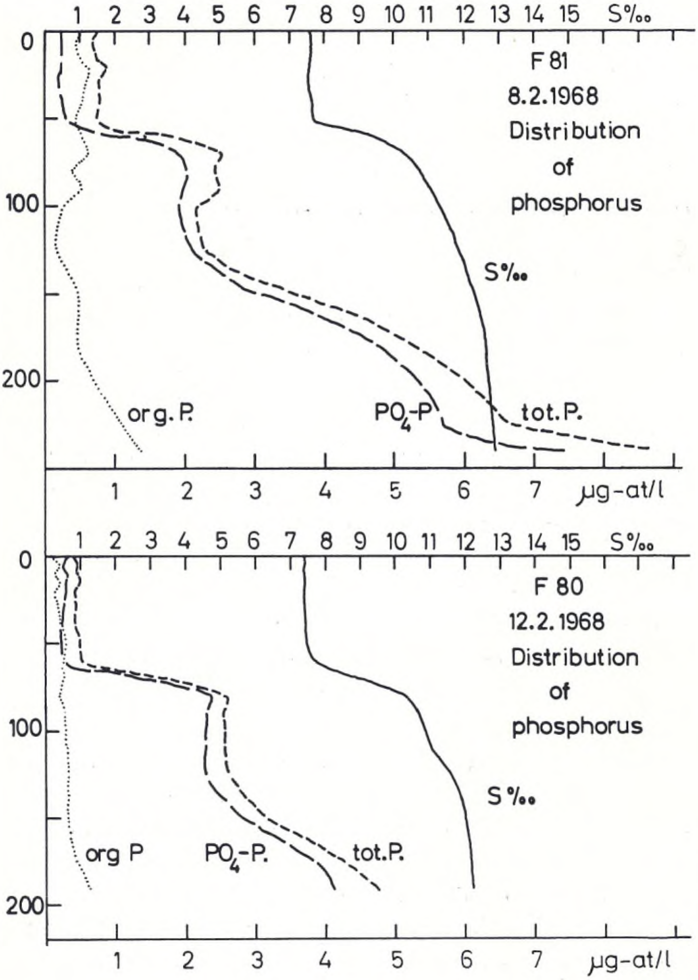


Fig. 51. The distribution of the phosphorus components in the Gotland Deep and the Fårö Deep in February, 1968.

the distribution of phosphorus at stations F 81 and F 80 in the Gotland basin during the February, 1968 expedition. Total phosphorus and phosphate were analyzed from the same sample on all standard depths. The difference between total P and phosphate (PO_4-P) gives the amount of "Organic P". All three parameters are shown in the figure. As can be seen the organic P is 40—60 % of the total P in the surface water. In the deep water it is only a small fraction of the total P. The main part of the P in the deep water consists of PO_4-P. The conditions were stagnant in the deep water at both stations during February, 1968 and H_2S was found below 150 m. The amount of organic P increases towards the bottom showing that the oxidation rate in the oxygen-free water is too slow to break down the organic compounds before they reach the bottom. In this manner organic matter is accumulated in stagnant deep basins.

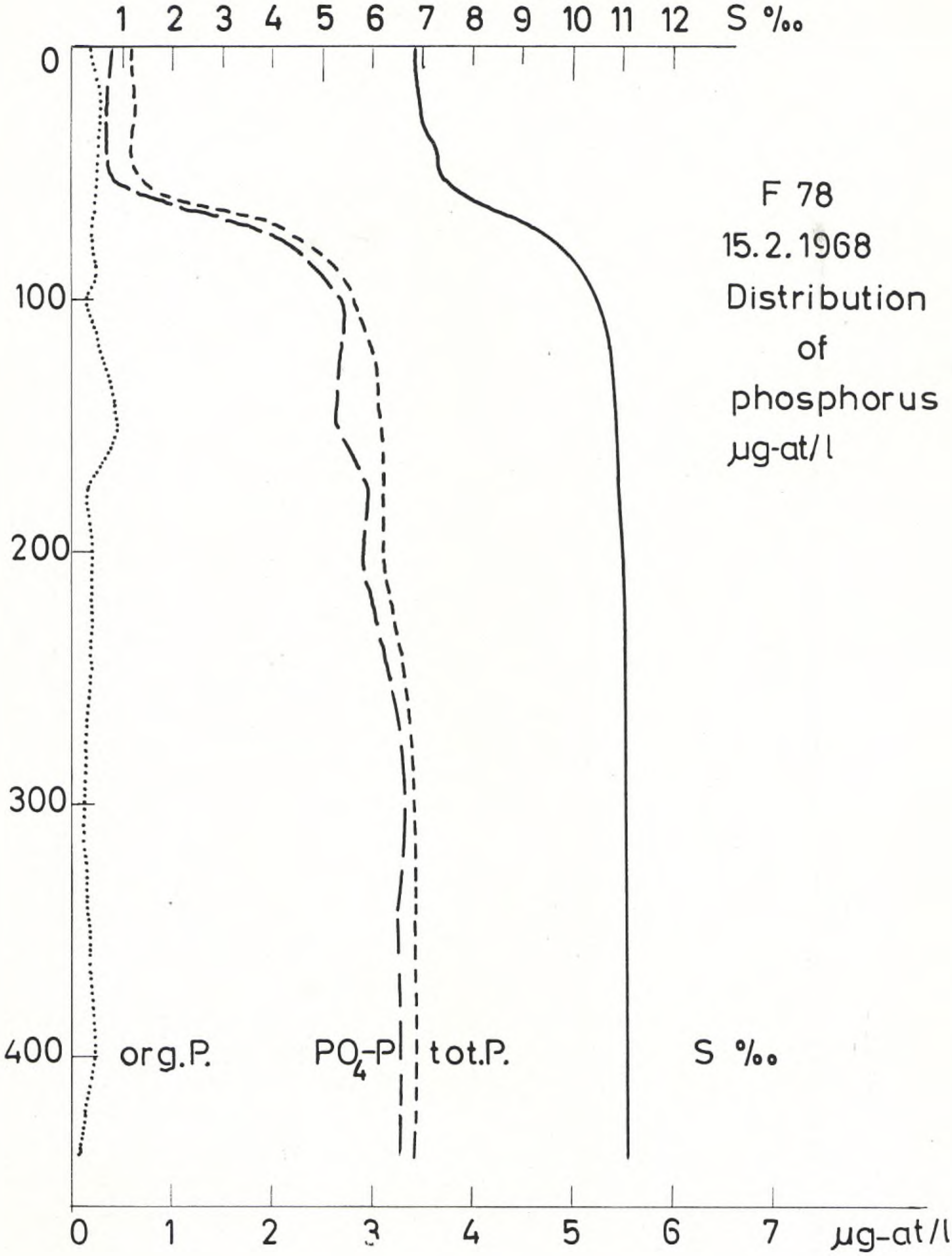


Fig. 52. The distribution of the phosphorus components in the Landsort Deep in February, 1968.

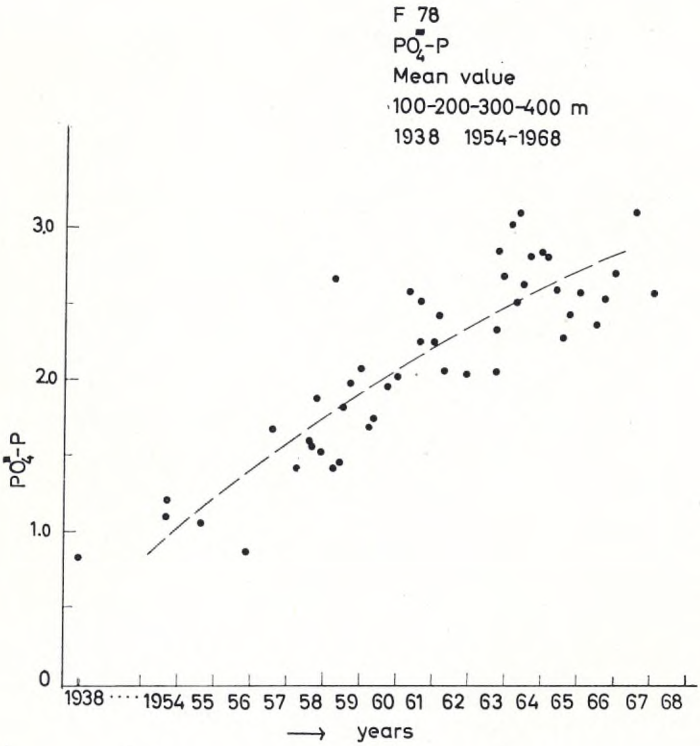


Fig. 53. Mean values of phosphate concentrations in the deep water of the Landsort Deep from 1954 to 1968 (including one value from 1938).

Fig. 52 shows the phosphorus components in the Landsort Deep during the same expedition. Here also the surface water contained more organic P than PO_4-P. In the Landsort Deep oxygen was still present in the deep water and the mixing there is relatively fast. Therefore no accumulation of organic P does occur in the deep water. The oxidation is also much faster in water containing dissolved oxygen than in oxygen-free water where the oxygen needed for the oxidation process has to be produced through bacterial reduction of nitrate and sulfate.

Unfortunately it is not possible to judge whether the amount of organic P has increased in the surface water because of the high amount of sewage and industrial wastes deposited in the Baltic during the last decades, or whether the values obtained by the author are normal for the Baltic. Past analyses of total P are too few and the methods used too crude for such comparisons.

It is, however, possible to make comparisons of the amounts of PO_4-P in the deep water of the Baltic during the last 15 years. Fortunately enough PO_4-P data are available for that purpose at several stations. Fig. 53 shows the mean values of PO_4-P in μg-at/l from the deep water of the Landsort Deep between 1954 and 1968. One value from 1938 is also included. It is

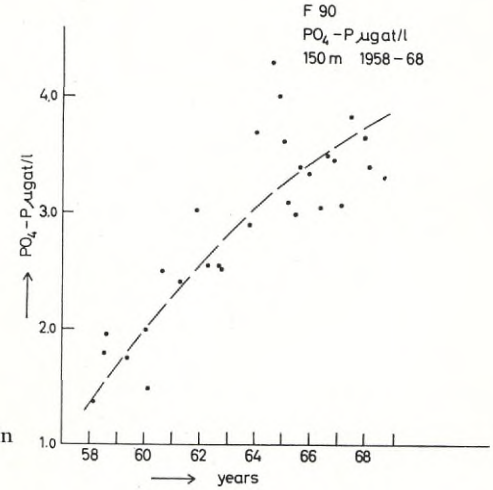


Fig. 54. Phosphate values at 150 m depth in the Norrköping Deep from 1958 to 1968.

clear that the PO_4-P during this time has increased continuously from about 1 µg-at/l to nearly 3 µg-at/l. The phosphate concentration in the Landsort Deep has increased almost 3 times during 14 years. Other stations show a similar tendency. Figures 54 and 55 are from the deep water of the Norrköping Deep (F 90) and the Karlsö Deep (S 41) for the last 10 years. A continuous increase of the PO_4 concentration has occured at both stations. The increase is higher here because of the fact that both stations are stagnant and contain H_2S in the deep water. The reason for the high phosphate concentrations in stagnant water has been described earlier (FONSELIUS 1967)

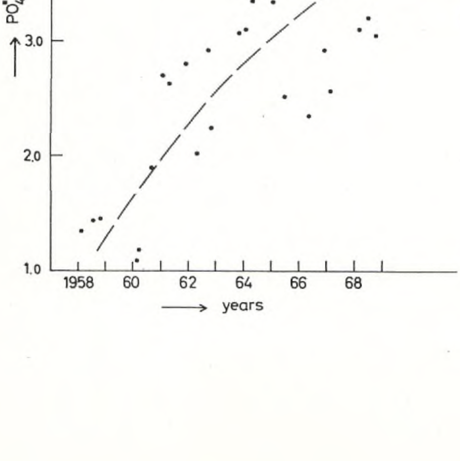


Fig. 55. Phosphate values at 100 m depth in the Karlsö Deep from 1958 to 1968.

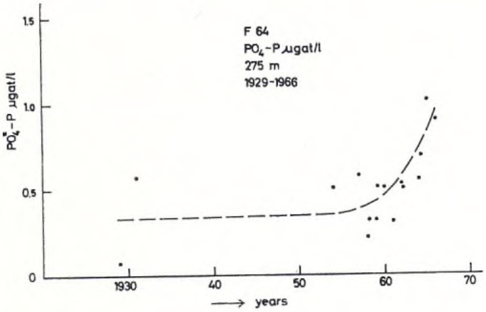
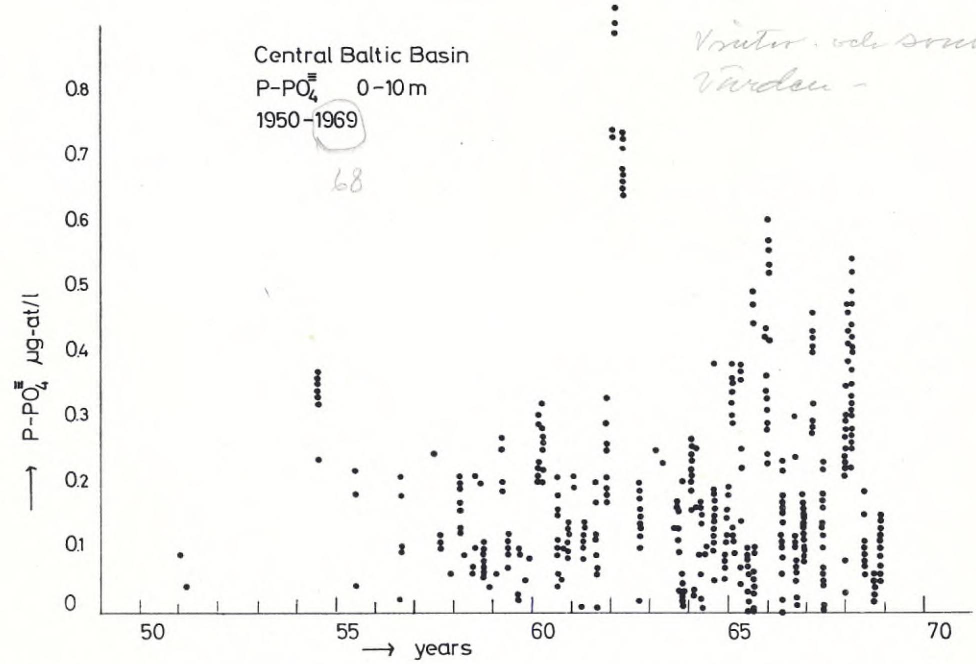


Fig. 56. Phosphate values at 275 m depth at station F 64 in the Åland Sea from 1929 to 1966.

and will be further discussed in chapter IX. Fig. 56 shows the phosphate concentration at station F 64 in the Åland Sea at 275 m depth. Two PO$_4$-P values from around 1930 are included in the figure. Here the P values seem to remain rather constant until 1960. Then a sharp increase of the values begins. The measurements from the Gulf of Bothnia are too scarce to allow any conclusions.

The phosphate concentration in the surface water of the Baltic proper between 1958 and 1964 has been investigated earlier (Fonselius 1967). During that short time it was not possible to see if the phosphate values had



Vinter- och sommar-värden -

Fig. 57. Phosphate values in the surface water of the stations in the Central Basin of the Baltic proper from 1951 to 1968.

increased. In order to check if a phosphate increase has occured in the surface water, all available PO_4 values from the surface water of the Central Basin have been plotted in Fig. 57. The values are rather scattered because of the seasonal variations of the phosphate. During the summer period the PO_4 values may decrease to zero because of the PO_4 uptake by micro-organisms in the surface water. During the winter the biological activity ceases and only the bacterial decomposition of organic matter continues. Therefore the PO_4 values increase in the surface water during the winter. The "fertilizations" of the surface water described by the author (FONSELIUS 1967) are easily recognized in the figure through the unusually high PO_4 values during these occasions. These fertilizations always occur during the winter when the thermocline disappears and the thermohaline convection reaches down to the primary halocline (FONSELIUS loc. cit.). From the figure it can be seen that the PO_4 values in the surface water generally have increased from 1951 to 1968 but it is difficult to judge the exact amount of the increase.

Fig. 58 shows the development of the phosphate situation from the middle of 1954 to the end of 1968 in the Landsort Deep. There are two clear "fertilizations" of the surface water to be seen, one in 1962 and the second in 1966. It is also obvious that the concentration of phosphate is increasing in the deep water. The frequency of situations with high phosphate concentrations in the deep water are increasing and when hydrogen sulfide (as has been shown in Fig. 36) is formed there, the concentrations will soon exceed 4 μg-at/l.

During the September, 1968 "Skagerak" expedition total P and PO_4-P were analyzed at all standard depths on all stations visited. The expedition started in Göteborg and ended in Piteå in the Bothnian Bay. A total of 47 stations were worked. There has not been any other expedition in the Baltic covering such a large area where both total P and PO_4-P have been analyzed simultaneously from the same sample. These results have been used for computing mean values of total P, PO_4-P and organic P for different parts of the Baltic on different depths. The author is aware that there is some uncertainty because the mean values do not cover all seasons, but it was not possible to find more complete measurements. This was especially true in the case of the Gulf of Bothnia. Fig. 59 shows the distribution of the phosphorus components in the different parts of the Baltic.

Four different water layers can be distinguished in the Baltic proper during the summer. The surface water is divided in two layers — a warm surface layer and below that a layer of cold winter surface water. These two layers are also found in the Gulf of Bothnia. The warm surface layer contains about 0.24 μg-at/l of total P in the Baltic proper. The amount is much lower in the Gulf of Bothnia and is only about 0.11 μg-at/l. The amount of inorganic P or PO_4-P is in the whole surface layer only 0.05 μg-at/l. The difference between total P and PO_4-P is considered to be organic P. The

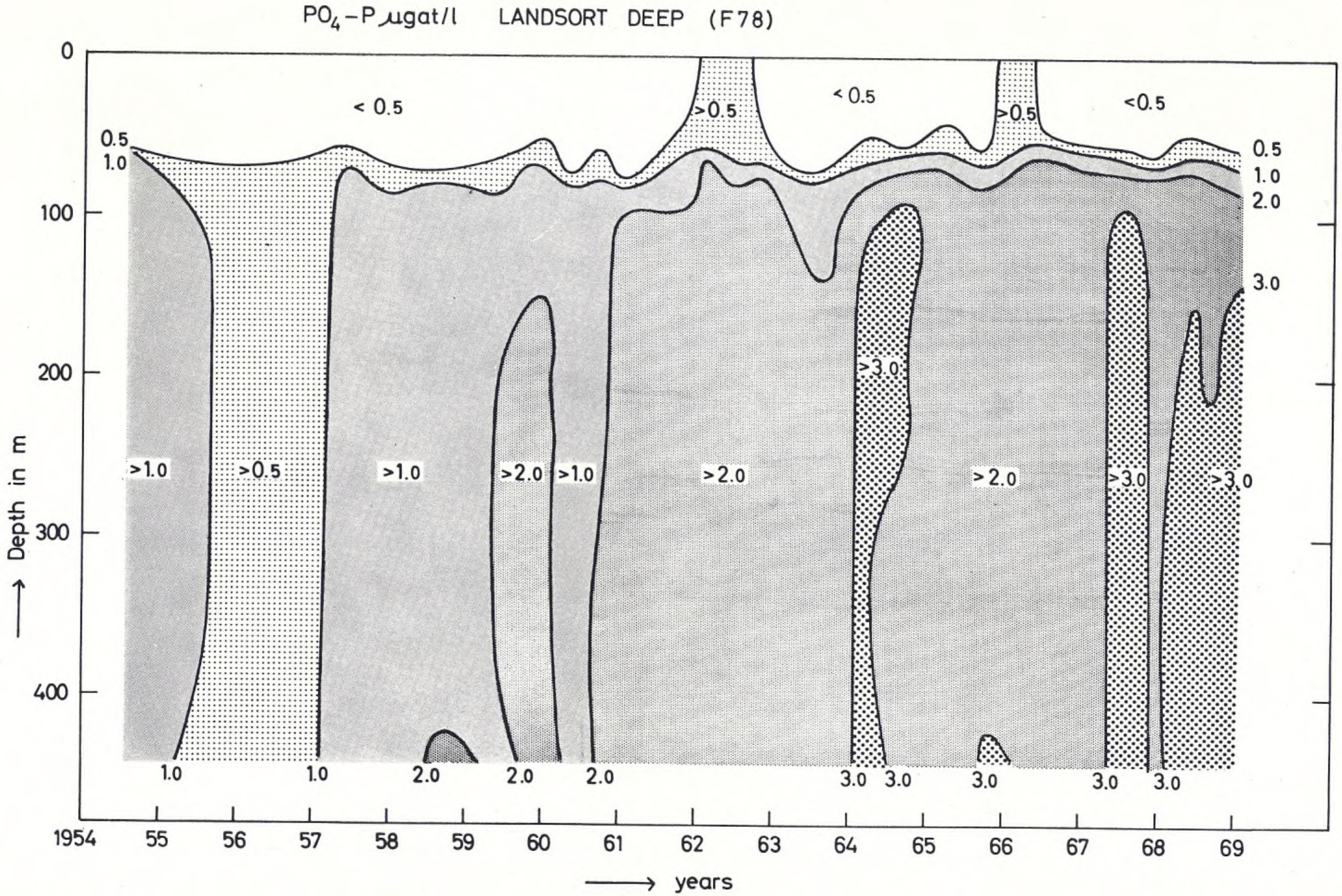


Fig. 58. The development of the phosphate accumulation in the deep water and the "fertilizations" of the surface water in the Landsort Deep from 1954 to 1968. (Smoothed values).

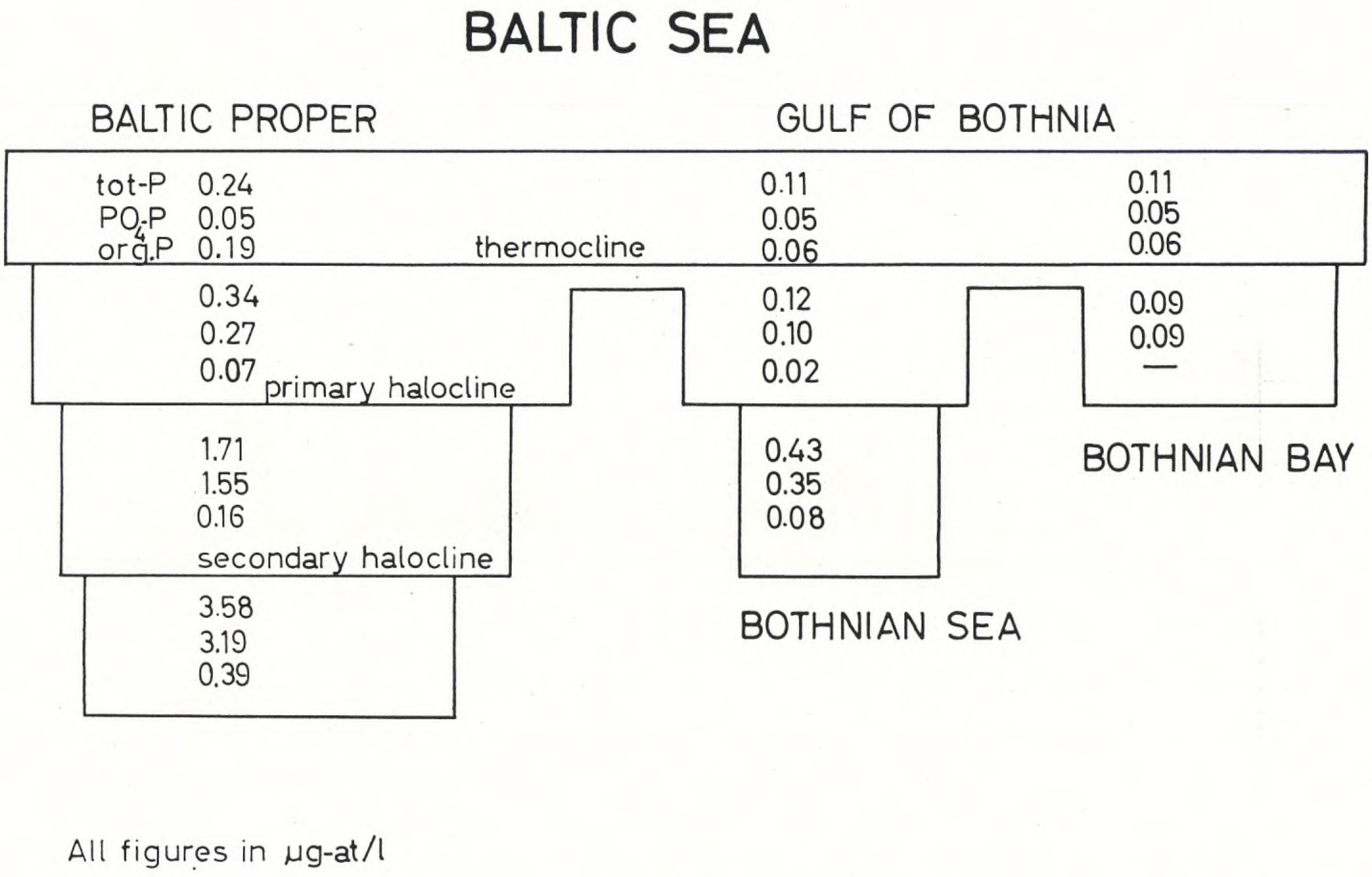


Fig. 59. Mean values of the phosphorus components in different parts of the Baltic in September 1968.

Table III. Mean values for the phosphorus components in the Baltic proper during 1968.

Water type	Total P µg-at/l	PO_4-P µg-at/l	Organic P µg-at/l
Surface water	0.45	0.16	0.25
Deep water	2.37	2.22	0.15
Stagnant water	5.19	4.64	0.51

amount of organic P in the surface layer of the Baltic proper is 0.19 µg-at/l. In the surface layer of the Gulf of Bothnia it is 0.06 µg-at/l. In the cold winter surface water below the thermocline the amount of total P in the Baltic proper is 0.34 µg-at/l. In the southern part of the Gulf of Bothnia, the Bothnian Sea, the amount is 0.12 µg-at/l and in the northern part, the Bothnian Bay, it is 0.09 µg-at/l. In the Baltic proper the corresponding concentrations of PO_4-P and organic P are 0.27 and 0.07 µg-at/l, respectively. In the Bothnian Sea the concentrations are 0.10 and 0.02 µg-at/l. In the Bothnian Bay the amount of PO_4-P is 0.09 µg-at/l or exactly the amount of total P. No organic P could be found there as the amount is below the limits of the analytical methods used for total P and PO_4-P. Below the primary halocline in the Baltic proper the concentrations of total P, PO_4-P and organic P are 1.71, 1.55 and 0.16 µg-at/l respectively. The corresponding values in the Bothnian Sea are 0.43, 0.35 and 0.08 µg-at/l. In the Bothnian Bay no distinct halocline could be found. In the stagnant water below the secondary halocline in the Baltic proper the corresponding P values were 3.58 µg-at total P/l, 3.19 µg-at PO_4-P/l and 0.39 µg-at organic P/l. The extremely low primary production in the Gulf of Bothnia is clearly demonstrated by these values. It was pointed out above that these mean values are only valid for the summer season.

During 1968 four expeditions have been carried out with the "Skagerak" in the Baltic. Two of them covered only the Baltic proper. The expeditions were done during February, June, September and November. On all cruises analyses of total P and PO_4-P were performed at the main international stations. It has been possible to compute for the year crude mean values for the phosphorus components in the Baltic proper from these measurements. These mean values are listed in table III.

It is a well-known fact that phosphate accumulates in the deep water of stagnant basins. This process has been described by RICHARDS in several papers (RICHARDS et al. 1956, RICHARDS 1965, RICHARDS et al. 1965). In the Baltic this process was studied by the author (FONSELIUS 1962, 1967). A constant relation should exist between the amount of phosphate accumulated in the basin and oxygen utilization (RICHARDS op. cit.). Sinking dead organic matter is oxidized to simpler compounds and its final form is as simple inorganic compounds such as; carbon dioxide, ammonia, nitrogen, phosphate etc. RICHARDS also gives the relation Apparent Oxygen Utilization (AOU) : P. It is 276: 1 expressed as atoms. It has been shown earlier by the author (FONSELIUS 1962, 1967) that this relation is not relevant for the conditions in the Baltic. The AOU there is about 550 atoms of oxygen per 1 atom of PO_4-P. (The utilization of oxygen from the NO_3^--ions has been omitted here because ammonia was not measured during the expeditions. This effect has been studied later by SEN GUPTA (1967)). Since phosphate seems to be the limiting nutrient salt for the primary production in the Baltic (FONSELIUS 1967), this probably means that the organisms in the Baltic survive with only half the amount of phosphorus normal for organisms in the open ocean. STRICKLAND (1960) claims that a phosphorus deficiency may develop in marine phytoplankton when the phosphate content of the surrounding water is low and that this is especially likely if nitrate is present in the water in excess. In this way cells of the organisms may have only 20 % of the normal value of phosphorus present. This may be the reason for the unusually high AOU : P ratio in the Baltic water where the phosphate content of the surface water is extremely low.

On some occasions there appeared to be a nitrate deficiency too in the Baltic surface water. Several intercalibration trials in the Baltic area (BUTLER 1967) have shown that the methods used are too uncertain to give reliable results with respect to the nitrate deficiency. In the best case, the intercalibration trial at Copenhagen in 1966, the standard deviation was ± 15.5 %. Many of the results which show zero nitrate concentration in the Baltic may be ascribable to analytical difficulties. According to SILLÉN (1966) the nitrogen cycle in sea water, especially the transformation processes in the surface water which regulate the amount of nitrate are not well understood. Nitrogen at thermodynamical equilibrium should exist in sea water almost completely as nitrate ions. Organisms may also partly use ammonia as a nitrogen source instead of nitrate (REDFIELD et al. 1963). It is difficult to judge if a real nitrogen deficiency exists in the surface water of the Baltic.

During stagnant conditions, however, the Baltic bottom water contains several times too much phosphate in comparison with the AOU. The relation AOU : P is then about 22 : 1 (FONSELIUS 1967). The reasons for this phosphate accumulation will be discussed in chapter IX.

If one looks at the phosphorus conditions in the central part of Skagerack one finds that this water contains about 1 µg-at PO_4-P/l at a salinity of about 35 ‰. Fig. 60 shows the phosphorus components at the station M 6 in the deepest part of Skagerack south of the Norwegian coast. In the deepest part where the salinity is close to 35 ‰ the PO_4-P concentration is 1 µg-at/l and the total P concentration about 1.25 µg-at/l. Unfortunately no measurements of total P in the Kattegat close to the Belts have been made except some series from the "Kullen" station in September and November 1968. This sta-

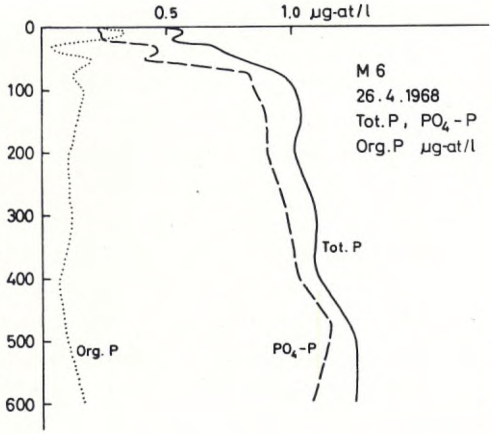


Fig. 60. The distribution of the phosphorus components at station M 6 in the Skagerack in April 1968.

tion is located in the outflowing Baltic current and so does not give much information about the P-content of the inflowing water. If it is assumed that the Skagerack water normally contains 1.25 μg-at total P/l at a salinity of 35 ‰, it is possible to compute the amount of P annually brought into the Baltic with the bottom current. To do so it is necessary to know the phosphorus concentration of the outflowing Baltic surface water. The mean value of the total P between 0 and 10 m at station S 12 (the Arkona Deep) measured during four expeditions in 1968 was 0.39 μg-at/l. This value is assumed to be representative for the outflowing water.

Kullenberg (1968) states that 2/3 of the inflowing water is Baltic water and only 1/3 is Skagerack water. Brogmus (1952) gives the amount of inflowing water to be 471 km^3/year. This means that $1.25 \times 1/3 \times 471 \times 10^{12} + 0.39 \times 2/3 \times 471 \times 10^{12}$ μg-at or about 9900 tons of P is annually added to the Baltic deep water. A total of 942 km^3 water flows out from the Baltic annually (Brogmus loc. cit.). Two-thirds of this water actually leaves the Baltic mixed with Skagerack water and one-third is recirculated. As was mentioned above this water returns with the inflowing water below the halocline. Actually 942 km^3 water leaves the surface layer of the Baltic. The concentration of total P was 0.39 μg-at/l there and $0.39 \times 942 \times 10^{12}$ μg-at or about 11400 tons of P annually leaves the Baltic surface layer. The excess of phosphorus in the outgoing surface current is about 1500 tons/year. It must be stressed that these values can only be viewed as approximate as long as no continuous daily measurements of total P are carried out in the Belts.

Fedosov and Zaitsev (1959) have estimated the amount of phosphorus brought to the Baltic with river water. They reported the value to be 3472 tons/year. The author arrived at a similar result (Fonselius 1967) by using the chemical denudation values given by Viro (1953) for Finland. These values give the amount of natural P in river water. The phosphorus released through human activity has to be added to this amount and it is assumed to be 3400 tons. VOIPIO (1968) estimated the amount of P in Finnish rivers including phosphorus from sewage systems to be about 20 µg P/l. He suggested that this value is valid for all rivers discharging in the Baltic. This seems to be too high an estimate. There is no evidence for instance that the Neva river contains such high amounts of phosphorus. The Neva is the largest river which discharges into the Baltic and it supplies 18 % of the river water to the Baltic. P values as high as those suggested by VOIPIO would probably be detected in the surface water of the Gulf of Finland. KOROLEFF (pers. comm.) claims no phosphorus contamination from the Neva river can be detected in the Gulf of Finland. It may be more realistic to calculate with a lower mean value for phosphorus in river water such as 15 µg/l. This value would give about 7100 tons of P/year for the whole Baltic. ODÉN arrived at a similar value (pers. comm.).

För låg förmodl. enl. Oppermann

It is extremely difficult to estimate the amounts of phosphorus released through sewage outlets. The amount of P in urban sewage water was according to "Miljövårdsforskning" (REXED et al. 1967) 1.5 g/person and day some 10 years ago in Sweden. Now it has increased to about 4 g/person and day. It is not easy to estimate the total amount of phosphorus discharged into the Baltic from these numbers. Only densely populated communities have sewage systems. In many cases the sewage is treated in sedimentation basins before it is released into the sea and through this process a part of the phosphorus is removed. The main reason for increased phosphorus values is the increasing use of synthetic detergents containing polyphosphates by households. It is not known if this is a trend in all countries around the Baltic. The use of synthetic detergents may not be as common in other countries as in Sweden.

In the present paper the amount of P released with river water is considered to be 15 µg/l or 7100 tons/year. The amount of phosphorus in precipitation over the surface of the Baltic amounts to 3000 tons/year (ODÉN, pers. comm.). The annual addition of phosphorus to the Baltic then amounts to 9900 + 7100 + 3000 = 20,000 tons. The annual loss will be 11,400 tons. It was shown earlier that 1/3 of the outflowing water returns with the inflowing deep current. Accordingly 3800 tons of phosphorus is recirculated. This amount should be subtracted from both incoming and outgoing phosphorus. The amounts will then be 16,200 respectively 7600 tons of P. The difference, 8600 tons is annually added to the Baltic. Most of this phosphorus is included in the biological life cycles in the water. Finally it is deposited in the bottom sediments. According to BUSHINSKI (1964) almost all dissolved phosphorus which is brought to the sea by rivers is immediately assimilated by the plankton and finally sedimented to the bottom. Very little is carried away into the deeper parts of the basin. This means that a biological filtering of the phosphorus takes place. If this were not true, the phosphorus content of the Baltic would continuously rise by several thousand tons per year.

Table IV. Phosphorus Balance of the Baltic in Tons/Year.

P added to the Baltic water		P removed from the Baltic water	
From the ocean	6100	To the ocean	7600
In river water	7100	To the sediments	8600
In precipitation	3000		
Total	16200	Total	16200

Table IV shows the phosphorus balance of the Baltic when it is assumed that the excess phosphorus is added to the sediments.

A large part of the phosphorus coming in through the Danish sounds is orthophosphate. The organic P will almost completely be oxidized to phosphate in the Baltic deep water. All this phosphate has to be absorbed in the bottom sediments or it has to be brought up into the surface water because there hardly is any primary production in the Baltic deep water.

It has been mentioned earlier (chapter II) that there is a certain mixing of water through the halocline which keeps the salinities of the deep water and the surface water at relatively constant levels. A rough calculation of this mixing can easily be made. Fig. 61 shows a "box model" of the Baltic. The halocline divides the Baltic into two boxes — a surface water box and a deep water box. Brogmus (1952) says the annual precipitation almost exactly equals the evaporation and for this reason they may be disregarded in the model. The annual river discharge is 471 km^3, the inflow from Kattegat is

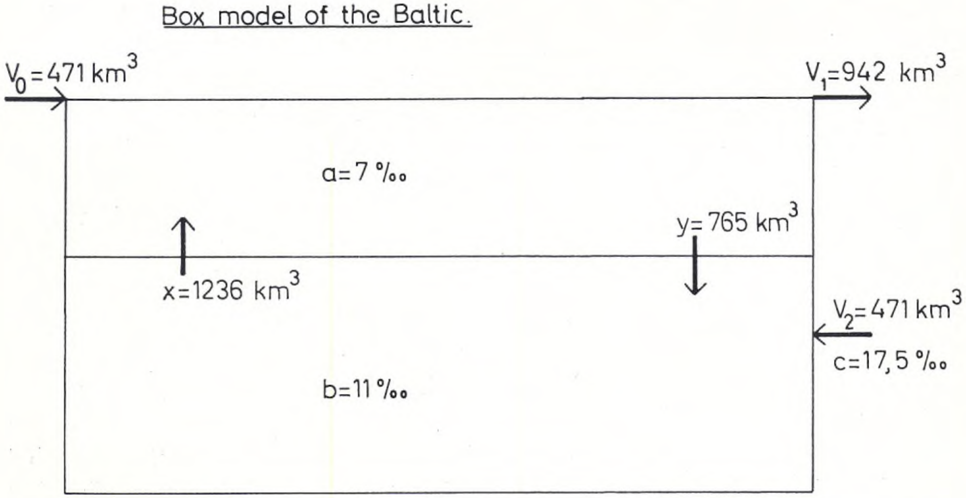


Fig. 61. A box model of the Baltic showing the water exchange through the halocline and the water balance of the Baltic.

also 471 km^3 and the outflow through the Danish sounds is 942 km^3 (BROGMUS loc. cit.). The salinity of the Baltic surface water is roughly 7 ‰ and the salinity of the deep water is supposed to be 11 ‰. The mean salinity of the incoming bottom current in the Belts is 17.5 ‰ (KULLENBERG 1968). The river discharge is called V_0, the outgoing current V_1 and the incoming current V_2. The amount of water mixed up through the halocline is marked X and the water mixed down is marked Y. The salinity of the surface water is a, the salinity of the deep water is b and the salinity of the incoming water in the Belts is c. The mixing through the halocline may be computed from the formulas:

$$V_0+X=V_1+Y \tag{1}$$

$$aY+cV_2=bX \tag{2}$$

Using the above mentioned values: $V_0=471$ km^3, $V_1=942$ km^3, $V_2=471$ km^3, $a=7$ ‰, $b=11$ ‰ and $c=17.5$ ‰. The use of these values in the formulas gives:

$$X=1236\ km^3/year$$
$$Y=765\ km^3/year$$

If a similar "box model" is used where the stagnant water is included as an additional box below the deep water box it is possible to construct a more complete phosphorus balance for the Baltic. Fig. 62 shows this balance

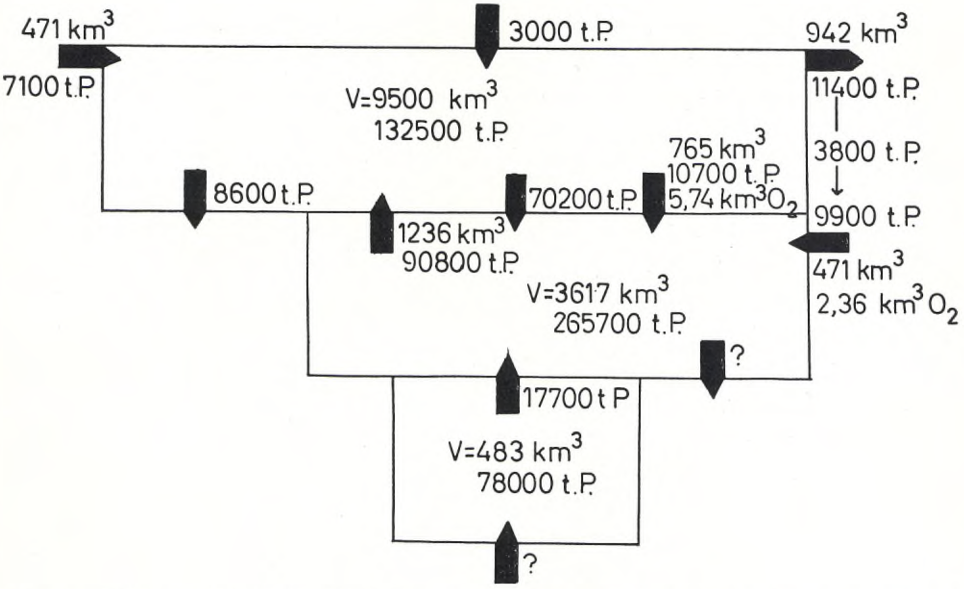


Fig. 62. A box model of the Baltic showing the phosphorus balance and the supply of oxygen to the deep water.

model for the Baltic. The amounts of phosphorus transported in and out from the Baltic were calculated earlier and are listed in table IV. The mean concentrations of phosphorus in the different water masses are given in table III. If these concentrations and the above calculated volumes of water mixing through the halocline are used the amounts of phosphorus brought up and mixed down through the halocline can be computed. Upmixing is $2.37 \times 1236 \times 10^{12}$ μg-at or 90,800 tons/year and downmixing is $0.45 \times 765 \times 10^{12}$ μg-at or 10,700 tons/year.

If the amount brought in to the deep water from the ocean is supposed to take part in this mixing the amount of phosphorus sinking through the halocline as particulate organic and inorganic matter is $90{,}800 - 9900 - 10{,}700 = 70{,}200$ tons.

Most probably relatively small amounts of suspended particulate inorganic phosphorus are transported down into the deep basins in the Baltic proper, (BUSHINSKI 1964); it may be assumed that at least 50 % of the sinking material arriving at the deep basins is organic P (see table III). About 40,000 tons of organic P is brought down into the deep water through the halocline if the total transport is 80,000 tons/year. In addition about 10,000 tons are added through the Belts. If it is assumed that 50 % of the material is organic P then the total annual organic P would be: $40{,}000 + 5000 = 45{,}000$ tons. This is 1452×10^{12} μg-at. Earlier it has been shown that the AOU is 550 : 1 in relation to released PO_4-P in the Baltic (FONSELIUS 1967). This means that 550 atoms of oxygen are needed in order to release 1 atom of PO_4-P from organic matter. The amount of oxygen needed for 1452×10^{12} μg-at of organic bound P is $798{,}600 \times 10^{12}$ μg-at. The oxygen supply to the deep water may be computed. From available oxygen data it can be judged that the inflowing bottom water contains about 5 ml O_2/l. Then the oxygen supply from the ocean will be $471 \times 5 \times 10^{12}$ ml/year $= 2360 \times 10^{12}$ ml. It appears from the oxygen concentration above the halocline that the maximum amount of O_2 mixed down through the halocline is about 7.5 ml/l. Annually $765 \times 7.5 \times 10^{12}$ or 5740×10^{12} ml are mixed down. The total supply ⋎ $\times 10^{12}$ of oxygen to the deep water is then 720,000 ⋎μg-at/year. If all organic P brought to the deep water were oxidized, the amount of oxygen needed for this is a little higher than the actual oxygen supply. This may explain the increasing oxygen deficit in the deep water. The values used are rough mean values but it is clear that small changes in the oxygen supply or in the phosphorus balance may influence the whole oxygen balance in the Baltic deep water. This may happen if the oxygen supply decreases through an increased stability of the halocline or if the phosphorus supply is increased through dissolution from the sediments or through increased waste disposal.

The amount of phosphorus in the different boxes have been calculated using the volumes of the boxes computed from table II. From Fig. 53 it was shown that the PO_4-P of the deep water had increased almost 3 times in about 14 years. If the increase of the whole deep water body is assumed to be 3 times the value 10 years ago the amount released from the sediments in the stagnant basins may be roughly computed: $2/3 \times 265{,}700 \times 1/10 = 17{,}700$ tons/year. This is the amount leaving the stagnant basins; a great part is also accumulated in the water of the basins. The accumulated amount is at present about 78,000 tons (see Fig. 62).

VIII. On silicate and the relation between silicate and phosphorus in the Baltic

It was noted earlier that the high silicate concentration in the Baltic is mainly due to the runoff. This has been investigated by VOIPIO (1961). He found that most of the silicate was brought to the Gulf of Bothnia with water from Swedish and Finnish rivers. The silicate is transported to the river water through weathering processes. It usually exists in fresh water as undissociated ortho-silicate but it can also exist as colloidal silicon or alumino-silicate ions. The silicate content increases towards the east. The water along the Baltic and German coast has low silicate concentrations. According to VIRO (1953), who analyzed the silicon content of Finnish rivers, the concentration is highest during the spring floods. The main component of the increase is suspended silicon.

Silicate may be regarded as a nutrient salt and is used by such organisms as diatoms as the main element in their shells. The biological activity of these algae removes silicate from the water. The opposite occurs in stagnant water where this salt is accumulated through the death and sinking of the diatoms (FONSELIUS 1962). The processes of decay and dissolution set free a part of the silicate but another large part is enclosed in the sediments.

Silicate analyses were carried out during the "Skagerak" expedition in September, 1968. The analyses were done according to STRICKLAND and PARSONS' technique (1965). The method was slightly modified for the conditions in the Baltic. The amount of sample water was decreased to 10 ml and the amounts of reagents were decreased proportionally. The colour was allowed to develop at least 4 hours and was measured in 1 cm cuvettes using a Hitachi Perkin-Elmer spectrophotometer. All reagents were added with Krogh-type automatic syringes.

The relation PO_4-P : Si has been plotted in Fig. 63 for the September expedition. The samples containing Kattegat water fall on line 1. The values below the line indicate mixing with Baltic water. These values are from surface water above the halocline. The samples from the Baltic proper fall on line 2. Close to the bottom of stagnant basins the PO_4-P values increase proportionally more than the silicate values. For this reason the line turns upward here. There does not seem to be any difference between surface water and deep water in the Baltic proper, except in stagnant basins. The samples from the Baltic proper are marked with crosses. The encircled

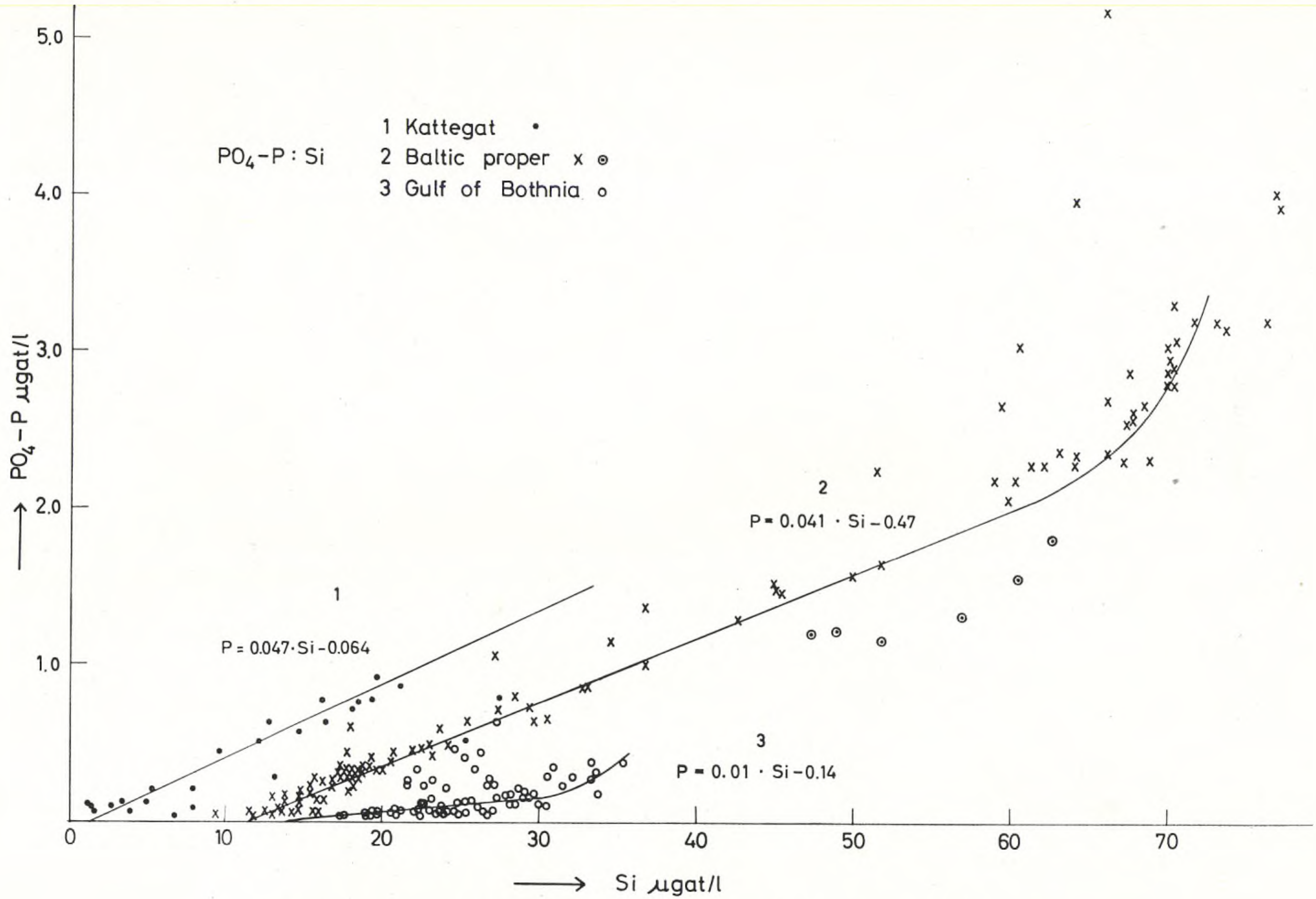


Fig. 63. The phosphate: silicate relation in different water masses in the Baltic.

dots are deep water samples from the southern Baltic proper. The reason for the proportionally low PO_4-P values there is not clear. The samples from the Gulf of Bothnia fall on line 3. They are marked as open circles. Samples influenced by water from the Baltic proper, e.g. water close to the bottom in the deeper parts of the Bothnian Sea, fall above the line. The equations for the lines are:

1. Kattegat water $P=0.047\times Si-0.064$ or $Si=1.35+21.1\times P$
2. Baltic proper water $P=0.041\times Si-0.47$ or $Si=11.5+24.4\times P$
3. Gulf of Bothnia water $P=0.010\times Si-0.14$ or $Si=14.0+100\times P$

If it is assumed that the average salinities of the inflowing Kattegat water, the surface water of the Baltic proper and the surface water of the Gulf of Bothnia are 17.5 $^{0}/_{00}$, 7 $^{0}/_{00}$ and 5 $^{0}/_{00}$ respectively, it can be shown that the silicate content of the Baltic proper is regulated by the silicate concentrations of the Kattegat water and the Gulf of Bothnia water:

$$5X+17.5(1-X)=7;\ X=0.8$$
$$(Si)_B=0.8\times 14+0.2\times 1.35;\ \ (Si)_B=11.5$$

The good agreement with the observed value in the Baltic proper is surprising. The reason may be that a part of the surface water from the Baltic proper is mixed into the surface water of the Gulf of Bothnia. This is caused by the counterclockwise current system of the Baltic surface water (PALMÉN 1930).

The curves in Fig. 63 show that phosphate and silicate are not accumulated in the stagnant bottom water in the same manner. The phosphate begins to increase when H_2S appears in the water, probably through dissolution from the bottom sediments. A similar dissolution of silicate does not seem to occur.

It can be seen that the water from the Baltic proper contains proportionally more silicate than the water from Kattegat; the water from the Gulf of Bothnia contains the most silicate. The reason for this is that the river water discharging into the Gulf of Bothnia contains the highest concentrations of silicate.

IX. On the exchange of nutrients between water and sediments

Normal sea water contains dissolved oxygen and is an oxidizing environment. SILLÉN (1961) has introduced to oceanography the conception pE, which is analogous to pH. It expresses the concentration of electrons in a solution in the same way pH expresses the hydrogen ion concentration. Thus pE is the negative logarithm of the electron concentration. Sea water has usually a pE of about 12.5 and a pH of about 8.2. The surface water of the Baltic is like normal sea water in this respect. In the deep water of the Baltic the oxygen concentration decreases rapidly downwards but the environment remains oxidizing as long as there is dissolved oxygen present in the water and no H_2S has been formed. The pH of the Baltic deep water may decrease to values a little below 7 because of the increasing amount of carbon dioxide formed. When H_2S appears in the water and the last traces of O_2 disappear a drastic change immediately occurs in the pE of the water. The environment becomes reducing and the pE decreases to negative values around —3.8 (SEN GUPTA 1969). The pH of the water changes only negligibly. It increases slightly when the H_2S concentration increases. The change may be about 0.2—0.3 pH units. This increase is probably because of the protolytic effect of the HS^- ions present in the water.

The surface layers of the sediments can be reducing long before the overlying water has lost its oxygen. Sediment samples often smell of H_2S even when the bottom water contains oxygen. In this case H_2S is oxidized at the sediment surface. Because the sediment itself is reducing, many sedimented substances may be transformed there into soluble form. In contact with interstitial water these substances will migrate up to the sediment surface. MANHEIM (1961) has investigated the chemical composition of stagnant sediments in the Baltic. He analyzed manganese nodules and suggested that these had grown on the surface of reducing sediments. Under reducing conditions minerals were dissolved in the interstitial water of the sediments. These minerals migrated to the surface of the sediment. When brought into contact with the oxygen-containing water above the sediment surface the minerals were again oxidized. The oxidized minerals could precipitate on suitable nuclei forming nodules. If the conditions in the water above the sediment are reducing conditions, then the minerals will remain in solution.

The properties of minerals and especially of nutrient salts have been studied by **Einsele** (1938), **Mortimer** (1941, 1942) and **Hayes** (1964). **Mortimer** has closely studied the mud-water interface both in nature in fresh water lakes and in a laboratory tank during oxidizing and reducing conditions. He observed that as long as oxygen was present in the water and the mud surface was oxidizing, inorganic nutrients were removed from the water phase and absorbed into the mud surface. Under these conditions iron was in the ferric form as $Fe(OH)_3$ and was precipitated from the water in colloidal form. Phosphate and silicate were absorbed by the mud also. The iron was observed partly to form phosphate salts. **Einsele** (1938) states that phosphorus coprecipitates with ferric hydroxide in the relation Fe: P = 7: 1. When the iron in the sediment is reduced and transformed to FeS because of the effect of excess H_2S, the phosphate is redissolved. It returns once more to the water phase and may be transported up from the sediments. There are two conditions under which the iron may be redissolved. If it comes into contact with oxygen again it may be transformed to hydroxide. If no oxygen is present, but only small amounts of H_2S and an excess of CO_2, then ferrous bicarbonate may be formed and this reaction may be expressed as:

$$FeS + 2\,H_2CO_3 = Fe(HCO_3)_2 + H_2S$$

The ferric hydroxide may dissolve in the same manner:

Y 2

$$2\,Fe(OH)_3 + H_2S + 4\,CO_2 = 2\,Fe(HCO_3)_2 + S \overset{4}{+} H_2O$$

When the supply of oxygen in **Mortimer**'s (1942) laboratory experiment was cut off by sealing the tank, the redox potential began to decrease. When all oxygen had disappeared from the water, nutrient salts began to dissolve from the mud surface. The whole system became reducing and Fe was transferred into ferrous form and it dissolved into the water. The P and Si concentrations increased enormously in the water phase. If sulfate was present in the water it was reduced to H_2S and Fe was precipitated as FeS. **Mortimer** observed the same phenomenon in fresh water lakes when the oxygen disappeared from the water.

Hayes (1964) made similar observations. He noted that organic matter which is present in sediments will decompose into inorganic form and can produce phosphate if oxygen is present in the sediments. If the pH of the sediment is between 5 and 7 this phosphate will be retained in the sediment. Sediments will also absorbe phosphate from the overlying water if oxidizing conditions exist and especially if iron is present. The maximum uptake occurs at pH 6 and it decreases only slightly with increasing pH. During oxidizing conditions the iron is in ferric form. During reducing conditions phosphate is released from the sediments. The iron is reduced to ferrous state and is released from the sediment. If H_2S is present it will be precipitated again as ferrous sulfide. It is this reaction which gives stagnant sediments their black colour.

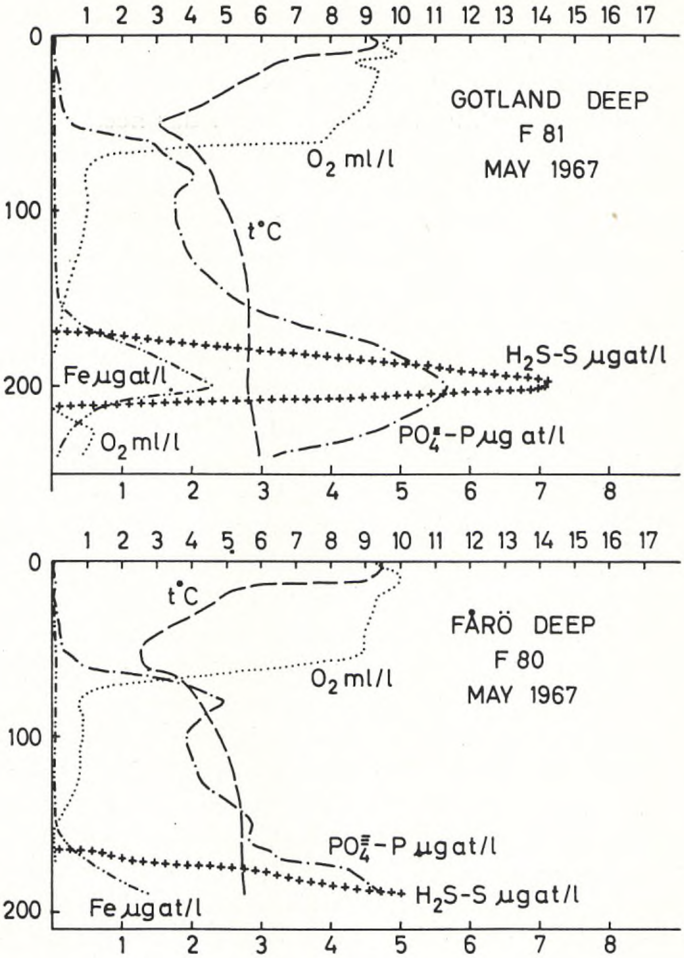


Fig. 64. The vertical distribution of dissolved iron in the Gotland Deep and the Fårö Deep in May, 1967. The upper scale shows S, t, O_2 and H_2S. The under scale shows PO_4-P and Fe.

The solubility product of FeS is much higher than that of $Fe(OH)_3$ and for this reason the amount of soluble iron increases when water becomes stagnant and contains H_2S (RICHARDS et al. 1965). At room temperature the solubility products in distilled water are: $FeS=10^{-19}$ and $Fe(OH)_3=10^{-36}$ (HÄGG 1946). RICHARDS calculated the apparent solubility product of FeS in Lake Nitinat to be 2.3×10^{-17}. KOROLEFF (1968 b) has measured iron concentrations in the Baltic. He calculated the apparent solubility product of FeS in the Baltic to be 1.1×10^{-18}. The author measured Fe in the Gotland Deep and the Fårö Deep in May, 1967. Fig. 64 shows the distribution of dissolved Fe and the other hydrographic factors in the two Deeps at that time. A renewal of the bottom water had just begun in the Gotland Deep and oxygen containing water was found below the stagnant H_2S containing water. This renewal is described in chapter IV. The concentration of dissolved Fe was very high in the stagnant water. It was about 2 μg-at/l in the Gotland Deep and about 1 μg-at/l in the Fårö Deep. These values are higher than the values reported by KOROLEFF in the Gotland basin (1968 b). The reason may be that dissolved humus has been extracted together with the iron by the organic solvent used (KOROLEFF 1968 b). This possibility has not been accounted for in the technique used (STRICKLAND et al. 1965). There may also be other reasons for the higher values. The filtering of FeS especially in dilute solutions, is not an easy task and some sulfide might have passed through the filter. KOROLEFF used a coprecipitation method in which the Fe was coprecipitated with $Mg(OH)_2$. Error in the calculation of the concentration of the dissolved Fe may occur because the forms in which iron occur in sea water are not well-known. There may be organic iron complexes which are not coprecipitated with hydroxides. RICHARDS et al. (1965) report more than 10 times higher particulate iron concentrations than dissolved iron values in Lake Nitinat. KOROLEFF's (1968 b) values of total Fe are of the same order of magnitude as the dissolved Fe values; in this case the particulate Fe is only a small fraction of the dissolved Fe. More investigations are clearly needed in this field.

Ca has been found to be dissolved in the deep water of the Baltic (GRIPENBERG 1937). In an earlier paper the author discusses the dissolution of Ca from the bottom sediments in detail (FONSELIUS 1967). It has been suggested by SILLÉN (1961) that a calcium compound, calcium phosphate, is dissolved from the sediments at the ocean bottom. It may be that Fe as well as calcium phosphate is dissolved from the sediments of the Baltic whose brackish water has the properties of both lake and sea water.

The dissolution of Ca is probably related to the lowering of the pH of the water below the halocline in the Baltic and not to the reducing conditions of the stagnant water. It is not clear whether the relation between the pH and the PO_4-P concentration in the Baltic is significant (FONSELIUS 1967). This relation is shown in Fig. 65 in which pH and PO_4-P values from the "Skagerak's" expedition in the Gotland Basin in February, 1967 are used. The PO_4-P values are plotted on a logarithmic scale and the pH values on a linear scale. The open circles in the upper left corner of the diagram are from the stagnant H_2S containing bottom water. The increase of pH with increasing PO_4-P values (and also H_2S values) in the stagnant water is clearly demonstrated. This increase is mainly ascribable to the protolythic effect of the HS^- ions.

y 2

$$Na_2S + H_2O \rightleftarrows HS^- + OH^- + Na^+$$

In a previous paper (FONSELIUS 1967) the author has discussed the reasons why the phosphate content of the stagnant Baltic water is higher than the phosphate content of the Cariaco Trench and the Black Sea and suggested that low pH and temperature caused a dissolution of phosphate in the Baltic.

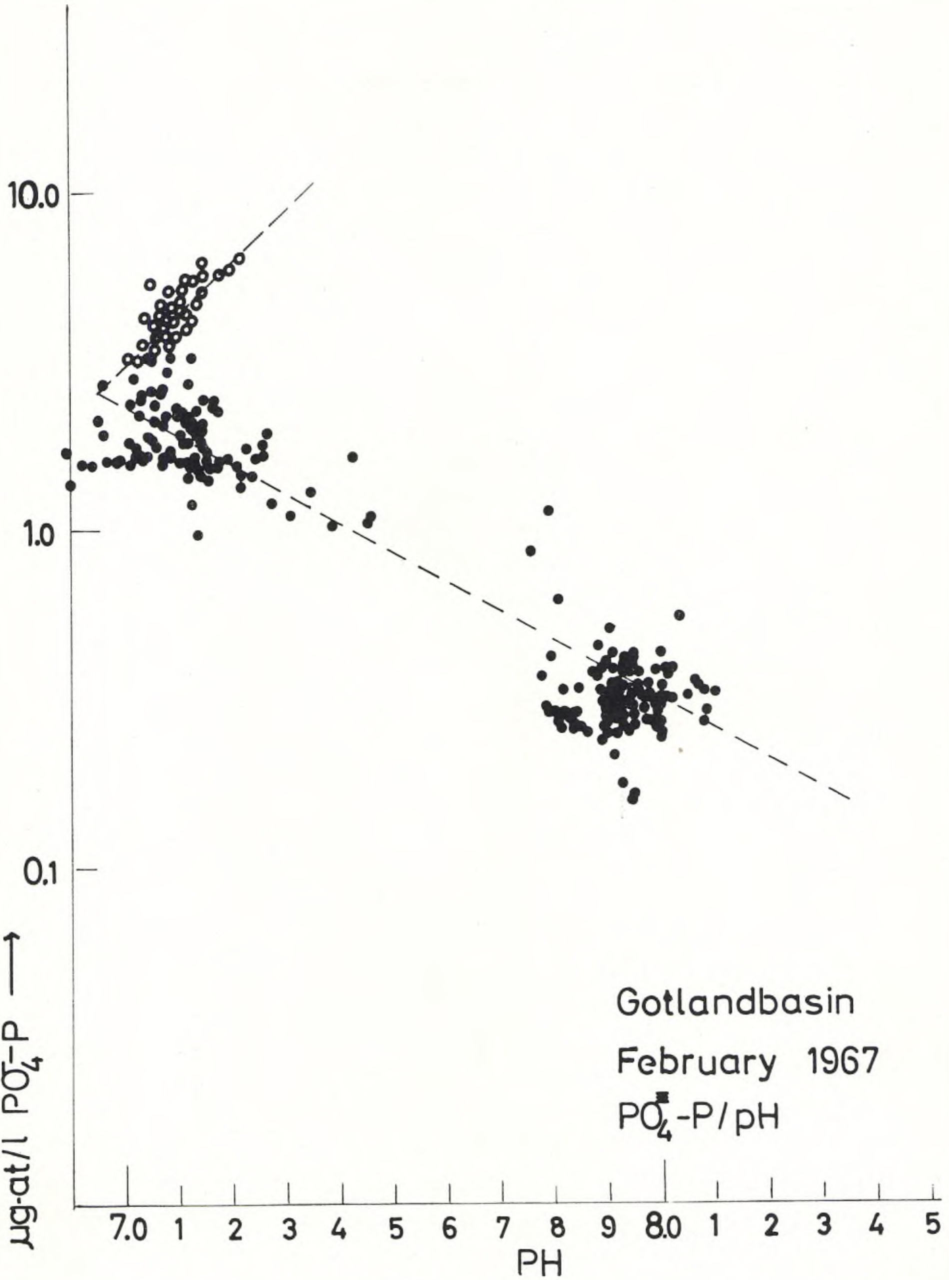


Fig. 65. The relation PO_4-P: pH in the Gotland Basin in February, 1967. The PO_4-P is on a logarithmic scale the pH on a linear scale.

There may be another reason for the high phosphate content of the stagnant water in the Baltic. Under normal conditions phosphorus is accumulated in the bottom sediments (MORTIMER 1942) and under stagnant conditions phosphate is released from the sediments. Phosphate concentrations up to 14 μg-at/l have been recorded in the stagnant water of the Baltic. It is surprising that phosphate values as high as this have not been observed in the Black Sea which has been stagnant for almost 6000 years (ZENKEVITCH 1963). The highest values reported from the Black Sea are around 9 μg-at/l. In the course of such a long period the sediments close to the sediment surface may have lost all soluble phosphate. Phosphate which comes from decaying matter increases very slowly in stagnant water where the oxygen needed for the oxidation is supplied through bacterial processes. For this reason there may be only a very small and gradual supply of phosphate to the deep water. The Baltic is only stagnant for short periods and every time the deep water is renewed and oxidizing conditions exist, new phosphate is absorbed into the sediment surface. It is because of these renewal periods that soluble phosphate is still present in the sediments. When conditions become reducing again the phosphate concentration increases very quickly showing that phosphate is released from the sediment surface (FONSELIUS 1967).

Phosphorus conditions which illustrate some of the principles discussed above can be mentioned here. Fig. 62 shows that the phosphorus content of the bottom current from the Kattegat is relatively high and that a fast absorption of phosphate into the sediments can occur during oxidizing conditions. The incoming bottom current in the Bosporus has a very low phosphorus content because the Mediterranean water has an extremely low phosphorus content.

In conclusion alternating oxidizing and reducing periods may be viewed as the reason for the high phosphate values in the bottom water of the Baltic during stagnant conditions.

X. Conclusions and discussion

The narrow and shallow connections with the ocean through the Belts and the Öresund and the high runoff are responsible for the ionic anomalies of the water in the Baltic. The climatic conditions in Northern Europe contribute also to the positive water balance in the Baltic. The positive water balance produces two water layers, a surface layer with a low salinity and a deep water layer with a higher salinity, separated by a permanent halocline. The halocline acts as a barrier and impedes the mixing of the water layers and the exchange of dissolved matter between them. Very little oxygen can be transported from the well aerated surface water down into the deep water through the halocline. The oxygen of the deep water is exhausted through oxidation processes. This results in a permanent oxygen deficit in the deep water.

The Baltic consists of a series of deep basins separated by sills. The topography of the Baltic forces the inflowing ocean water to pass through the different deep basins in a counterclockwise movement around Gotland. The shallow sill between the Baltic proper and the Gulf of Bothnia prevents greater amounts of heavy bottom water from passing into the Gulf of Bothnia. No permanent halocline has developed there except close to the bottom of the Bothnian Sea. A deep narrow channel through the sill allows small amounts of deep water from the Baltic proper to stream down into the Åland Sea and along the bottom of the Bothnian Sea. A weak halocline seems to prevent thermohaline convection down to the bottom in these areas. Stagnant conditions develop in some of the deep basins of the Baltic proper. All oxygen may then be exhausted and H_2S formed in the bottom water.

The only effective renewal of the deep water occurs through inflow of oxygen-rich water with a relatively high salinity from Kattegat. Occasionally greater inflows caused by special meteorological conditions may occur. These inflows can completely renew the stagnant bottom water of the deep basins. The new water is unable to renew the stagnant bottom water if it does not have a higher density than the old water.

Incoming water which renews the stagnant water may remain in the deep basin for such a long time that it in its turn eventually loses it oxygen and stagnates. If the stagnant water acquires a very high density, inflowing water of lower density fails to renew the stagnant water because it passes over the basin through an intermediate layer and leaves the bottom water undisturbed. Once a body of water becomes stagnant the condition tends to perpetuate itself and even worsen because when an inflow of new, aerated water does occur its oxygen quickly reacts with H_2S and so anoxic conditions develop shortly. At present the situation in the Baltic appears to be that oxygen conditions in the whole deep water body are deteriorating and that one deep water basin after another is loosing its oxygen and stagnating.

There is a connection between this oxygen decrease and a salinity increase in the Baltic which has occured during the present century. (This connection is particularly clear for the deep stations in the northern Baltic proper). The reasons for the salinity increase are: the decreased runoff to the Baltic from the rivers which discharge into it; the decreased water exchange through the Danish sounds and the increased intensity of the bottom current in the Belts and Kattegat. Meteorological factors are responsible for these phenomena.

The stability of the halocline has been increased by the greater salinity. This diminishes the water and oxygen exchange through the halocline. The exchange of water will be about 10 $l/m^2/day$ or counted as oxygen 70 $ml/m^2/day$. Even though the little exchange that does take place is much greater than the exchange through the Danish sounds, the exchange through the halocline is significant because it affects the whole Baltic proper. Small decreases in the oxygen supply can cause anoxic conditions in the deep water if the decrease continues over a long period. There are some long period variations in the runoff but the trend indicates a general decrease for the 20th century. The present salinity and oxygen conditions are possibly similar to the conditions during the middle of the 19th century.

There has been an accumulation of phosphorus in the Baltic deep water. This trend has been noted for the 15 years in which phosphate has been regularly measured there. The increasing oxygen deficit in the Baltic increases the accumulation of dissolved phosphorus in the deep water because the formation of H_2S creates reducing conditions which cause phosphate to be released from the bottom sediments. The low pH of the deep water causes a dissolution of phosphate from inorganic particulate matter containing phosphorus as well. A noteable example of this process occurs with apatite. Another reason for the increasing phosphorus values may be that there is a great amount of phosphorus in sewage water which is emptied into the Baltic from communities and industries.

There is a phosphorus deficit in the Baltic's surface water. One reason for this deficit is the fact that the river water that flows into this area has low concentrations of phosphate. Also the halocline impedes the mixing of the surface water with the deep water which is rich in phosphate. The surface water is occasionally "fertilized" by "upwelling" of phosphate from the deep water. "Fertilizations" are caused by salt water inflows from Kattegat and normal turbulence and diffusion through the halocline. The increasing phosphorus values of the deep water are eventually reflected in the surface water whose phosphorus concentration increases because of the "fertilizations". The release of sewage directly to the surface water also brings about an increase in the phosphorus concentration there. This greater amount of phosphorus increases organic production in the surface layer because phosphorus seems to be one of the limiting nutrients for primary production in the Baltic.

Increased primary production implies an increased number of dead organisms in the surface water. The dead organic matter sinks to the deep water and decays and through this process consumes oxygen in the deep water. Increased phosphorus concentrations in the surface water is in the way just described related to an increased oxygen consumption in the deep water.

In summary the oxygen deficit in the Baltic can be attributed to the following:

1) The increased salinity which has increased the stability of the halocline and has diminished the supply of oxygen to the deep water through the halocline.
2) The increased amount of phosphorus in the Baltic which has increased primary production and through this has increased the oxygen consumption in the deep water.

The salinity increase is the primary reason for the oxygen deficit and the phosphorus increase is the secondary reason. The secondary effect may have been increased by the enormously increased waste disposal into the Baltic during the 20th century.

Acknowledgements

The author wishes to express his sincere thanks to Miss K. AHLNÄS, M. Sc. who has carried out a great part of the analysis work aboard and in the laboratory during 1968 and to Mr. K. RANDERS who has collected and compiled data, drawn figures, carried out computations on stabilities and calculated the volumes of the deep basins. The author wishes to thank the master, Captain S. RONGE, the officers and crew of the "Skagerak" and the staff of the Hydrographic laboratory for their work at sea. Thanks are also due to Prof. D. DYRSSEN, Dr. E. ERIKSSON, Prof. B. KULLENBERG, Dr. A. LINDQUIST, Dr. S. ODÉN, Dr. E. OLAUSSON, Dr. A. SVANSSON and Prof. P. WELANDER for valuable discussions and suggestions.

The method for phosphate analysis has been worked out together with Mr. S. ENGSTRÖM from our laboratory. Mrs. C. MALKIN has corrected the English of the manuscript.

During 1968 the work has been supported with grants from "Statens Naturvetenskapliga Forskningsråd".

References

AHLNÄS K. 1962. Variations in salinity at Utö 1911—1961. — Geophysica 8: 2 p 135.

ANTONOV A. E. 1964. Oceanographic basis for fishing industry forecasts in the southern Baltic. — Kaliningrad 1964. (in russian).

BAARS J. K. 1930. Over sulfatreductie door bacterien. — Dissertation, Delft, 1930.

BANSE K. 1957. Die Verteilung von Sauerstoff, Phosphat und suspendierter Substanz. Ergebnisse eines hydrographisch-produktionsbiologischen Längschnitte durch die Ostsee im Sommer 1956. II. — Kieler Meeresforsch. IX.1.

BROGMUS W. 1952. Eine Revision des Wasserhaushaltes der Ostsee. — Ibid. IX.1.

BUCH K. 1917. Über die Alkalinität, Wasserstoffionenkonzentration, Kohlensäure und Kohlensäuretension im Wasser der Finnland umgebenden Meere. — Soc. Scient. Fenn. Finnländische hydrographisch-biologische Untersuchungen Nr 14.

— 1931. Eine biologisch-chemische Studie im Hafenwasser von Helsingfors. — Cons. perm. int. p. l'explor. de la mer. Rapp. et proc. verb. LXXV.

— 1932. Untersuchungen über gelöste Phosphate und Stickstoffverbindungen in den nordbaltischen Meeresgebieten. — Havsforsk. Inst. Skrift No 86.

— 1933. On boric acid in the sea and its influence on the carbonic acid equilibrium. — J. du Cons. III: 3.

— 1934. Det biokemiska kretsloppet i Östersjöbäckenet. Soc. Scient. Fenn. XII: 6.

— 1945. Kolsyrejämvikten i Baltiska havet. — Fennia 68: 5.

— 1954. Physikalische und chemische Verhältnisse in Beziehung zur biologischen Aktivität im Wasser des südwestlichen Schärenmeeres von Finnland. — Havsforsk. Inst. Skrift No 159.

— und GRIPENBERG S. 1938. Jahreszeitlicher Verlauf der chemischen und biologischen Faktoren im Meerwasser bei Hangö im Jahre 1935. — Havsforsk. Inst. Skrift No 118.

BUSHINSKI G. I. 1964. Shallow water origin of phosphate sediments. — Developments in Sedimentology Vol. I. Deltaic and shallow marine deposits. Edit. L. M. J. U. VAN STRAATEN, 1964.

BUTLER E. I. 1967. Report on the analysis of nitrate and nitrite at the ICES intercalibration of chemical methods held at Copenhagen 1966. — ICES C. M. 1967/C (mimeo.).

CHERNOVSKAYA E. N. 1962. Distribution of free carbonic acid in the Baltic. — Rep. Soviet. Inst. Oceanolog. (in russian).

COX R. A. 1966. Salinity and chlorinity results, Copenhagen intercalibration trials, 1966. — Report on intercalibration measurements. Unesco techn. papers in mar. sci. no 9, pp 43—52.

DERYUGIN K. M. 1923. Hydrology and Benthos in the eastern part of the Gulf of Finland. — Hydrological and hydrobiological investigations in the Neva bight. — Petrograd. (in russian).

— 1947. Hydrological revue of the Neva bight. — Soviet Inst. of Ocean. (in russian).

DICKSON R. R. 1968. Long-term changes in hydrographic conditions in the North Atlantic and adjacent seas. — ICES. C. M. 1968/C: 27 Hydrography Comm. (mimeo.).

EINSELE W. 1938. Über chemische und colloidchemische Vorgänge in Eisen-Phosphatsystemen unter limnochemischen und limnogeologischen Gesichtspunkten. — Archiv f. Hydrobiologie 33.

Ekman F. L. 1893. Den svenska hydrografiska expeditionen 1877, I. — Kgl Svenska Vetensk. Akad. Handl. Bd 25: 1.

Ekman G., Pettersson O. and Trybom F. 1907. Resultaten av den internationella havsforskningens arbete under åren 1902—06. — Kgl. Jordbruksdepart. XIV, 1907.

Eriksson E. 1959. The yearly circulation of chloride and sulfur in nature. — Tellus XI: 4 p. 67.

Fedosov M. and Zaitsev G. 1959. Water balance and chemical regime of the Baltic Sea and its gulfs. — ICES. C. M. 1959, Hydrogr. Comm. No 66 (mimeo.).

Fonselius S. H. 1962. Hydrography of the Baltic deep basins. — Fishery Board of Sweden, series Hydrography, No 13, 41 pp.

— 1965. The oxygen analysis during the informal intercalibration meeting in Copenhagen. June, 1965. — Report on the intercalibration measurement in Copenhagen, 9—13 June 1965 organized by ICES. Unesco techn. papers in mar. sci. no 3, pp 3—5.

— 1966 a. The results of the phosphate intercalibration measurements. Leningrad 24 May 1966. — Report on intercalibration measurements. Ibid. no 9, pp 34—39.

— 1966 b. The intercalibration of the Winkler method for dissolved oxygen. Copenhagen, September 1966. — Report on intercalibration measurements. Ibid. no 9, pp 53—62.

— 1967. Hydrography of the Baltic deep basins II. — Fishery Board of Sweden, series Hydrography, No 20, 31 pp.

Fox Ch. J. J. 1907: On the coefficients of absorption of the atmospheric gases in destilled water and sea water and of atmospheric carbonic acid in seawater. — Trans. Faraday Soc. 5. 68.

Gessner F. 1933. Phosphat, Nitrat und Planktongehalt in Arkonabecken. Ein Beitrag zur Produktionsbiologie der Ostsee. — J. du Cons. VIII, pp 181—194.

— 1940. Produktionsbiologische Untersuchungen im Arkonabecken und den Binnengewässern von Rügen. — Kieler Meeresforsch. III: 2.

Gieskes J. 1966 a. The pH measurements at the intercalibration meeting, Leningrad May, 1966. — Report on intercalibration measurements. Unesco techn. papers in mar. sci. no 9, pp 24—33.

— 1966 b. The pH measurements during the intercalibration meeting in Copenhagen, September 1966. — Report on intercalibration measurements. Ibid. no 9, pp 90—98.

Granqvist G. 1938. Zur Kenntnis der Temperatur und des Salzgehaltes des Baltischen Meeres an den Küsten Finnlands. — Havsforsk. Inst. Skrift No 122.

— 1952. Harmonic analysis of temperature and salinity in the sea off Finland and changes in salinity. — Ibid. No 152.

Grasshoff K. 1965. The results of the chlorinity and salinity intercalibration measurements during the informal meeting in Copenhagen June, 1965. — Report on the intercalibration measurements in Copenhagen, 9—13 June 1965 organized by ICES. Unesco techn. papers in mar. sci. no 3, pp 6—8.

— 1966 a. The results of the chlorinity and salinity intercalibration measurements, Leningrad, May 1966. — Report on intercalibration measurements. Ibid. no 9, pp 9—18.

— 1966 b. General conclusions of the intercalibration measurements. — Report on intercalibration measurements. Ibid. no 9, pp 111—114.

Gripenberg S. 1937. The calcium content of Baltic waters. — J. du Cons. XII: 3.

— 1960. On the alkalinity of Baltic waters. — Ibid. XXVI: 1.

Hayes F. R. 1964. The mud-water interface. — Oceanogr. Mar. Biol. Ann. Rev. 1964, 2. pp 121—145.

Hela I. 1958. A hydrographic survey of the waters in the Åland Sea. — Geophysica VI: 3—4, Meteorology, pp 219—242.

— 1966. Secular changes in the salinity of the upper waters of the Northern Baltic Sea. — Comm. phys.-mat. Soc. Scient. Fenn. XXXI: 14.

Hägg G. 1946. Kemisk reaktionslära. — Almqvist et Wiksells Boktryckeri AB, Uppsala.

Jones P. G. V. and Folkard A. R. 1966. Report on the analysis of phosphate at the ICES intercalibration trials of chemical methods held in Copenhagen 1966. — Report on intercalibration measurements. Unesco techn. papers in mar. sci. no 9, pp 63—79.

Kalle K. 1932. Phosphatgehaltuntersuchungen in der Nord- und Ostsee im Jahre 1931. — Ann. Hydrogr. 60: 1, pp 6—17.

— 1943. Die grosse Wasserumschichtung im Gotlandstief vom Jahre 1933—34. — Ann. Hydrogr. 71: 4—6.

Knudsen M. 1901. Hydrographical Tables. Second edit. 1931.

Koroleff F. 1965 a. Report on the intercalibration measurements in Copenhagen, 9—13 June, 1965, organized by ICES. — Unesco techn. papers in mar. sci. no 3, pp. 1—2.

— 1965 b. The results of alkalinity intercalibration measurements in Copenhagen, June 1965. — Report on the intercalibration measurements in Copenhagen, 9—13 June, 1965 organized by ICES. Ibid. no 3 pp 9—11.

— 1965 c. The results of the phosphate intercalibration measurements in Copenhagen, June 1965. — Report on the intercalibration measurements in Copenhagen, 9—13 June 1965 organized by ICES. Ibid. no 3 pp 12—14.

— 1966. The intercalibration of alkalinity. — Report on intercalibration measurements. Ibid. no 9 pp 99—107.

— 1968 a. Determination of total phosphorus in natural waters by means of persulfate oxidation. — ICES. C. M. 1968/C: 33 (mimeo.).

— 1968 b. A note on the iron content of Baltic water. — ICES. C. M. 1968/C: 34 (mimeo.).

Kullenberg B. 1955. Restriction of the underflow in a transition. — Tellus VII, pp 215—217.

— 1968. Anteckningar i oceanografi för 1-betygstuderande, Ht 1968. (mimeo.).

Kwiecinski B. 1965 a. The sulfate content of Baltic water and its relation to the chlorinity. — Deep-Sea Res. Vol. 12, pp 797—804.

— 1965 b. The relation between the chlorinity and the conductivity in Baltic water. — Ibid. Vol. 12, pp 113—120.

Lebedintsev A. A. 1910. Hydrological and hydrochemical investigations in the Baltic in August—September 1908. — Trudy Baltiskoj Ekspedicii. Vol. 1, 1910. St. Petersburg.

Lindquist A. 1959. Studien über das Zooplankton der Bottensee II. — Inst. Mar. Res. Lysekil. Series Biology. Rep. No 11. Fishery Board of Sweden.

Manheim F. T. 1961. A geochemical profile in the Baltic Sea. — Geochim. Cosmochim. Acta, Vol. 25, pp 52—70.

Meyer P. F. and Kalle K. 1950. Die biologische Umstimmung der Ostsee in den letzten Jahren — eine Folge hydrographischer Wasserumstimmungen? — Archiv f. Fischerei-Wissenschaft. Jg 2, H. 1/2 1950, pp 1—9.

Miezis V. and Ozoliņš J. 1940. Die Lettische Terminfahrten in den Jahren 1935, 1936, 1937 und 1938. — Zemkopibas Ministrijas Zvenjniecibas Rakstu Krojums XIX burtnica.

Mortimer C. H. 1941. The exchange of dissolved substances between mud and water in lakes. — J. of Echology, Vol. XXIX: 2, pp 280—329.

— 1942. The exchange of dissolved substances between mud and water in lakes. — Ibid. Vol. XXXI: 1, pp 147—201.

Murphy J. and Riley J. P. 1962. A modified single solution method for the determination of phosphate in natural waters. — Anal. Chim. Acta 27, pp 31—36.

Nehring D. 1966. The results of the oxygen intercalibration measurements. Leningrad, May 1966. — Report on intercalibration measurements. Unesco techn. papers in mar. sci. no 9, pp 19—23.

— and ROHDE K. 1967. Weitere Untersuchungen über anomale Jonenverhältnisse in der Ostsee. — Beiträge zur Meereskunde 20, pp 10—33.

PALMÉN E. 1930. Untersuchungen über die Strömungen in den Finnland umgebenden Meeren. — Comm. phys.-math. Soc. Scient. Fenn. V: 12.

PALMORK K. H. 1966. The intercalibration of the methods for silicate determination, Copenhagen 1966. — Report on intercalibration measurements. Unesco techn. papers in mar. sci. no 9, pp 80—90.

PALOSUO E. 1964 a. The Gulf of Bothnia in winter time, I. Data from winter cruises 1959—63. Havsforsk. Inst. Skrift No 208.

— 1964 b. A description of the seasonal variations of water exchange between the Baltic proper and the Gulf of Bothnia. — Ibid. No 215.

PETTERSSON O. 1889. Methode zur volumetrischen Bestimmung der im Wasser gelösten Gase. — Berichte d. deutsch. chem. Gesellsch. 22, 1434.

REDFIELD A. C., KETCHUM B. H. and RICHARDS F. A. 1963. The influence of organisms on the composition of sea-water. — The Sea, Vol. II. Edit. M. N. HILL. Interscience Publishers, New York, London, 1963, p 38.

REXED B., BOLINDER E., BROHULT S., EIDEM I., JOHANSSON A., LANE S., LÖNNGREN R., LUNDHOLM B. and STENRAM H. 1967. Miljövårdsforskning. — Betänkande avgivet av 1964 års naturresursutredning, p 59.

RICHARDS F. A. 1965. Anoxic basins and fjords. — Chemical Oceanography, I. Edit. J. P. RILEY and G. SKIRROW. Academic Press, London and New York 1965, pp 611—645.

— and VACCARO R. 1956. The Cariaco Trench, an anoxic basin in the Caribbean Sea. — — Deep-Sea Res. 3, pp 214—28.

— CLINE, J. D., BROENKOW W. W. and ATKINSON L. P. 1965. Some consequences of the decomposition of organic matter in Lake Nitinat, an anoxic fjord. — Limn. and Oceanogr., ALFRED REDFIELD 75th Anniversary Vol. November 1965. Supplem. to Vol. X.

ROHDE K. 1966. Untersuchungen über die Calcium- und Magnesiumanomalie in der Ostsee. — Beiträge zur Meereskunde 19, pp 18—31.

SCHULZ B. 1922. Hydrographische Untersuchungen insbesondere über die Kohlensäure in der Ostsee im Jahre 1922. — Ann. Hydrogr. 50, pp 244—251.

— 1923. Hydrographische Untersuchungen besonders über den Durchlüftungszustand in der Ostsee im Jahre 1922. — A. d. Arch. d. Deutschen Seewarte 41, no 1.

— 1932. Einführung in die Hydrographie der Nord- und Ostsee. — Die Tierwelt der Nord- und Ostsee, Bd. I, Leipzig 1932, pp 45—88.

— 1956. Hydrographische Untersuchungen in der Ostsee 1925 bis 1938 mit dem Reichsforschungsdampfer "Poseidon". — Ergänzungsheft zur Deutsch. Hydrogr. Zeitschr. Reihe B, 4.

SEGERSTRÅLE S. 1953. Further notes on the increasing salinity of the inner Baltic and its influence on the fauna. — Soc. Scient. Fenn. XIII, p 15.

SEN GUPTA R. 1967. Inorganic nitrogen compounds in the Baltic. — Thesis for the degree of Fil. lic. at Göteborgs University, 50 pp (mimeo).

— 1969. Biochemical relationships and inorganic nitrogen equilibrium in semi-enclosed basins. — Tellus XXI: 2 (in press).

SILLÉN L. G. 1961. The physical chemistry of sea water. — Oceanography, edit. M. Sears. Publ. no 67 AAAS, Washington D.C. pp 549—581.

— 1966. Regulation of O_2, N_2 and CO_2 in the atmosphere; thoughts of a laboratory chemist. Tellus XVIII: 2—3, pp 204—205.

SIMONOV A. I. 1965. The hydrochemical state of the Baltic. — The Hydrometeorological Press, Leningrad (in russian).

Sirén A. 1958. Eräistä pisimmistä Suomea koskevista hydrologisita havaintosarjoista (Some of the longest hydrological observation series on Finland, engl. summ.). — Medd. fr. Hydrografiska Byrån XVI, pp 32—35.

Skopintsev B. 1957. Studies of redox potential in waters of the Black Sea. — Gidrokhim. Materialy 24, pp 21—36 (in russian).

Soskin I. M. 1963. Continuous changes in the hydrological characteristics of the Baltic Sea. Hydrometeorological Press, Leningrad (in russian).

Strickland J. D. H. 1960. Measuring the production of marine plankton. — Fisheries Board of Canada, Bull. No 122, p 20.

— and Parsons T. R. 1965. A manual of sea water analysis. — Ibid. No 125 (Second revised edition).

Sverdrup H. U., Johnson M. W. and Fleming R. H. 1942. The Oceans. — Prentice-Hall Inc. Englewood Cliffs, N. J. pp 416—418.

Viro P. 1953. Loss of nutrients and the natural nutrient balance of the soil in Finland. — Comm. Inst. Forest. Fenn. 42: 1, p 51.

Voipio A. 1961. The silicate in the Baltic Sea. — Ann. Acta Scient. Fenn. ser. A II, chemica 106.

— 1968. On the cycle and balance of phosphorus in the Baltic. — ICES C.M. 1968/C: 32 (mimeo.).

Wattenberg H. 1940. Der hydrographisch-chemische Zustand der Ostsee im Sommer 1939. — Ann. Hydrogr. 68, pp 184—194.

— and Meyer H. 1936. Der jahreszeitliche Gang des Gehaltes des Meerwassers an Planktonnährstoffen in der Kieler Bucht im Jahre 1935. — Kieler Meeresforsch. I: 1, pp 264—278.

Winkler L. 1888. The determination of dissolved oxygen in water. Berichte d. deutsch. chem. Gesellsch. 21, 2843.

Wittig H. 1940. Über die Verteilung des Kalziums und der Alkalinität in der Ostsee. — Kieler Meeresforsch. III, pp 460—496.

Wyrtki K. 1954. Der grosse Salzeinbruch in die Ostsee im November und Dezember 1951. — Kieler Meeresforsch. X: 1, p 19.

Zenkevitch L. 1963. Biology of the seas of the U.S.S.R. — George Allen et Unwin LTD London, p 383.

Reports from the Fishery Board of Sweden.

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