GÖTEBORGS UNIVERSITET

HYDROGRAPHY OF THE BALTIC DEEP BASINS II

BY

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Sida 21, stycke b rad 8: "P constant" skall vara "P con-
centration".

Sida 27: Texten till fig. 22 hör till fig. 23.

Sida 29, rad 13: "0.0 µgAt/l" skall vara "30.0 µgAt/l".

Sida 78, rad 32: "720,000 µg-at" skall vara "720.000 x 10
µg-at."

Sida 84, rad 20: I formeln står det H_2O, skall vara $2H_2O$.

Sida 86, rad 38: I formeln står det Na^+, skall vara $2Na^+$.

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I. Introduction

In an earlier work the author has described the unusually long stagnation period in the Gotland basin, which was caused by the big salt inflow into the Baltic in December 1951 (FONSELIUS 1962). The inflowing Kattegat water filled up the deep basins with heavy high saline water. This water remained in the Gotland basin for 10 years under continuous dilution, until it was replaced by new water in the middle of 1961. The long residence time for the Kattegat water in the Gotland basin caused stagnation there, and H_2S was formed in the stagnant water when all the oxygen had been used up. During the stagnation large amounts of phosphate were accumulated in the deep water. The author estimated the accumulated amount of phosphate-phosphorus in the Gotland basin to be over 40,000 tons. The phosphorus concentration of the bottom water exceeded 10 µgA/l. Normally the concentration is between 1 and 2 µgA/l in the Baltic bottom water. When the stagnation was broken, all this phosphorus was released and brought up in the overlying water levels. An increase of the phosphate content of the Baltic surface water was therefore predicted by the author.

From the thirties a similar but smaller stagnation period is known. This stagnation has been described by KALLE (1943), and it is even mentioned in Dietrichs "Allgemeine Meereskunde" as a classic example on stagnation. Phosphate measurements were carried out during the stagnation, and KALLE estimated the accumulated amount of phosphate-phosphorus to be 30,000 tons. Unfortunately, only sporadic hydrographic measurements were carried out in the Gotland basin during the thirties, and therefore the development of the stagnation and the inflow of new water could not be studied in detail.

The author has described the variations in salinity, temperature and oxygen content at 200 m in the Gotland basin from 1902 to 1961 (FONSELIUS loc. cit.). From these diagrams it can be seen that the oxygen suddenly increased from 0 ml/l in 1933 to around 3.5 ml/l in 1934. It is, however, difficult to detect any significant changes in temperature and salinity at that occasion. How this amount of oxygen could be brought down in the deep water without visible changes in the hydrographical factors is not easy to understand. KALLE (loc. cit.) has tried to explain this turnover of the deep water. Anyhow, this stagnation did not cause any big changes in the Baltic deep water and cannot be compared to the big stagnation and turnover during 1951 to 1961.

MEYER and KALLE (1950) suggested that the phosphate which had been brought up from the Gotland basin in 1933 had "fertilized" the water of the Baltic and that this fertilization had increased the yield of the fishing in the southern Baltic in a high degree. MEYER and KALLE estimated that 1/4 of the 50 m thick surface layer of the Baltic water had got a phosphorus increase of about 0.20 μgA/l and that this increase of nutrient salts would cause an increase in the amount of fish, amounting to 150,000 tons of food fish per year in the eastern Baltic. They even show diagrams of fishery statistical catch yields from different Baltic countries and show an enormous increase in the catch of cod, especially during 1939—45. The conditions in the world were, however, far from normal during the world war, and it is doubtful if any direct conclusions concerning the relation between the phosphate increase and statistical fishing data can be drawn during this time.

LINDQUIST (1960) explains the increase in the catch of cod by Swedish fishing vessels during the last decades through the increase of the salinity in the Baltic during this time. This seems to be a more probable explanation than the release of phosphate after the stagnations. Of course, this might be a contributing factor, but the main factor is certainly the increased salinity which also means improved conditions for several types of plankton organism. Another contributing factor is certainly the improved fishing technique during the last decades. Earlier, bottom trawls were not used in the Baltic.

II. Phosphate variations in the surface water

Fig. 1 shows the amount of phosphate-phosphorus in μgA/l in the surface water of the Baltic proper from 1958 to 1965. The values are taken from the hydrographic measurements of the Fishery Board of Sweden in the central Baltic. The phosphate was measured spectrophotometrically, first according to WOOSTER and RAKESTRAW (1951), and from 1964 according to MURPHY and RILEY (1962). As can be seen from the figure, the phosphate concentration suddenly increased in the beginning of 1962 at all stations. In a few months this extra phosphate again disappeared, and the surface values returned to normal concentrations.

The author had predicted (loc. cit.) that the phosphorus content of the surface water should rise to around 0.40 μgA/l when the released phosphate from the Gotland basin reached the surface layers. The increase was, however, 0.65—0.90 μgA/l. The reason for this is obviously that the accumulated amount of phosphate was estimated too low, due to inaccurate information regarding the volume of the stagnant area. A better estimate was made by FEDOSOV and ZAITSEV (1959). They calculated the accumulated phosphorus to amount to 110×10^3 tons. This should increase the 50 m thick surface
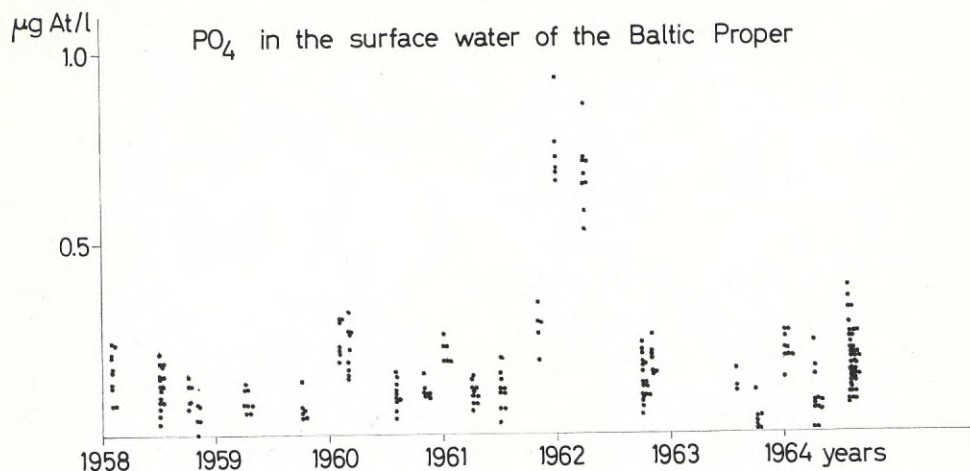
Fig. 1. The phosphate concentration in the surface water of the Baltic proper from 1958 to 1964.

layer of the Baltic proper with 0.35 µgA/l, which means that the concentration during the winter, when the normal concentration is 0.20—0.30 µgA/l, really would amount to values around 0.60 µgA/l. How could this "extra" phosphorus disappear in a few months? The brutto transport of water out from the Baltic through the Belts and Öresund to Kattegat is according to BROGMUS (1952), about 1000 km³ per year. The volume of the surface layer down to 50 m in the Baltic proper is about 10⁴ km³. The mean height of the primary halocline in the Baltic proper is 50 m, and the water above this depth is considered to be the outflowing brackish surface water. It is obvious that it would take around 10 years to bring out all the "extra" phosphate from the Baltic in this way. The phosphate must have disappeared through another mechanism.

The Baltic surface water is considered to be near the starving limit regarding nutrient salts. The phosphate has been suggested to be one of the limiting factors for organic life, and, especially in the Baltic, it may be the limiting factor. Therefore it is tempting to assume that the extra phosphate, which in the winter 1962 was mixed up in the photosynthetic layer, allowed the organic production of phytoplankton to increase, and that the phosphate in that way was removed from the water phase.

Unfortunately, no measurements of the primary production using the C-14 method by STEEMANN-NIELSEN were carried out in the Baltic proper during this period. C-14 measurements were carried out in the Gulf of Bothnia at the light ship "Finngrundet", but the results can hardly be considered significant for the Baltic proper. The Gulf of Bothnia is covered by ice during the winter, and "Finngrundet" is in action only during the ice-free part of the year.

SJÖBLOM (1964) reports, however, that the intestinal fat content of Baltic herring caught in 1962 and 1963 was unusually high, and that there was no difference in the relative amounts of intestinal fat between young and old herrings, as there is in years of low fat content. This might be an indication of an increased primary production in 1962, which has given the herring more to eat. SJÖBLOM even reports that the "condition" coefficient of the herring was unusually high in 1962, and that there were unusually few herrings with no stomach content.

NIKOLAEV et al. (1962) found that zooplankton during 1962 increased enormously, especially in August. They got values exceeding 180 $\%$ of the long time means. For instance, the average abundance of Crustacea in the 0—100 m water was in August 1962 in the Baltic 17,430 ind./m^3, which is 187 $\%$ of the long period mean value. The biomass amounted to 318 mg/m^3 during the same time. This is 159 $\%$ of the long period mean. NIKOLAEV et al. explain this extraordinarily high plankton increase by an unusually high river discharge that spring, which brought out an excess of nutrients into the surface water. This cannot, however, explain the high concentration of phosphate in the surface water. According to FEDOSOV et al. (loc. cit.), the total amount of phosphorus brought into the Baltic annually by river water is 3472 tons. The increase in the Baltic proper during the winter 1962 was about 110,000 tons. It can hardly be assumed that the discharge of river water should have been 30 times the normal during 1962. FEDOSOV et al. do not indicate how they calculated the river discharge of phosphorus. A rough calculation of the chemical denudation in the area which discharges its water into the Baltic supports, however, FEDOSOV's data. If we assume that the area is 10^6 km^2 and take VIRO's (1953) value for the denudation in Finland, 10 ton/km^2/year, as an average, we get a total denudation of 10^7 tons. POLDERVAART (1955) gives the amount of P$_2$O$_5$ in the sediments as 0.15 $\%$. This gives an annual amount of P discharged into the Baltic of 3250 tons.

Therefore it is much more tempting to assume that the phytoplankton during the spring has used up all the extra phosphate and in this way been able to increase so much that the zooplankton during the summer has had enough food to be able to almost double its amount.

III. The origin of the surface phosphate

The reason why the released phosphate reaches the surface layers only during the winter is that the thermocline in the Baltic is very stable during the summer and effectively isolates the deep water from the surface water. It might here be proper to repeat some of the main features of the hydrography of the Baltic. The inflowing salt bottom water and the outflowing

brackish surface water are separated by a halocline, called the "primary halocline". This halocline remains throughout the year in the Baltic proper. A "secondary halocline" may be formed during stagnant conditions in the deep basins, and it may remain for long times, but it is not a permanent phenomenon and disappears when the stagnation is broken. In the brackish surface water a thermocline is formed during the spring close to the surface, and it moves slowly downward during the summer, getting more and more stable. During the autumn it is weakened through the cooling of the surface water, and during the winter it disappears completely. This causes a homo-thermal mixing of the surface water down to the primary halocline.

When the secondary halocline is destroyed and the stagnant water is lifted up from the basin, it seems by some mechanism to penetrate even the primary halocline. Exactly how this happens is not clear, but it seems that the phosphate slowly is mixed through the halocline in a 20—30 m thick layer. The halocline seems to have been moved 25 m up in November at the station F 80 north of the Gotland basin (Figs. 2 and 3).[1] Buch (1932) has shown that nutrients are transported up to the surface in the Gulf of Finland through "upwelling". The deep water moves along the bottom into the Gulf of Finland and is there pressed upwards and mixed with the out-flowing surface water. There are however no measurements from the Gulf of Finland during this time; the area is covered by ice during the winter. No extra phosphate reached the surface layer before January 1962, when the thermocline had disappeared and there occured total convection down to the primary halocline. Fig. 4 shows how the phosphate in January is evenly spread out in the whole water mass down to the halocline. This homothermal mixing shows how important the disappearence of the thermo-cline is during the winter for the nutrient salt supply of the Baltic surface water. Very little phosphate is brought down into the surface water by runoff; the deep water is the main source for nutrient salts in the Baltic. The river discharge of about 3,500 tons annually increases the surface layer of the Baltic proper by 0.01 µgA/l. When a new thermocline is formed during the spring close to the surface, the surface water again is isolated from the deeper waters, and the phosphate in the surface layer is the only nutrient source for the plankton bloom. As can be seen from fig. 5, all the extra phosphate has been used up during the spring and summer, and the surface values for phosphate are again normal in October.

Glowinska (1961) has described the conditions in the Bornholm basin and the Gdansk basin during 1959. According to her figures, there was an accumulation of phosphate in the deep water of the Bornholm basin during January 1959. The phosphate concentration decreased in February, and there was instead an increase of phosphate extending up to the surface in the Gdansk basin.

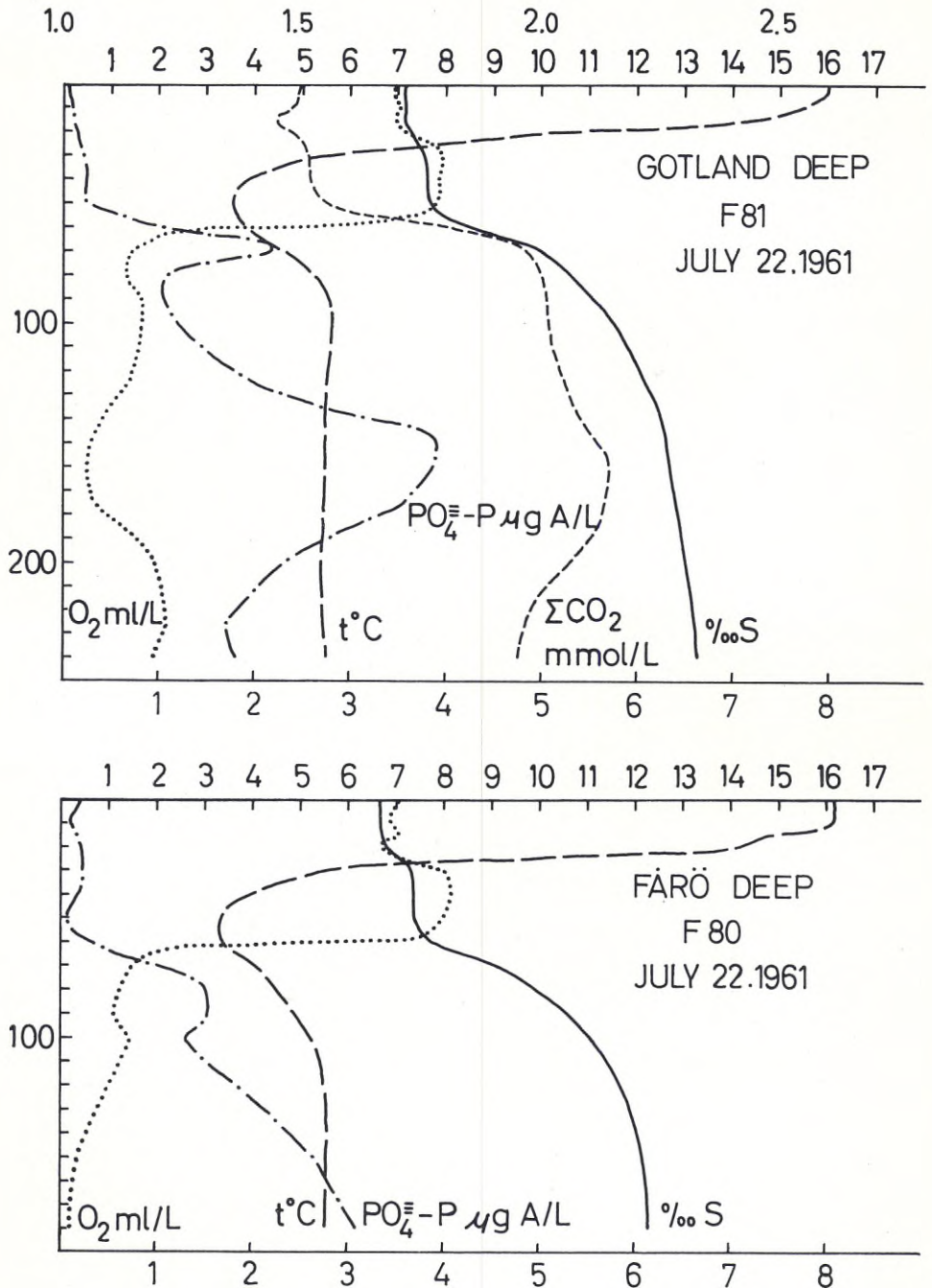[1] There is of course also the possibility that this was an unusually big internal wave.

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Fig. 2. The hydrographic conditions at the Gotland Deep and the Fårö Deep, July 22, 1961. Swedish data. The under scale $PO_4 \equiv -P$, the upper S, t, O_2, CO_2, H_2S, ΣCO_2.
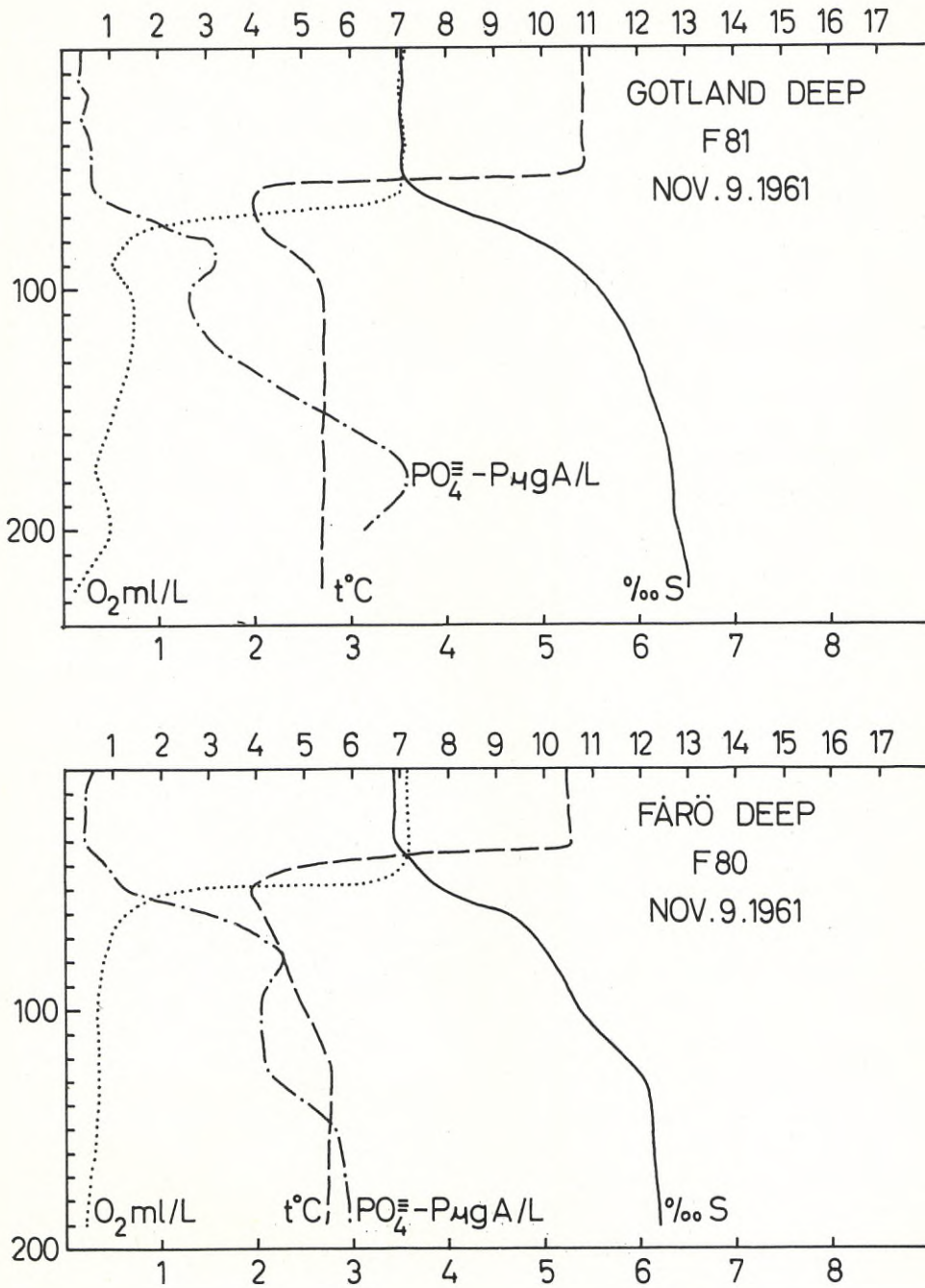
Fig. 3. The hydrographic conditions at the Gotland Deep, and the Fårö Deep, November 9, 1961. Swedish data. The under scale $PO_4\equiv-P$, the upper S, t, O_2, CO_2, H_2S.
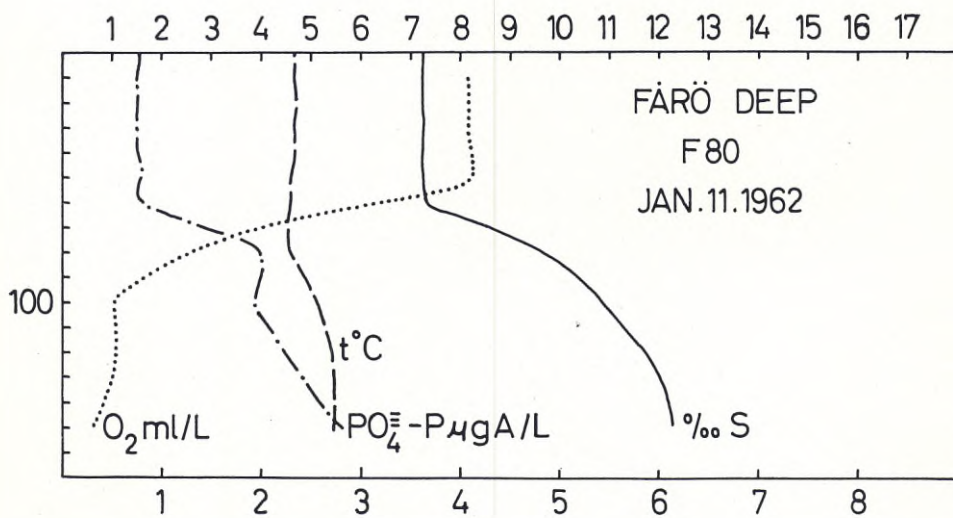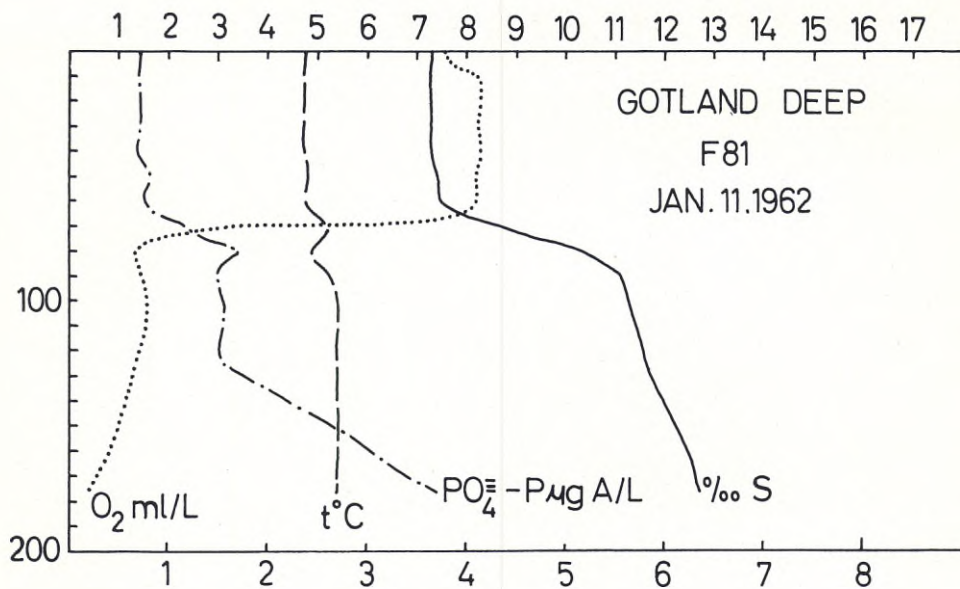
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Fig. 4. The hydrographic conditions at the Gotland Deep and the Fårö Deep, January 11, 1962. Swedish data. The under scale $PO_4\equiv-P$, the upper S, t, O_2, CO_2, H_2S.
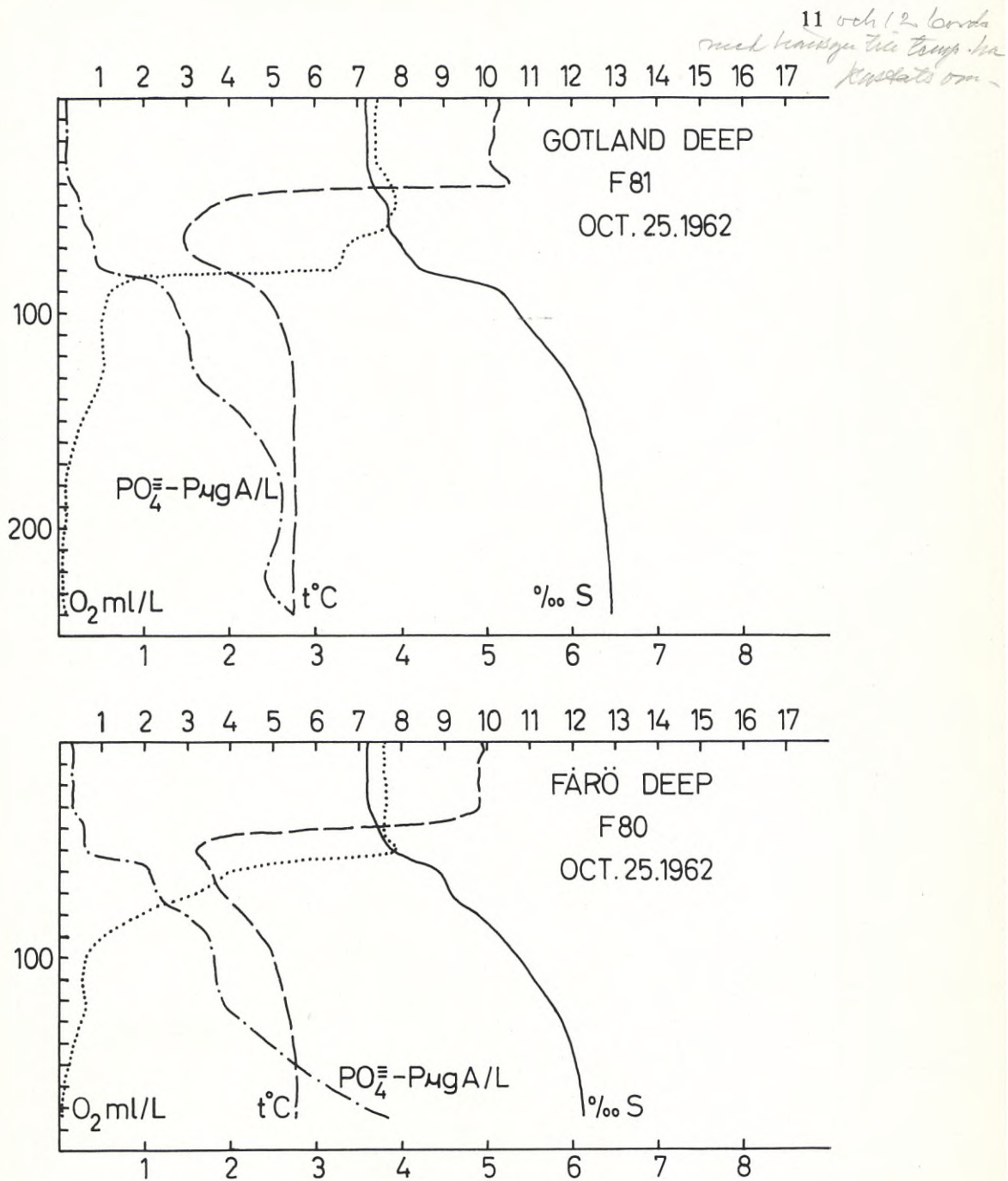
Fig. 5. The hydrographic conditions at the Gotland Deep and the Fårö Deep, October 25, 1962. Swedish data. The under scale $PO_4^{\equiv}-P$, the upper S, t, O_2, CO_2, H_2S.
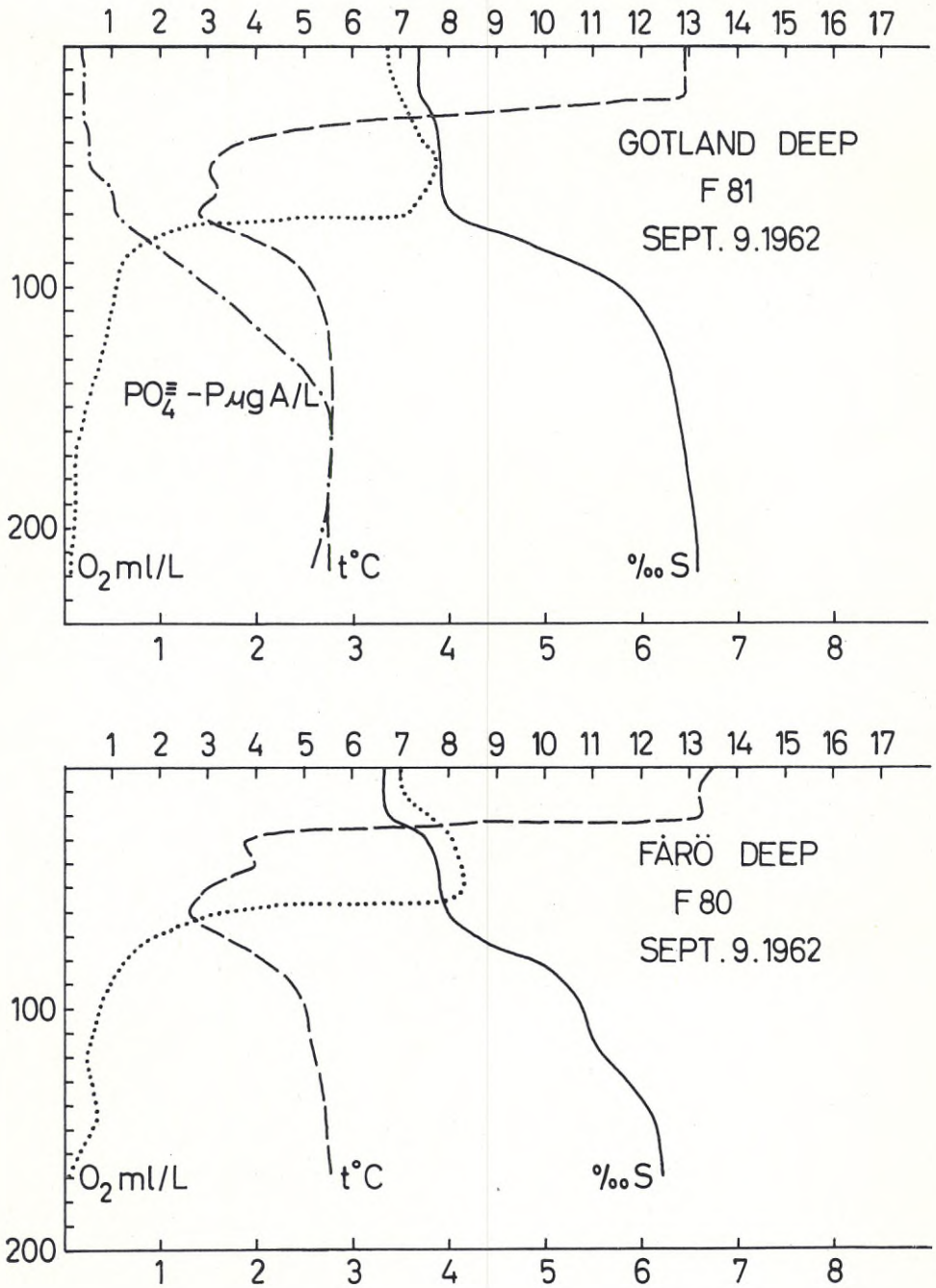
Fig. 6. The hydrographic conditions at the Gotland Deep and the Fårö Deep, September 9, 1962. Swedish data. The under scale $PO_4^{\equiv}-P$, the upper S, t, O_2, CO_2, H_2S.

Even in this case there has been an inflow of new water into the Bornholm basin in January—February. This inflow has been described by the author (Fonselius loc. cit.). The released phosphate from the Bornholm basin seems to have been transported over to the Gdansk basin and mixed through the whole water column. Due to the winter conditions with vertical convection, the mixing occured quickly. Even in this case the "extra" phosphate disappeared in a short time.

IV. The 1963 stagnation in the Gotland Basin

During 1963 there occured a new short stagnation period in the Gotland basin (FONSELIUS 1964). The stagnation was probably caused by an inflow of water from the Bornholm basin. The bottom water in the Bornholm basin was replaced by a relatively strong influx of high saline water from the Kattegat in January 1962 (THOMSEN 1962). The old bottom water was slowly forced out from the Bornholm basin and reached the Gotland basin during the summer. In September the salinity exceeded 13 $^0/_{00}$ in the Gotland basin and reached 12.5 $^0/_{00}$ in the Fårö Deep (fig. 6). From the figure
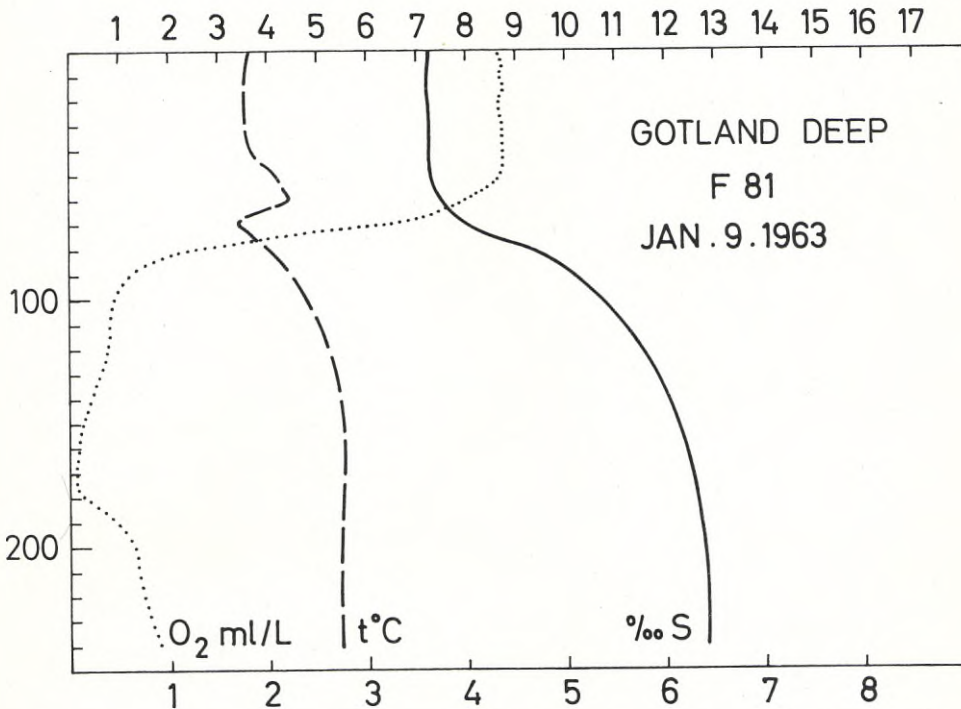

Fig. 7. The hydrographic conditions at the Gotland Deep, January 9, 1963. Swedish data. The under scale $PO_4 \equiv -P$, the upper S, t, O_2, CO_2, H_2S.

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it can be seen that this inflow did not improve the oxygen conditions in the deep water, indicating that the high saline water was almost oxygen-free during the inflow. The conditions in the Gotland basin and the Fårö Deep in October 1962 were shown in fig. 5. The salinity had decreased a little, and the oxygen concentration was still very low. The phosphate increase close to the bottom indicates beginning stagnation. In January 1963 the Gotland Deep was again visited by the "Skagerak" (fig. 7). Surprisingly the oxygen in the deep water had increased to values over 1 ml/l. No changes in temperature and salinity could be detected. Unfortunately, the phosphate could not be measured this time, due to faulty reagents. In February KALEIS and ALEXANDROVSKAYA (1963) reported hydrographic data from the Gotland basin (fig. 8). No high oxygen values were found in the bottom water and the phosphate values had increased (5.6 µgA/l) in comparison to the October values, at the same depth (230 m). KALEIS et al. (loc cit.) reported H_2S in the Gotland basin in May (fig. 9). The phosphate had now increased to around 7 µgA/l at 230 m. In August they reported 16 µgA/l H_2S and 9 µgA/l $PO_4^{\equiv}-P$ at 230 m (fig. 10). Three days later the Gotland Deep was visited by the "Skagerak", and the results confirmed the USSR results (fig. 11). We found, however, that the H_2S layer began at 175 m while KALEIS
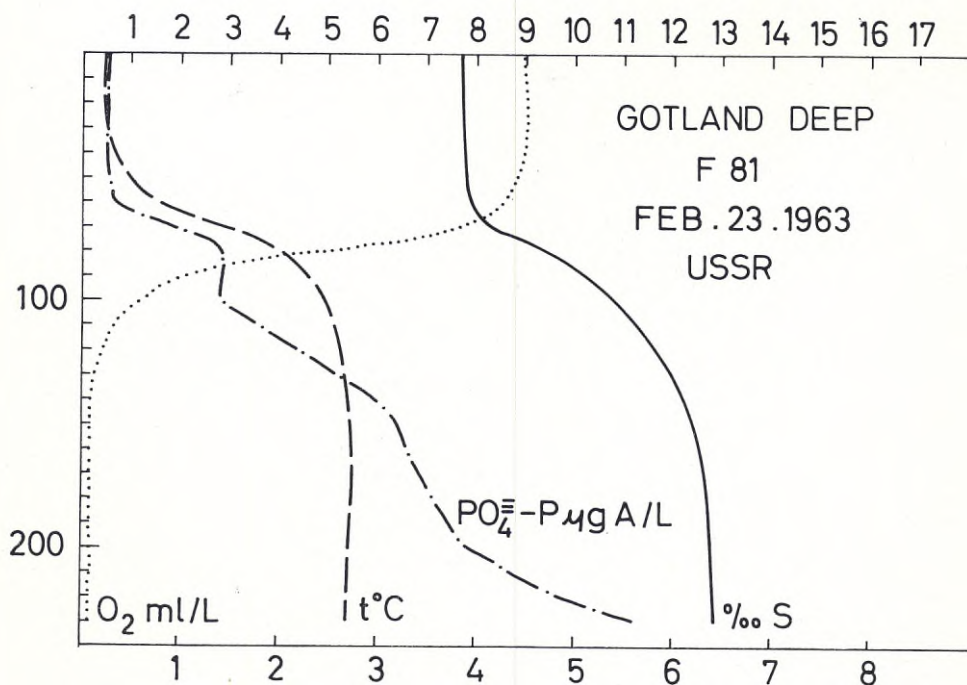

Fig. 8. The hydrographic conditions at the Gotland Deep, February 23, 1963. USSR data. The under scale $PO_4^{\equiv}-P$, the upper S, t, O_2, CO_2, H_2S.
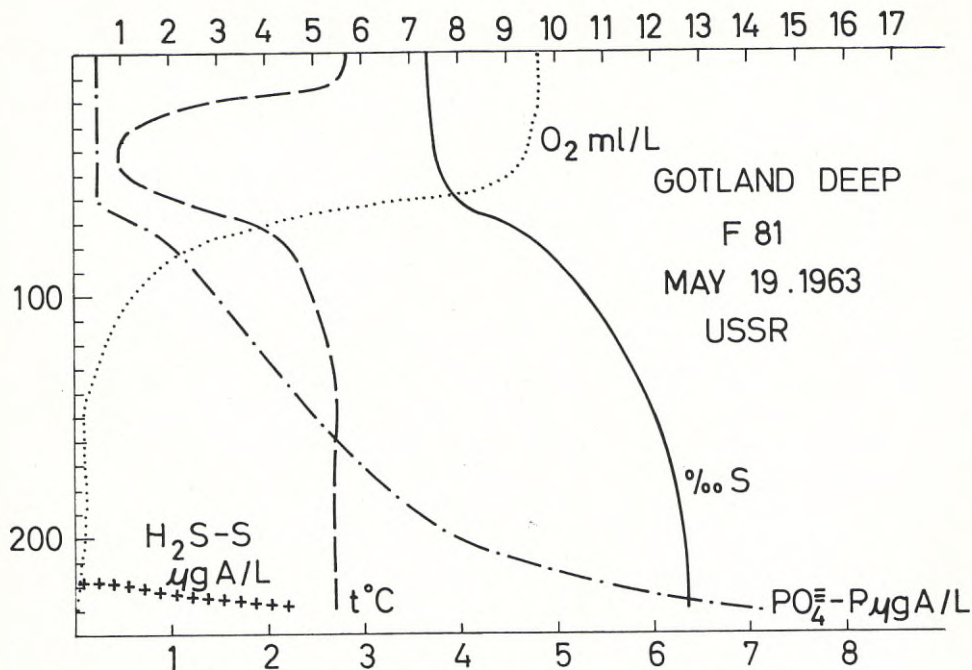
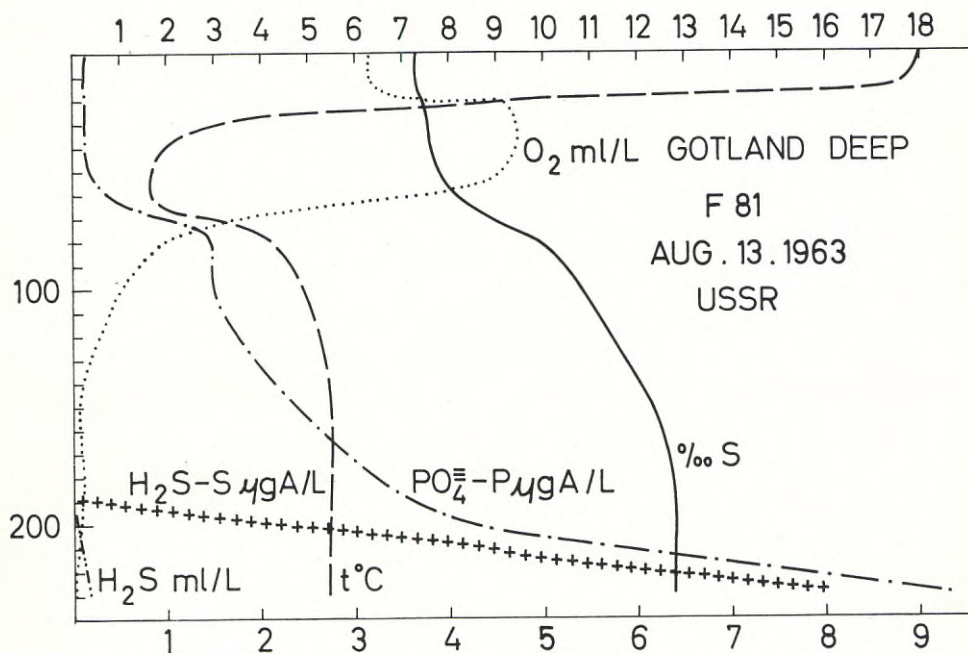Fig. 9. The hydrographic conditions at the Gotland Deep, May 19, 1963. USSR data. The under scale $PO_4\equiv-P$, the upper S, t, O_2, CO_2, H_2S.

Fig. 10. The hydrographic conditions at the Gotland Deep, August 13, 1963. USSR data. The under scale $PO_4\equiv-P$, the upper S, t, O_2, CO_2, H_2S.
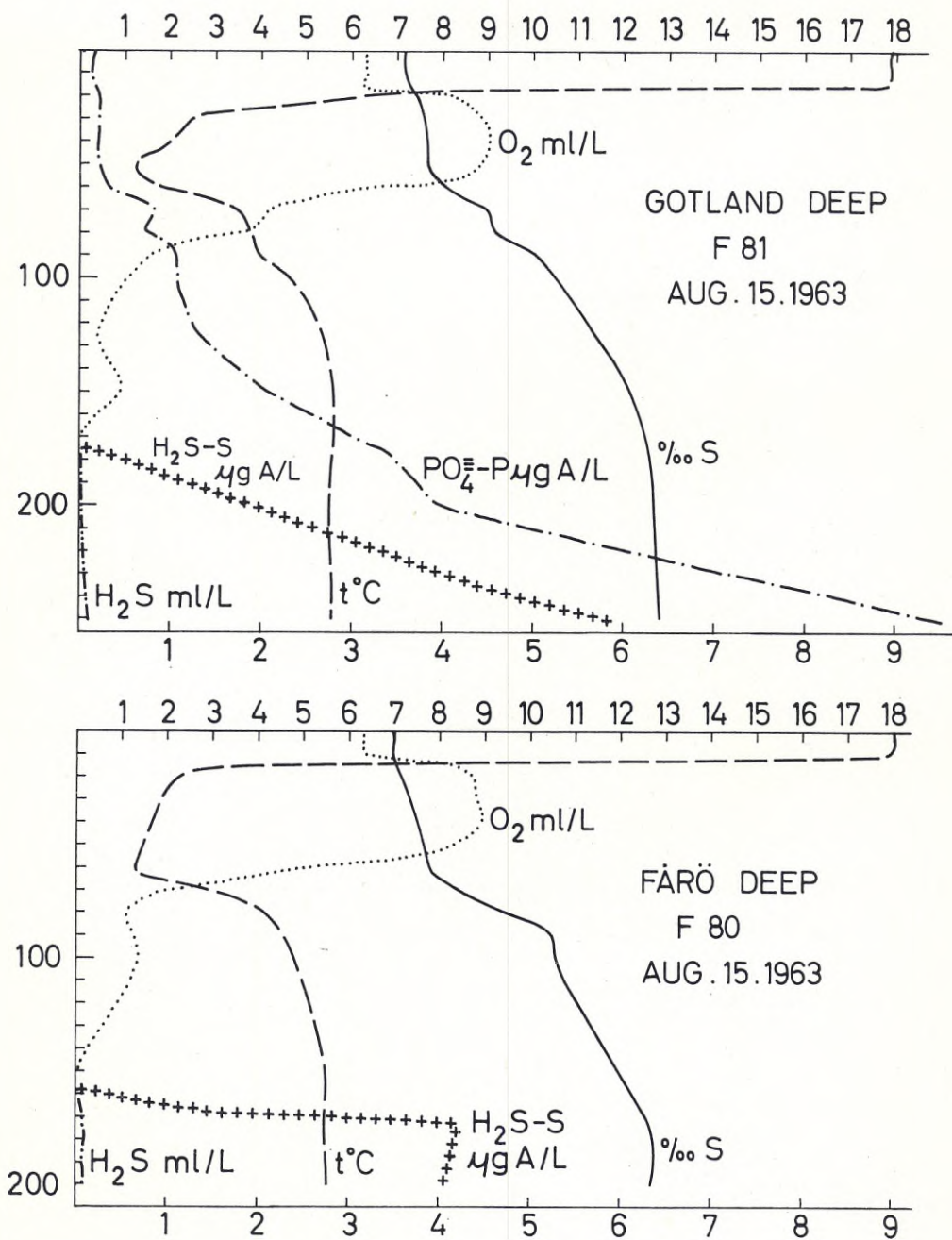
Fig. 11. The hydrographic conditions at the Gotland Deep and the Fårö Deep, August 15, 1963. Swedish data. The under scale $PO_4^{\equiv}-P$, the upper S, t, O_2, CO_2, H_2S.

et al. did not sample that depth. Surprisingly KALEIS et al. report oxygen together with relatively high values for hydrogen sulfide. Evidently there are some analytical differences in the methods. We have never found more than traces of oxygen together with H_2S in the same sample. An inter-calibration of the methods should, if possible, be carried out. The figure shows even the conditions in the Fårö Deep on the same occasion. There is an indication of a small influx of new water. The H_2S values are lower at 200 m than at 175 m. No phosphate was measured here. KALEIS et al. (loc. cit.) again reported values from the Gotland Deep in September (fig. 12). The H_2S had increased to 18 µgA/l, but the phosphate had decreased a little. The H_2S layer began above 150 m. In October the "Skagerak" again visited the Gotland Deep and the Fårö Deep. The results again supported KALEIS data (fig. 13). The hydrogen sulfide had again increased to 18 µgA/l in the Fårö Deep, and the phosphate concentration was 5 µgA/l at 190 m. In Ja-nuary 1964 the "Skagerak" visited the Gotland Deep and the Fårö Deep and found that a new influx now was going on (fig. 14). From the figure it can clearly be seen how the H_2S layer is lifted up by the new water. The phos-phate shows a corresponding decrease at 225 m. Even in the Fårö Deep this decrease of H_2S and phosphate can be seen, but the sampling depths are to few to give any details. During the "Skagerak"s visit in April, oxygen
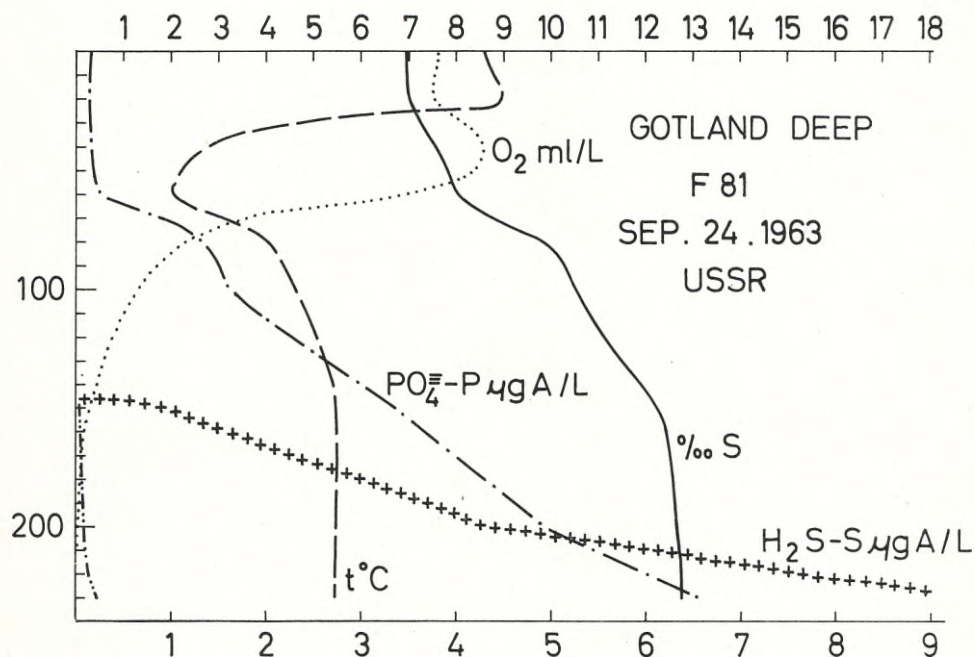

Fig. 12. The hydrographic conditions at the Gotland Deep, September 24, 1963. USSR data. The under scale $PO_4 \equiv -P$, the upper S, t, O_2, CO_2, H_2S.
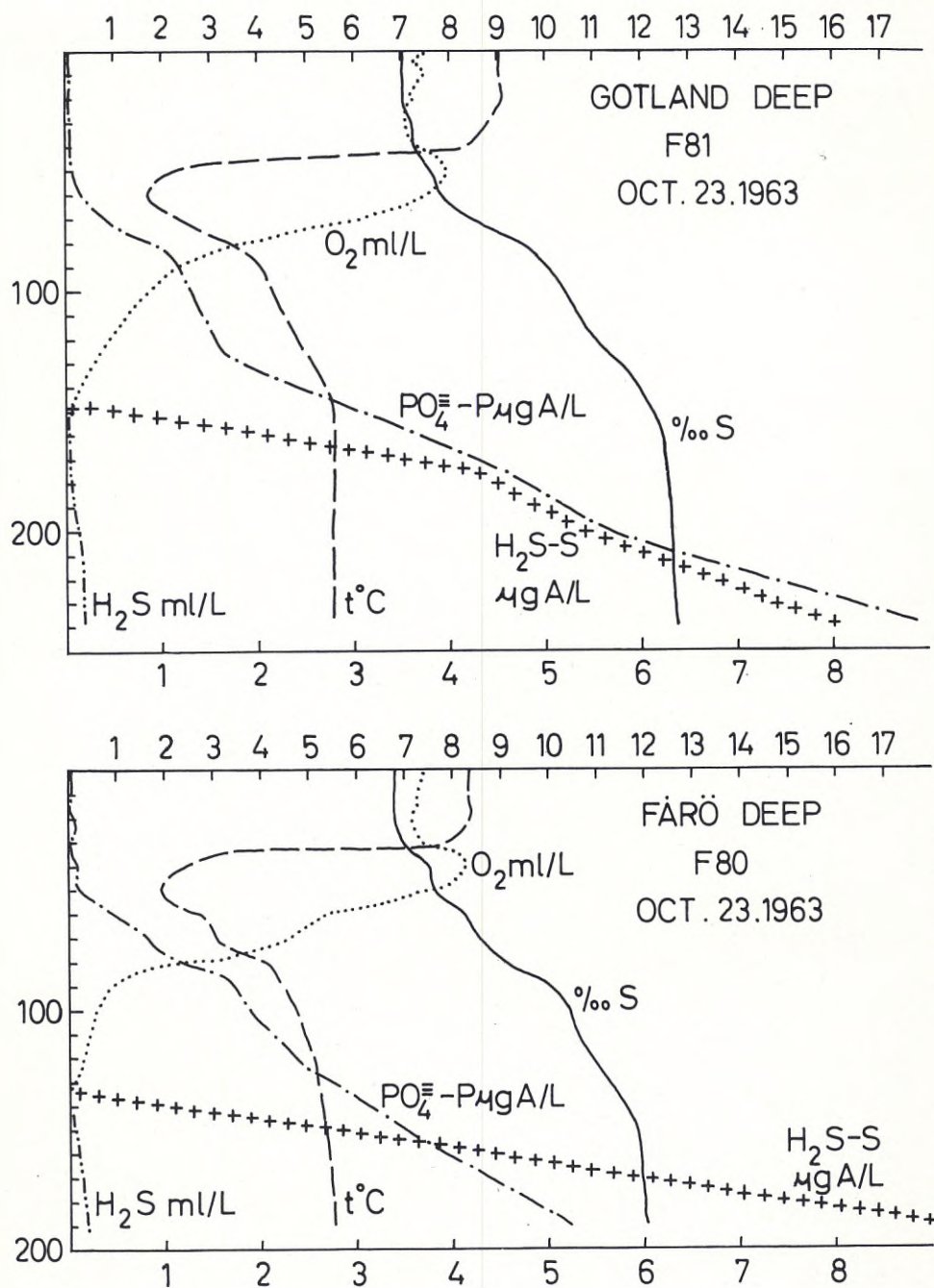
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Fig. 13. The hydrographic conditions at the Gotland Deep and the Fårö Deep, October 23, 1963. Swedish data. The under scale $PO_4^{\equiv}$—P, the upper S, t, O_2, CO_2, H_2S.
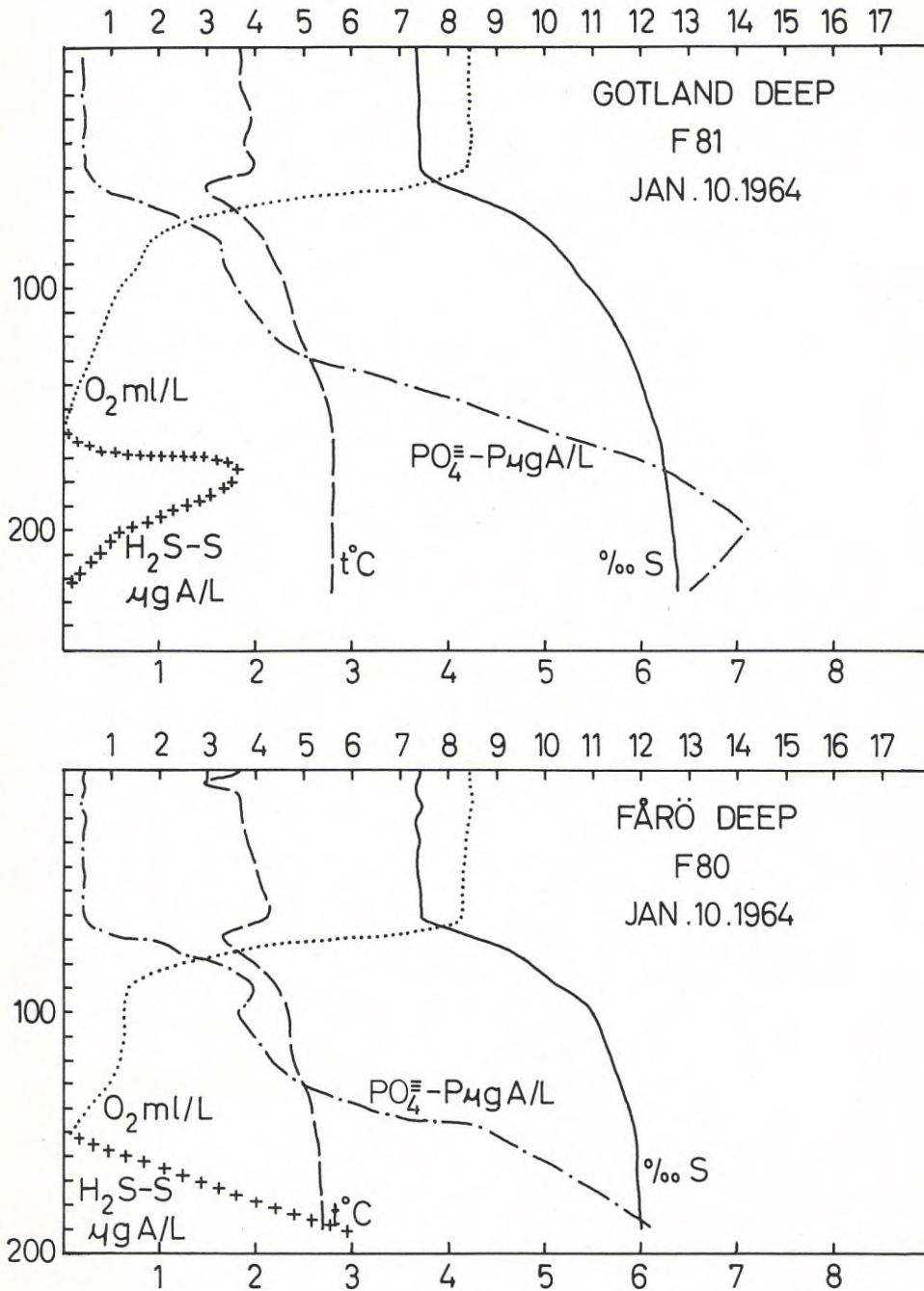
Fig. 14. The hydrographic conditions at the Gotland Deep and the Fårö Deep, January 10, 1964. Swedish data. The under scale $PO_4^{\equiv}$—P, the upper S, t, O_2, CO_2, H_2S.
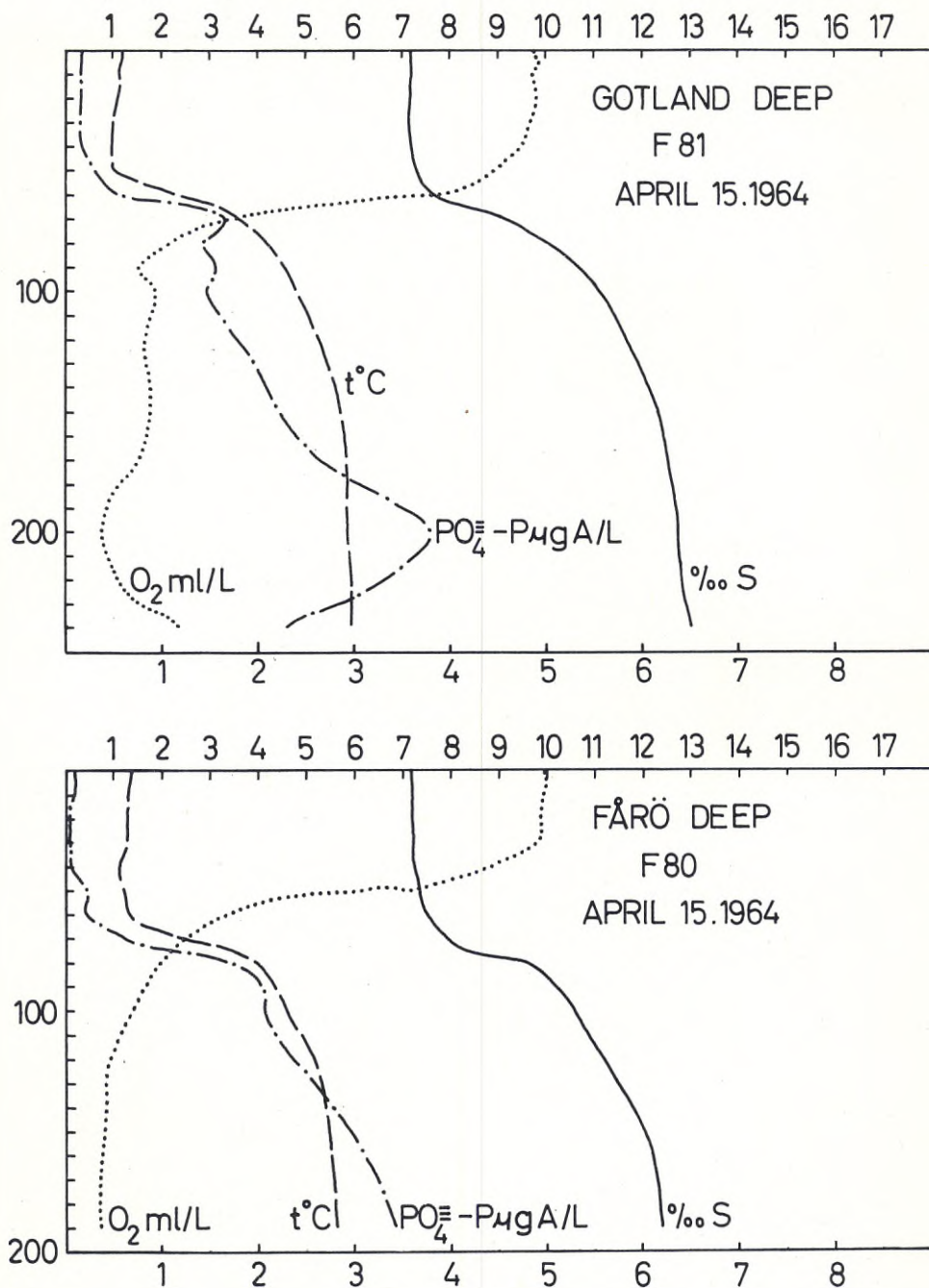
Fig. 15. The hydrographic conditions at the Gotland Deep and the Fårö Deep, April 15, 1964. Swedish data. The under scale $PO_4^{\equiv}$—P, the upper S, t, O_2, CO_2, H_2S.
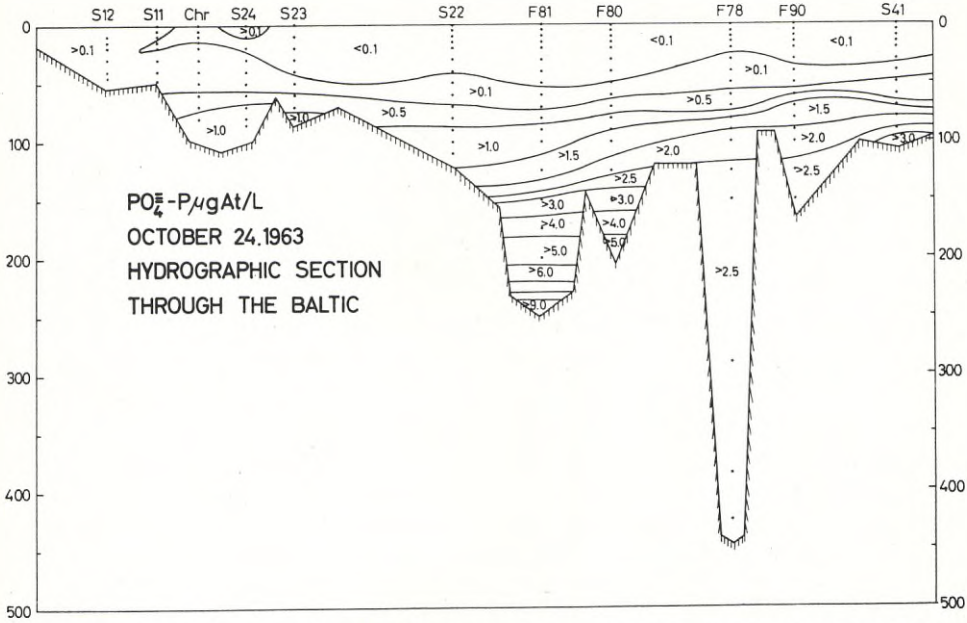
Fig. 16. Longitudinal section through the Baltic proper, showing the phosphate concentration during October 1963. Swedish data.
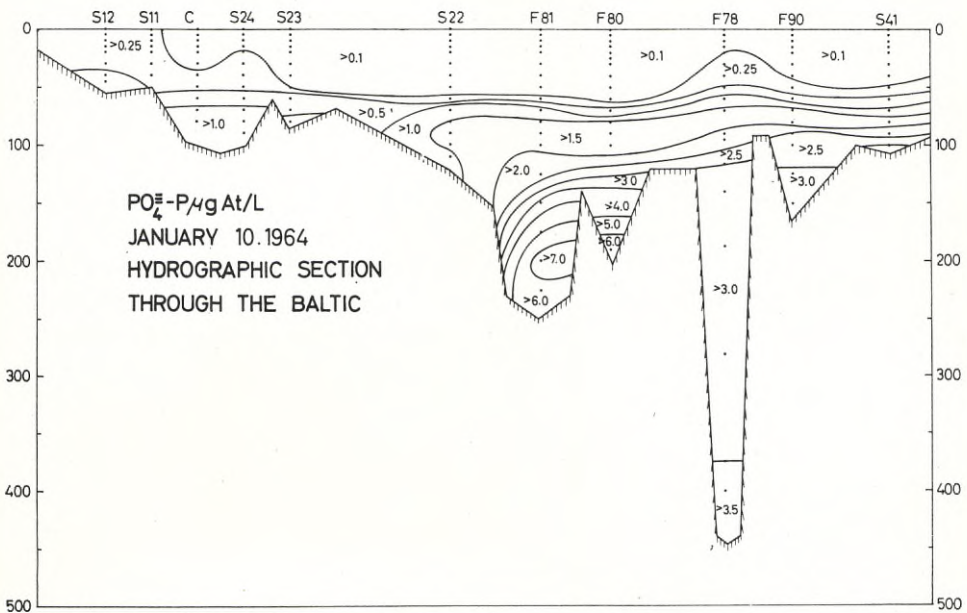

Fig. 17. Longitudinal section through the Baltic proper, showing the phosphate concentration during January 1964. Swedish data.

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was present at all depths in both the deeps (fig. 15). In the Gotland Deep there was an oxygen maximum close to the bottom at 240 m and a corresponding minimum in phosphate. No hydrogen sulfide was found. Now the salinity at 240 m again reached 13 $^0/_{00}$. Fig. 16 shows a longitudinal section through the Baltic proper according to FONSELIUS (1962). The figure gives the phosphate distribution in October 1963 during the stagnation period. The accumulation of phosphate in the Gotland basin and the Fårö Deep can clearly be seen. Fig. 17 shows the phosphate distribution in the same section in January 1964 during the inflow of new water, and fig. 18 shows the conditions in April 1964. The overturn of the stagnant water is indicated in these figures, and they show the development of the inflow. The inflow is a relatively slow process which continues during the whole of 1964. It is surprising to notice that almost no detectable changes in temperature and salinity occur during the inflow. The density of the new water is almost the same as the density of the old stagnant water. Therefore, the above mentioned high oxygen values close to the bottom found by the "Skagerak" in January 1963 evidently have to be regarded as true. It is almost impossible for an experienced oceanographer to get such a big error in the oxygen analysis. There must have occurred a small new inflow of oxygen rich water, which only can be detected by help of the oxygen values.

In December 1965 the "Skagerak" worked a section from Landsort, at the
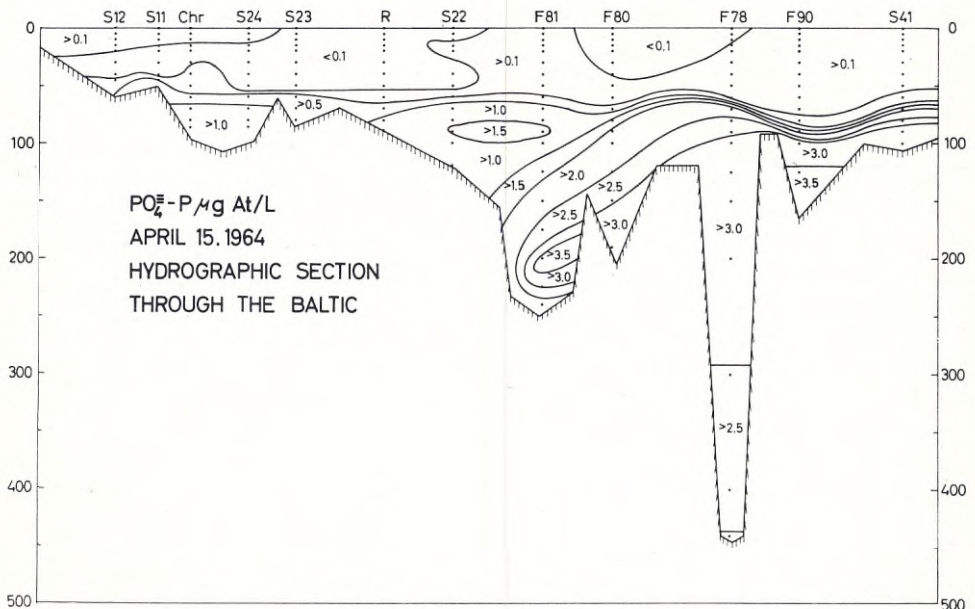

Fig. 18. Longitudinal section through the Baltic proper, showing the phosphate concentration during April 1964. Swedish data.

Swedish coast, to Lovisa, in the Gulf of Finland. Phosphate analyses were carried out over the whole Baltic proper and in the Gulf of Finland. High phosphate values were found in the northern and western parts of the Baltic and especially in the Gulf of Finland in the surface water. At one station in the Gulf of Finland high phosphate values appeared through the whole water column down to the primary halocline. This gives evidence for how the phosphate from the stagnation during the winter 1963—1964, now two years later was mixed up into the surface layers especially in the Gulf of Finland (fig. 19). The figure is a typical example of a river mouth or an estuary, with out flowing brackish water in the surface layer and a compensation current in the deep water. Such a mechanism will always transport dissolved matter from the deep water to the surface water, but the winter convection will increase the effect very much. The change in salinity during the turnover of the water in the stagnant basin is so small that it can not be detected as a change of the surface salinity. Therefore the phosphate is a much better indicator for such processes.

We may now expect a new "fertilization" of the Baltic surface water, and consequently there should occur a new phytoplankton bloom during the spring and a corresponding increase of zooplankton in the late summer. The result of this would be a new good Baltic herring stock during 1966. Unfortunately, the severe winter and the ice conditions in the Baltic has made all hydrographic work impossible for us during this spring.
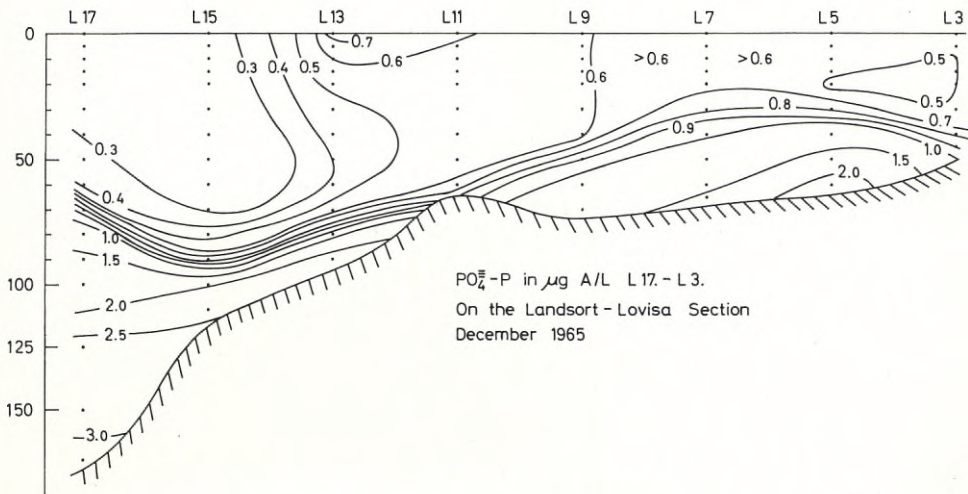

Fig. 19. The phosphate concentration on the section Landsort—Lovisa in the Gulf of Finland, December 1965. Swedish data.

V. The accumulation of phosphate in the deep basins

One may of course ask, from where this accumulated phosphate in the deep basins originates. There are several explanations. The most commonly accepted theory is that the phosphate released from sinking and decaying organic matter produced in the surface regions is accumulated in the water of the stagnant basin. RICHARDS and VACCARO (1956) have investigated the stagnant conditions in the Cariaco trench off the coast of Venezuela. They showed that the relation between the AOU (Apparent Oxygen Utilization) and the accumulated phosphate in the stagnant water was close to the relation in plankton. According to FLEMING (1940) the relation between carbon, nitrogen and phosphorus $(C : N : P)$ expressed in atoms is $106 : 16 : 1$ in plankton. When the plankton dies, it will decay through oxidation. The organic carbon, nitrogen and phosphorus will be oxidized to CO_2, NO_3^- and $PO_4^{\equiv}$ by the dissolved oxygen in the water. According to RICHARDS and VACCARO, the stagnant water of the deep basins should contain these constituents accumulated in the same proportions as in living plankton. Oxygen would have been consumed in accordance to these oxydation processes. The formation of hydrogen sulfide is explained as an oxydation process using the oxygen of the $SO_4^{\equiv}$-ions in the water when all free oxygen of the
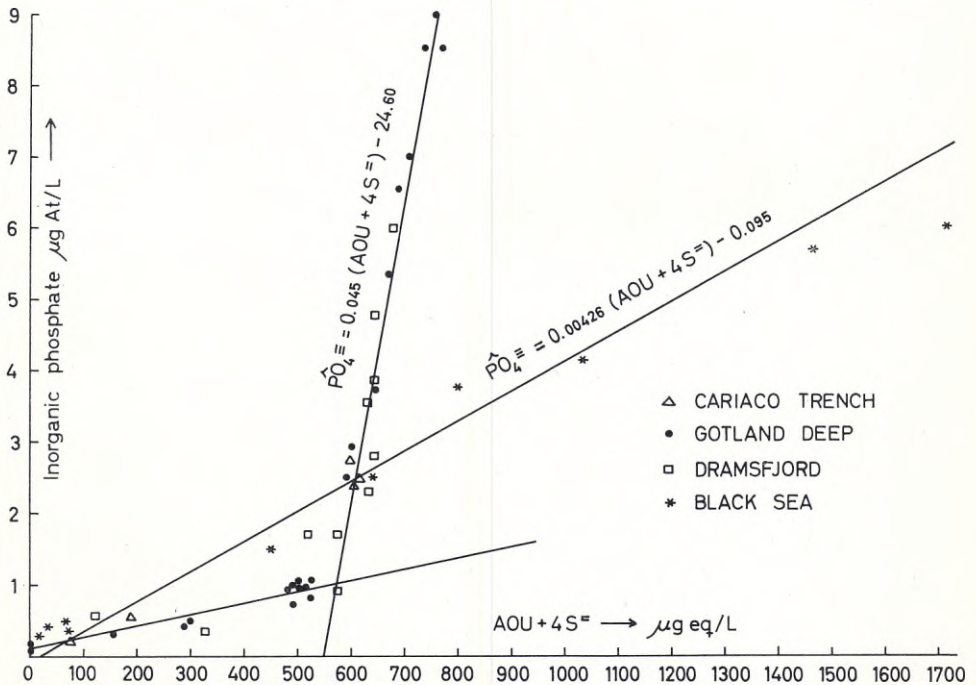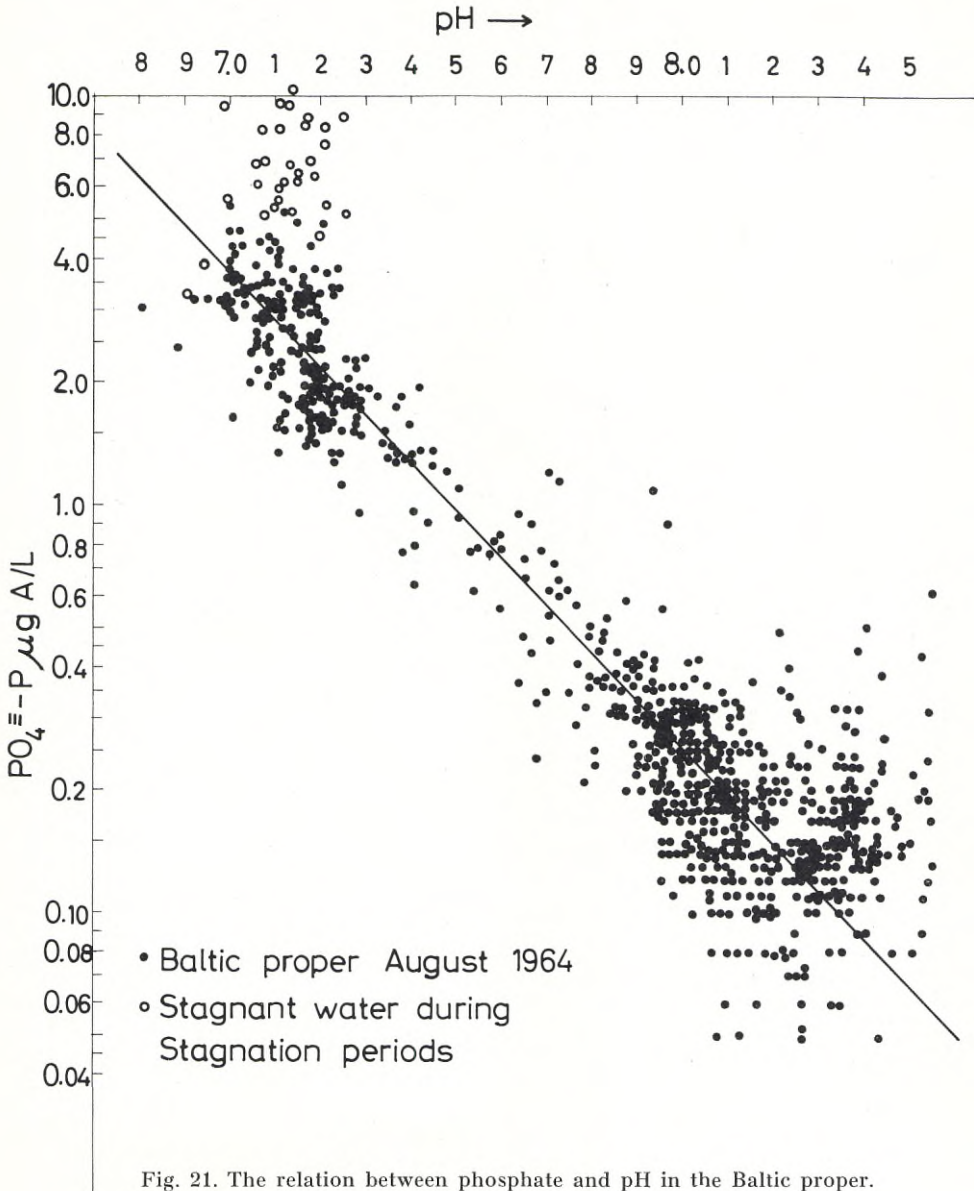

Fig. 20. The relation between phosphate and AOU in different Seas.

Fig. 21. The relation between phosphate and pH in the Baltic proper.

water has been utilized. The sulfate is reduced to sulfide, and every sulfide ion formed is as an oxydant equivalent to four atoms of oxygen. Before the sulfate oxydation begins, the nitrate is, through denitrification, transformed to ammonia and free nitrogen. RICHARDS and VACCARO got for the Cariaco trench the relation 235 : 1 between utilized oxygen and released phosphate, when both constituents were expressed in μgA/l. In plankton the

theoretical relation should be 276 : 1. This relation may change in phosphate-poor water, and in the Baltic surface water, where the phosphate concentration is very low, this relation is close to 550 : 1 (fig. 20). This figure is taken from the author's previous work (1962) and shows the relation in stagnant areas in different seas. When the conditions change to stagnant, the relation $AOU : PO_4^{\equiv}$ in the Baltic changes completely and is now 22 : 1. This ratio shows that there must exist another quite different mechanism for the accumulation of phosphate in the water. If the phosphate had been released directly from the decaying organic matter, it should have required an enormous amount of oxygen, and that has not been accounted for in the figure. It is therefore much more tempting to assume that the phosphate by some means has been dissolved from the bottom sediments.

In fig. 21 the phosphate in μgA/l in the Baltic proper has been plotted against the pH of the water, using semilogarithmic paper with the phosphate on the logarithmic scale. The values are quite scattered, but there is an indication of a straight line for the relation between phosphate and pH. The reason for the scattering is certainly due to bad precision in the pH measurements. The open circles at the top of the figure indicate stagnant water containing H_2S. As can be seen, the pH remains close to 7 when H_2S is present even if the phosphate values still increase. This may be due to protolysis by HS^- ions. Evidently phosphate is released from the bottom all over the Baltic proper if the pH is close to 7. During stagnation it will, of course, be accumulated in the stagnant water, and therefore there should not be any constant relation between the utilized oxygen and the accumulated phosphate. It should not, however, be forgotten, that a part of the phosphate certainly must originate from the decaying organic matter as suggested by RICHARDS and VACCARO (loc. cit.).

The mechanism suggested would explain the abnormally high phosphate values in the Baltic deep water. This water has been shown to be the most important source of phosphate for the Baltic surface water. Without this mechanism a great deal of the organic phosphate would be deposited into the sediments and in that way removed from the phosphorus cycle in the Baltic.

VI. Discussion of the phosphate accumulation

KOCZY (1952) found during the "Albatross" expedition that the water layers close to the bottom (3—50 m from the bottom) in the Pacific had a higher phosphate content than the layers above them. He explained this as a dissolution of phosphate from the sediments. Organic matter contains phosphorus and during the decay of organic matter in the surface layers of the bottom sediments, phosphate will dissolve into the water just above the

bottom. Because this process demands oxygen, a corresponding decrease of the oxygen in the sediment surface or in the water above it should occur. From the "Albatross" values it is not, however, possible to find such a correlation.

The dissolution of apatite seems to be correlated to the pH of the water. Its solubility curve is very similar to the carbonate solubility curve, and it runs almost parallel to it (KRUMBEIN and GARRELS 1952). It has been suggested by OLAUSSON (1966) that the dissolution of phosphate from the bottom sediments increases with decreasing of the pH of the environment. AMES (1959) has investigated in the laboratory the formation of carbonate-apatite through replacement of calcite at low temperatures. He found that the system Na_3PO_4-$CaCO_3$-H_2O was strongly dependent on pH, and the higher pH was, the more phosphate replaced calcite in the chrystal gitter forming carbonate-apatite. A pH higher than 7 seems to be necessary for the reaction. Alkaline phosphate solutions will hence cause a fast replacement of calcite by phosphate. The most important characteristics of the environment during the sedimentation of natural phosphates are: 1) a pH higher than 7, 2) presence of calcareous material and a system which is saturated with calcium with regard to its HCO_3^- content, 3) $PO_4^=$-concentrations over 1 µgA/l. The replacement is hardly influenced by great amounts of alkali, and, according to ARRHENIUS (1963), only the exchange of trace elements in the carbonate-apatites is influenced by Eh (pE). An increase of the grain size will reduce the effectivity of the phosphate metasomatism, while an increase of the temperature will increase the reaction speed. DEGENS (1965) suggests that the reaction may still continue when the chalk stone has been completely phosphatized so that the phosphatized chalk stone gradually changes in the direction of ordinary apatite.

As mentioned, AMES experiments were carried out in the laboratory, and the real limits in nature for these reactions are not exactly known. In ordinary sea water the pH is close to 8, and therefore it is not of great importance if the phosphatizing begins exactly at pH 7. In stagnant basins the conditions may, however, be different, and in these the pH can decrease to values close to 7.

This may lead to the opposite reaction. Phosphate may be dissolved from carbonate apatite or directly from the sedimenting apatite. Three examples from stagnant basins show the influence of pH on the phosphate accumulation. 1) The Cariaco trench off the coast of Venezuela in the Caribbean Sea. According to RICHARDS and VACCARO (1956), the pH of the stagnant water is not below 7.8. The temperature is around 17°C down to the bottom. The relation AOU : $PO_4^=$ is almost normal in regard to the relation for decaying organic matter. This indicates that almost all phosphate in the basin originates from decay of plankton organisms. No phosphate is released from the sediments and probably a slow transport of phosphate down into the

sediment is occurring as suggested by AMES. The process seems, however, to be too slow to be detected as a decrease of phosphate close to the bottom. 2) The Black Sea has a very high H_2S content, and it has been stagnant for a very long time. The pH of the deep water is 7.5 and the temperature $8.8°C$ (Pillsbury results, unpublished). The phosphate concentration is much higher than in the Cariaco trench, but the relation $AOU : PO_4^{\equiv}$ seems to be right with regard to the relation for plankton. There is evidently no release of phosphorus from the sediments and probably a very low precipitation to the sediments. 3) The Gotland basin, which can be compared to many stagnant Norwegian fjords. During the stagnation the H_2S concentration in the Gotland basin was relatively low, but the phosphate concentration was enormously high compared to the AOU. The pH was 7.1—7.2, and the temperature was around $5.5°C$. Obviously there occurs a dissolution of phosphorus from the bottom, or the AOU value has to be increased incredibly much in order to get a proportion between oxygen utilization and phosphorus increase fitting the conditions in living matter. In the Baltic the proportions between the elements seem anyhow to be displaced so that the organisms need only half of the phosphate amount which is normally needed in the oceans. As mentioned earlier, the Baltic is almost on the starving limit regarding phosphate, and the organisms seem to have adopted themselves to this condition, according to REDFIELD, RICHARDS and KETCHUM (1963). The pH is generally close to 7 in the Baltic deep water. This would explain the abnormally high phosphate concentration in the deep water as a constant releasing of phosphate from the bottom sediments.

Summary

Irregular inflows of Kattegat water through the Belts are known to cause stagnation in some of the Baltic deep basins, especially in the Gotland basin. During the stagnation all oxygen in the deep water of the basin may be exhausted. In this case hydrogen sulfide will be formed in the oxygen free water. The phosphate concentration in the deep basin increases enormously during the stagnation. When the stagnation is broken, this accumulated phosphate is released and during the winter it seems to be brought up into the surface water through vertical mixing. The increase of nutrient salts in the surface water seems to cause an unusually rich phytoplankton bloom in the spring, which will be followed by a corresponding increase of the zoo-plankton in late summer. This would then be mirrored in a high quality of the Baltic herring stock. The high phosphate values of the surface water will go back to normal values in a few months.

A short stagnation period during 1963 can be studied in detail. That year the Gotland basin was visited regularly by research ships from USSR and Sweden, in some cases only few days apart. The fast development of the stagnation and the turnover of the water could therefore be followed closely. The results of the observations from the two countries support and complete each other very nicely. The released phosphate from the Gotland basin seems to have reached the surface water in December 1965, especially through vertical mixing in the Gulf of Finland. A new plankton bloom and a corresponding good Baltic herring stock may be expected in 1966.

The accumulated phosphate in the deep basins originates only partly from decaying organic matter in the surface layers above the stagnant water. The main part of the phosphate seems to come from the bottom sediments in the basin. The bottom water of the Baltic has a very low pH, and this seems to favor a releasing of phosphate from the sediments. Some stagnant basins in other parts of the world do not show such a high phosphate accumulation, and consequently they show higher pH values in their deep water.

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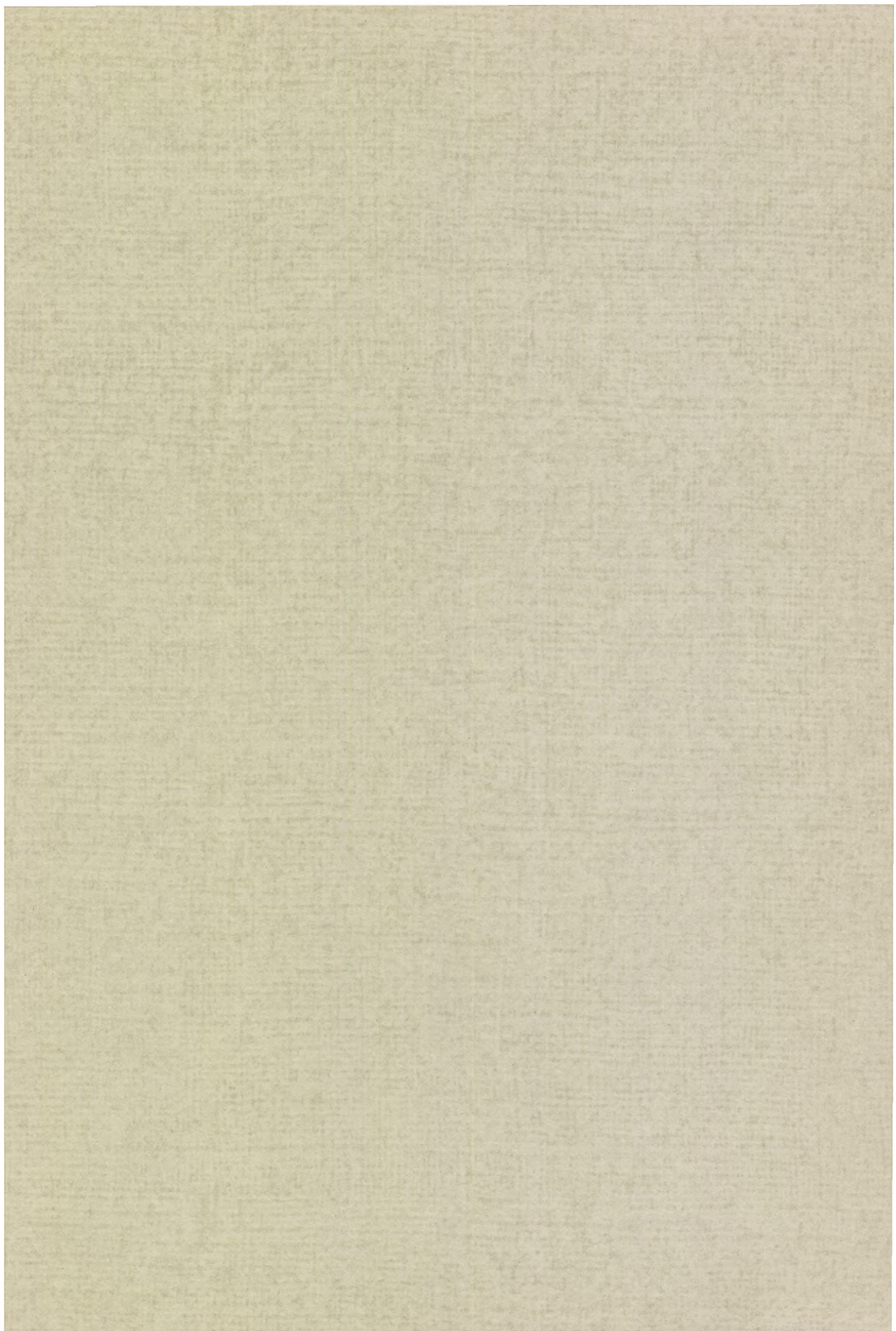
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