Water renewal in a semi-stagnant sea studied by means of chemical parameters

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ABSTRACT

A general description of the properties of stagnant and semi-stagnant seas is given. The Baltic Sea is used as an example of a semi-stagnant environment and the water inflows into the Baltic Sea are described. The main water masses in different water layers and seasonal changes are shown. Examples of variations in the density/oxygen (or hydrogen sulphide) relationship in the Gotland Deep are given. The chemical changes taking place in the water during stagnation periods are described and discussed and the effects of inflows of oxygen containing water on the hydrogen sulphide containing deep basins are shown. The relationship between phosphate and inorganic nitrogen compounds is illustrated for different parts of the Baltic Sea. Finally, the frequency of stagnation periods during the years 1965–1985 in the Gotland Deep is described.

INTRODUCTION

Stagnant or semi-stagnant seas are generally partly landlocked with a restricted connection to the open sea. They have narrow and shallow entrances with a sill. The water balance is positive with an excess of fresh water. Therefore they have an outgoing current in the surface through the entrance. Examples of such basins are many Norwegian and Canadian fjords, the Black Sea and the Baltic Sea (Fonselius 1969b, Grasshoff 1975). If the entrance is very shallow and narrow in comparison to the volume of the landlocked area, the basin becomes permanently stagnant. Examples of such areas are the Black Sea and certain fjords. Examples of semi-stagnant areas are the Baltic Sea and the Idefjord at the Swedish west coast (Fig. 1).

In this paper the author describes the renewal processes and chemical properties of the Baltic Sea which may be considered a prototype of semi-stagnant seas.

PHYSICAL MECHANISM FOR STAGNATION

The physical reasons for stagnant conditions are that water with high density (usually high salinity) fills the basin. On top of this heavy water low density surface water flows out from the basin through the entrance over the sill. This water consists of fresh water mixed with salt water from below. A permanent halocline is formed between these two layers. A compensation current flows along the bottom over the sill below the outgoing current. This current keeps the density of the stagnant water mass at a permanent level. The Black Sea is an excellent example of such a basin (Grasshoff 1975). In semi-stagnant basins the volume of the basin is too small in comparison to the entrance area to maintain a constant density in the stagnant water. The stagnation is caused by occasional inflows of water with high density. The reason for this may be e.g. that long lasting storms force
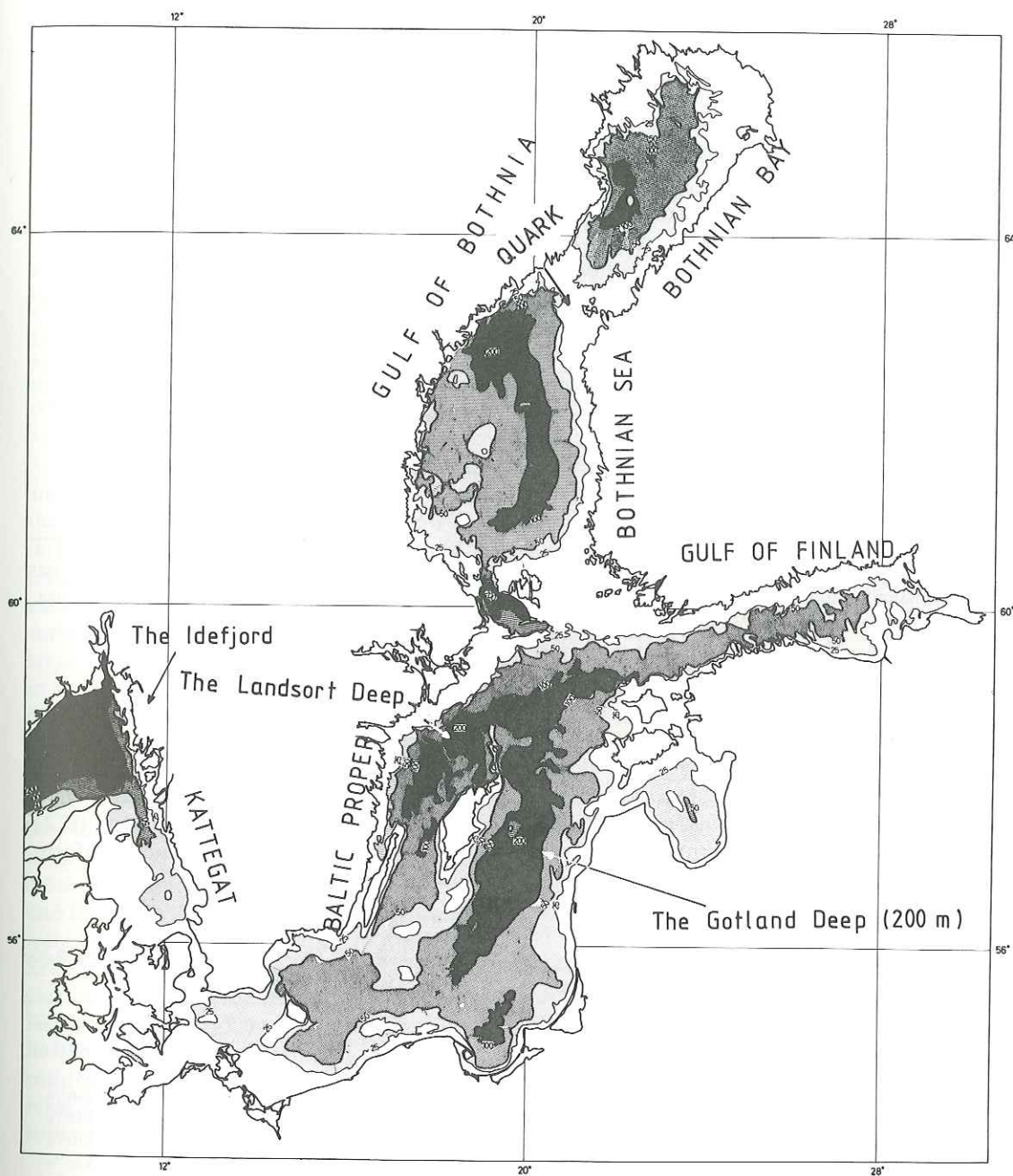
Fig. 1.   Map of the Baltic Sea with the names of the different subareas. The sites of the Gotland Deep in the central Baltic Proper and the Idefjord at the Swedish west coast are marked on the map.

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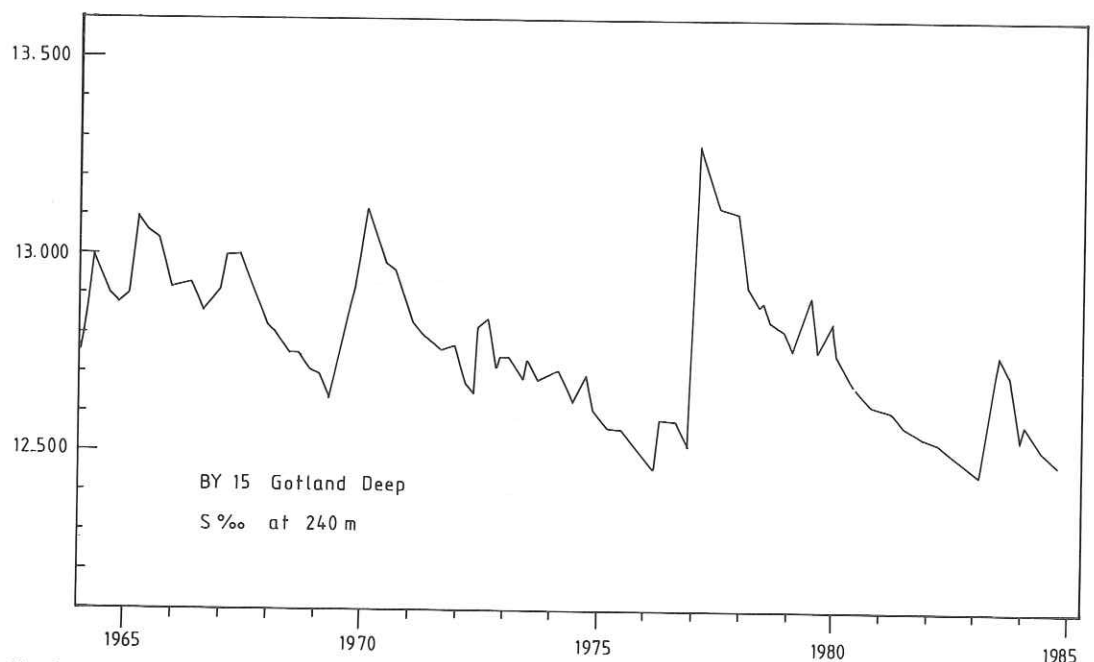t water. The
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Fig. 2. Salinity variations in the Gotland Deep at 240 m caused by inflows of water from the Kattegat 1964–1984.

high salinity water over the sill into the basin. It then flows along the bottom of the basin filling up cavities and sub-basins. New smaller inflows with lower density will flow over this heavy bottom water. The salinity of the stagnant water will slowly decrease due to turbulence and diffusion. Finally the density gets so low, that a new inflow can replace the stagnant water forcing it out from the sub-basin. Often the density difference between the old and the new water is so small that it is almost impossible to see it from single salinity and temperature measurements, but the large inflows are easily recognised by the sudden increase in the salinity. Figure 2 shows such inflows in the Baltic Sea in the period 1964–1984. It can clearly be seen how the salinity suddenly increases and how it then slowly decreases until a new inflow occurs.

WATER BALANCE

The water balance of the Baltic Sea has been calculated by several authors, for example, Brogmus (1952), Fedosov and Zaitsev (1959), Fonselius (1969b), Mikulski and Majewski (1970), Sjöberg et al. (1972). Table 1 gives general hydrographic information on the Baltic Sea.

TABLE 1

Geographical and hydrographical features of the Baltic Sea according to Fonselius (1969b).

Surface area	$366{,}000 \text{ km}^2$
Volume	$21{,}900 \text{ km}^3$
Mean depth	60 m
River discharge	$471 \text{ km}^3/\text{a}$
Precipitation	$183 \text{ km}^3/\text{a}$
Evaporation	$183 \text{ km}^3/\text{a}$
Outflow of water to Kattegat	$942 \text{ km}^3/\text{a}$
Inflow of water from Kattegat	$471 \text{ km}^3/\text{a}$
Mean salinity of the surface water	7.0
Mean salinity of the deep water	11.0
Mean salinity of the outflowing water	8.7
Mean salinity of the inflowing water	17.4

Box model of the Baltic.

$V_0 = 471$ km^3 $V_1 = 183$ km^3 $V_1 = 942$ km^3

$V_4 = 183$ km^3

$d = 8,7$ ‰

$a = 7$ ‰

$y = 765$ km^3

$x = 1236$ km^3

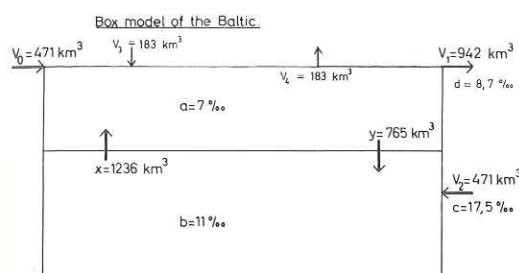$V_2 = 471$ km^3

$c = 17,5$ ‰

$b = 11$ ‰

Fig. 3. Box model of the Baltic Sea showing the water balance. V_0 = River discharge, V_1 = Outflowing water, V_2 = Inflowing water, V_3 = Precipitation, V_4 = Evaporation, a = Salinity in the surface water box, b = Salinity in the deep water box, c = Salinity of the inflowing water, d = Salinity of the outflowing water. (From Fonselius 1969b).

Precipitation and evaporation are equal and can be disregarded. The Baltic Sea has then a positive water balance, with an annual excess of fresh water supply, which creates a surface layer with low salinity. The excess flows out from the Baltic Sea as a surface current together with an equally large amount of Kattegat water which flows in along the bottom of the Belts. A "box model" of the Baltic Sea is shown in Figure 3. From the salinities given in Table 1, it is seen that one third of the outflowing water returns to the Baltic Sea and is mixed with the inflowing Kattegat water. Since the deep water of the Kattegat has a salinity close to 34 salinity units, it is clear that only one third of the inflowing water is Kattegat water. If we divide the volume of the Baltic Sea, 21,900 km^3 by the annual net outflow, ($\frac{2}{3}$) · 944, we find the residence time of the Baltic Sea water to be 35 years. Evaporation has here been disregarded, because residence times are generally used for material balances and evaporation does not remove anything but water from the system.

WATER MASSES AND THEIR SEASONAL VARIATIONS

In the Baltic Proper we can distinguish four different water masses. The two main

water masses are the surface water and the deep water. Both of them contain temporary water masses, in the surface water the warm summer surface layer, and in the deep water the stagnant bottom water (see Fig. 4). A primary halocline separates the two main water masses. The surface water has a very low salinity, around 6–8 salinity units and the deep water has a higher salinity, around 8–13 units. The temperature of the surface water is very low during the winter, close to 0°C. The temperature of the deep water is around 3–5°C and is hardly influenced by seasonal variations. During the spring a thermocline begins to build up in the surface water separating a warm surface layer from the cold winter surface water. This thermocline disappears during the winter and a total vertical convection occurs

Sea Surface

Winter				Summer				0 m
S	7.2 – 7.7 ‰			S	6.4 – 7.2	NO$_2$	<0.02 – 0.23	
t	0.1 – 5.5 °C			t	5.5 – 18	tot.P	0.25 – 0.63	
pH	8.03 – 8.30 units			pH	8.1 – 8.5	tot.N	15 – 19	
A	1.36 – 1.63 meqv/l			A	1.34 – 1.54	NH$_4$	0 – 2.7	
PO$_4$	0.36 – 0.92 µmol/l			PO$_4$	0.02 – 0.35	SiO$_2$	4.3 – 13	
NO$_3$	0.9 – 4.6 – " –			NO$_3$	<0.1 – 1.0	O$_2$	80 – 120	
NO$_2$	0.11 – 0.31 – " –							0 – 30 m
tot.P	0.54 – 1.23 – " –							
tot.N	17 – 21 – " –							
NH$_4$	0 – 0.8 – " –							
SiO$_2$	11 – 24 – " –							
O$_2$	96 – 100 %							

The thermocline is generally accompanied by a weak secondary halocline.

Primary halocline — 50 – 60 m

S	8 – 11	‰	
t	3 – 5	°C	
pH	7.9 – 7.2		
A	1.6 – 1.7		
PO$_4$	1.0 – 3.4	µmol/l	
NO$_3$	4.4 – 8	"	
NO$_2$	0.02 – 0.14	"	
tot.P	1.0 – 3.9	"	
tot.N	18 – 22	"	
NH$_4$	0.05 – 0.27	"	
SiO$_2$	26 – 70	"	
O$_2$	76 – <3	%	
H$_2$S	0	µmol/l	

Secondary halocline — 150 – 400 m

S	11 – 12.5 ‰		tot.P	4.0 – 7.3	µmol/l	
t	4.8 – 5.6 °C		tot.N	16 – 34	"	
pH	7.27 – 7.30 units		NH$_4$	2 – 12	"	
A	1.7 – 2.0 meqv/l		SiO	80 – >150	"	
PO$_4$	4.0 – 5.9 µmol/l		O$_2$	0 – 3	%	
NO$_3$	0 "		H$_2$S	0 – 54	µmol/l	
NO$_2$	0 "					

440 m

Sea bottom ///////////////////

Fig. 4. Diagram of the vertical stratification of chemical variables in the Landsort Deep showing winter and summer conditions.

down to the primary halocline. The temperature of the warm summer water may reach 18–19°C. When an inflow of unusually high saline water occurs through the Danish Sounds, this water which has a high density will fill up the deep basins of the Baltic Proper, forming a stagnant bottom water, separated from the deep water by a secondary halocline. This water has of course a slightly higher salinity and also the temperature may vary a little from the temperatures of the deep water (Fonselius 1969b).

Chemically the four water masses show very different properties for some parameters. In the surface water the nutrients almost disappear during the summer after the spring plankton bloom. The oxygen values show around 100% saturation both during summer and winter. In the deep water high nutrient concentrations are found due to decomposition of sinking dead plankton. The oxygen concentration decreases to low values due to utilization by decomposition of dead matter, and in the stagnant water the oxygen disappears completely and hydrogen sulphide is formed. The phosphate, ammonia and silicate concentrations increase, but nitrate and nitrite disappear completely. Figure 4 shows the chemical properties of the different water masses in the Baltic Proper. The variables shown in the figure are from the Landsort Deep, the deepest spot in the Baltic Sea.

CHEMICAL CHANGES IN THE STAGNANT ENVIRONMENTS

The best way to study the stagnation is to follow changes in the chemical parameters. Dead organic matter formed during the plankton production sinks downwards and is broken down into simpler compounds through bacterial oxidation. The end products are simple inorganic compounds: carbon dioxide, water and nutrient salts. These reactions have been described e.g. by Richards (1965). Because nutrient salts in the surface water are taken up by plankton, the downward transport of particulate matter strips the surface water of the nutrients, which instead are accumulated in the deep water. The surface water becomes oligotrophic.

The most important nutrient salts are phosphate, nitrate, nitrite, ammonia and for the diatoms silicate. Normally nutrients are brought back to the surface in upwelling areas. In stagnant basins the nutrients are accumulated in the bottom water and remain there. In semi-stagnant basins, the nutrients are released, when the stagnant water is forced out of the deep basin. The oxidation of organic matter requires oxygen and in that way the dissolved oxygen of the water is used up, causing oxygen deficiency in the stagnant water. If the stagnation continues for so long time that almost all oxygen disappears, nitrate reducing bacteria begin to oxidize organic matter by using the oxygen from nitrogen ions, reducing them to free nitrogen gas as shown by Richards (1965). Thus nitrate disappears from the water. This can very often be seen in the Baltic Sea (Fig. 5). We find low concentrations in the surface water, especially during summer, when plankton has utilized almost all nitrate. Below the halocline we can see the accumulation of nitrate and also how the nitrate values decrease, when the oxygen begins to disappear.

When hydrogen sulphide is present in the water, all nitrate has disappeared. The hydrogen sulphide is formed through another bacterial process. Sulphate reducing bacteria reduce the sulphate ions to hydrogen sulphide, using the oxygen of the sulphate ions for oxidation of the organic matter. Hydrogen sulphide is a poisonous gas and it kills the benthic fauna, transferring the area into a dead oceanic desert where no fish can live. Figure 5 shows the disappearance of the oxygen, the formation of hydrogen sulphide close to the bottom,

BY 15 A Gotland Deep 26.5 1972
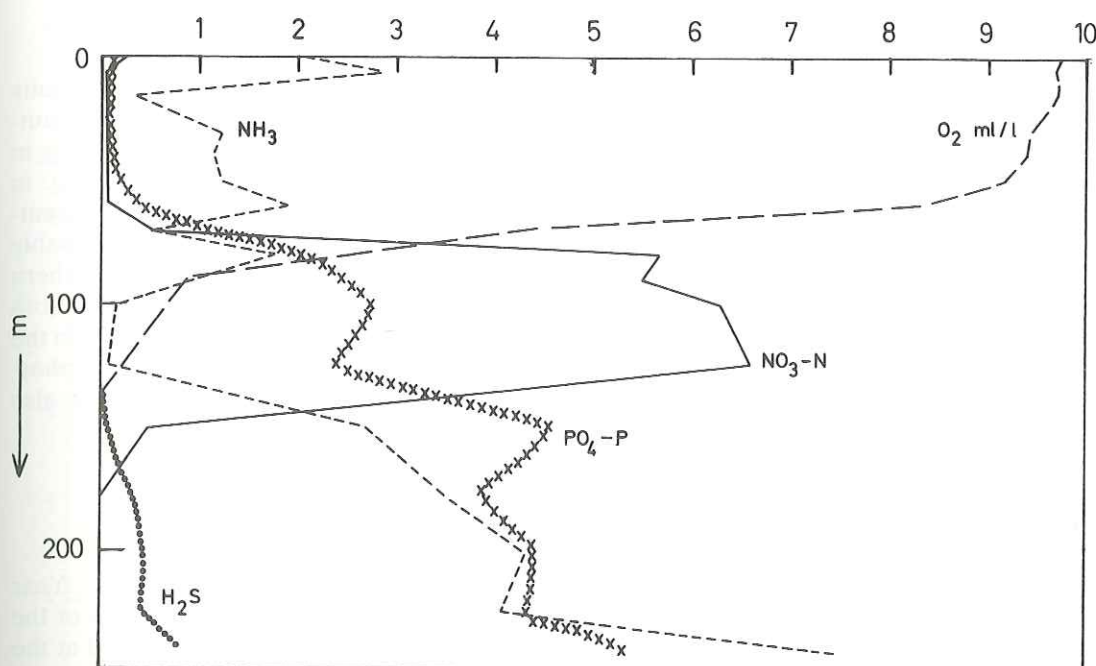Inorganic N, PO_4-P µg-at/l, O_2 and H_2S ml/l

Fig. 5. Vertical distribution of different chemical variables in the Gotland Deep durnig stagnant conditions (From Fonselius 1976).

the reduction of the nitrate and accumulation of phosphate. We can also see the accumulation of ammonia in the hydrogen sulphide containing water. During the decay of organic matter the organically bound nitrogen in proteins is released as ammonia. In oxygen containing water the ammonia is oxidized to nitrate. When no oxygen is present in the water, the ammonia will accumulate in the hydrogen sulphide containing water.

Phosphate is also accumulated in the stagnant basins. It is interesting to note that the phosphate concentration increases enormously, when hydrogen sulphide begins to form. The reason for this is that in normal oxygen containing water, phosphate is coprecipitated with ferric hydroxide, which is practically insoluble in the water

and flocculates. Phosphate is in that manner brought down into the sediment surface layer. When the environment becomes reducing through hydrogen sulphide formation, the ferric hydroxide is dissolved. Ferrous ions are formed which react with sulphide ions forming ferrous sulphide. The phosphate goes into solution and therefore the phosphate concentration suddenly increases in the water. The bacterial chemo-oxidation is a much slower process than the oxidation using free dissolved oxygen in the water and therefore the sediments in stagnant basins are rich in organic material (Fonselius 1969b; Deuser 1975).

When the stagnant water is replaced by new water, the nutrients and the hydrogen sulphide are brought out from the deep basin with the old water and are mixed with
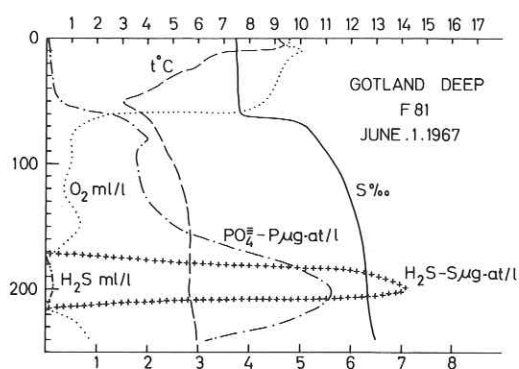
Fig. 6. Vertical distribution of hydrographical factors during an inflow of oxygen containing water along the bottom in the Gotland Deep in June 1967. The upper scale shows salinity, temperature, oxygen and hydrogen sulphide. Hydrogen sulphide is expressed both in ml/l and μgat/l. The lower scale shows phosphate (From Fonselius 1969b).

the water above the basin and around it (Fig. 6). The hydrogen sulphide reacts with the oxygen of this water and reduces its oxygen content. The ammonia is oxidized into nitrate. The nutrients may ultimately during the winter convection reach the surface wat-

er enriching it with nutrients, or we may say fertilizing it (Fig. 7).

NUTRIENT RELATIONSHIPS

It is a well known fact that normally phosphate is the production limiting nutrient in fresh water and nitrate is limiting in the open ocean. In brackish water, e.g. in the Baltic Sea, we find that nitrate is limiting in the southern parts and most probably in the entire Baltic Proper. In the southern Gulf of Bothnia, the Bothnian Sea, both nutrients seem to be equally limiting. In the northern part of the Bothnian Bay, phosphate is clearly limiting (Fig. 8. See also Fonselius 1981).

VARIATIONS IN STAGNATION

During the International Baltic Year 1969–1970 a research ship from one of the participating countries was anchored at the station BY 15 (The Gotland Deep) for one
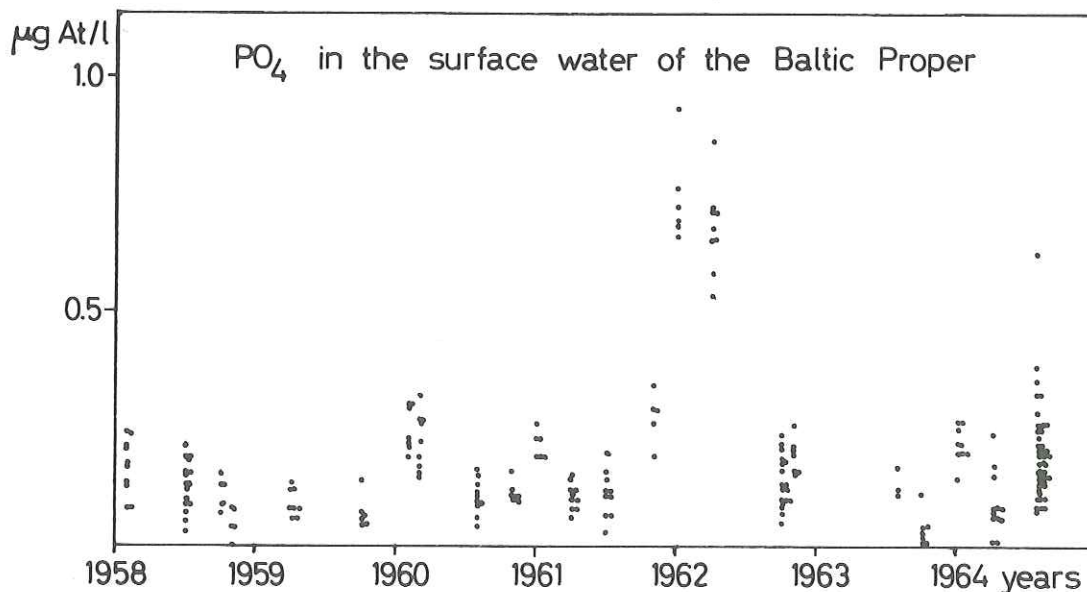

Fig. 7. The phosphate concentration in the surface water of the Baltic Proper from 1958–1964. A large inflow has in the winter of 1961/62 mixed phosphate up to the surface layer (From Fonselius 1967).

Relation Σ inorg N: PO₄-P in the Baltic proper and the Gulf of Bothnia.
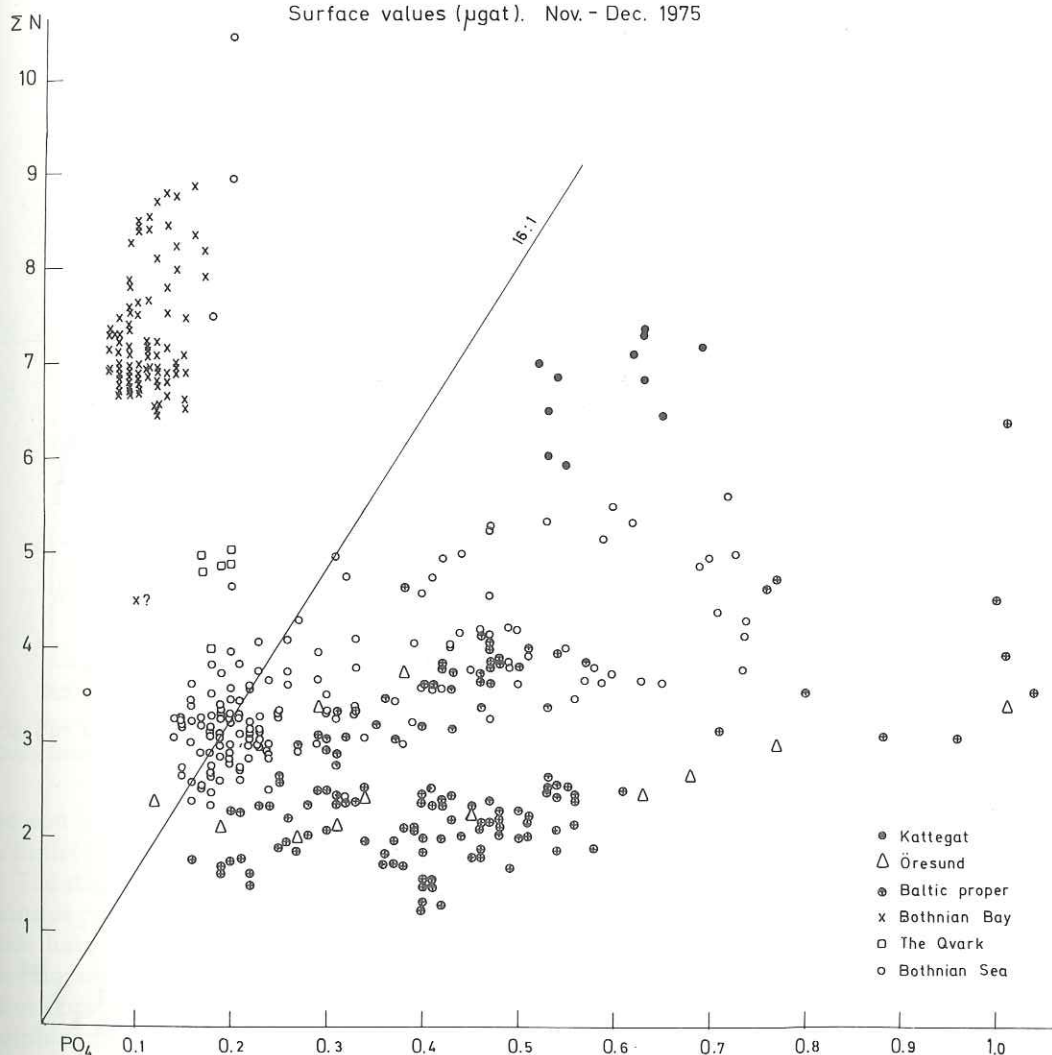Surface values (μgat). Nov. – Dec. 1975

Fig. 8. Relation between total inorganic N ($NO_2^- + NO_3^- + NH_4^+$) and phosphate in the Baltic Sea. The straight line shows the theoretical relation between N and P (by atoms) in plankton organisms (From Fonselius 1978).

week almost every month, measuring salinity, temperature, dissolved oxygen, hydrogen sulphide and phosphate every third hour. Figure 9 shows results from these measurements in the form of density/oxygen or hydrogen sulphide diagrams. Only four occasions are shown in the figure. In the third diagram (Penck) it can be seen how oxygen rich water is replacing the old hydrogen sulphide containing water. The deepest parts have received new water, containing up to 2 ml/l oxygen. Above this water we find hydrogen sulphide water and also water with oxygen in thin layers. On top of these layers we again find water with high oxygen content. In the fourth diagram
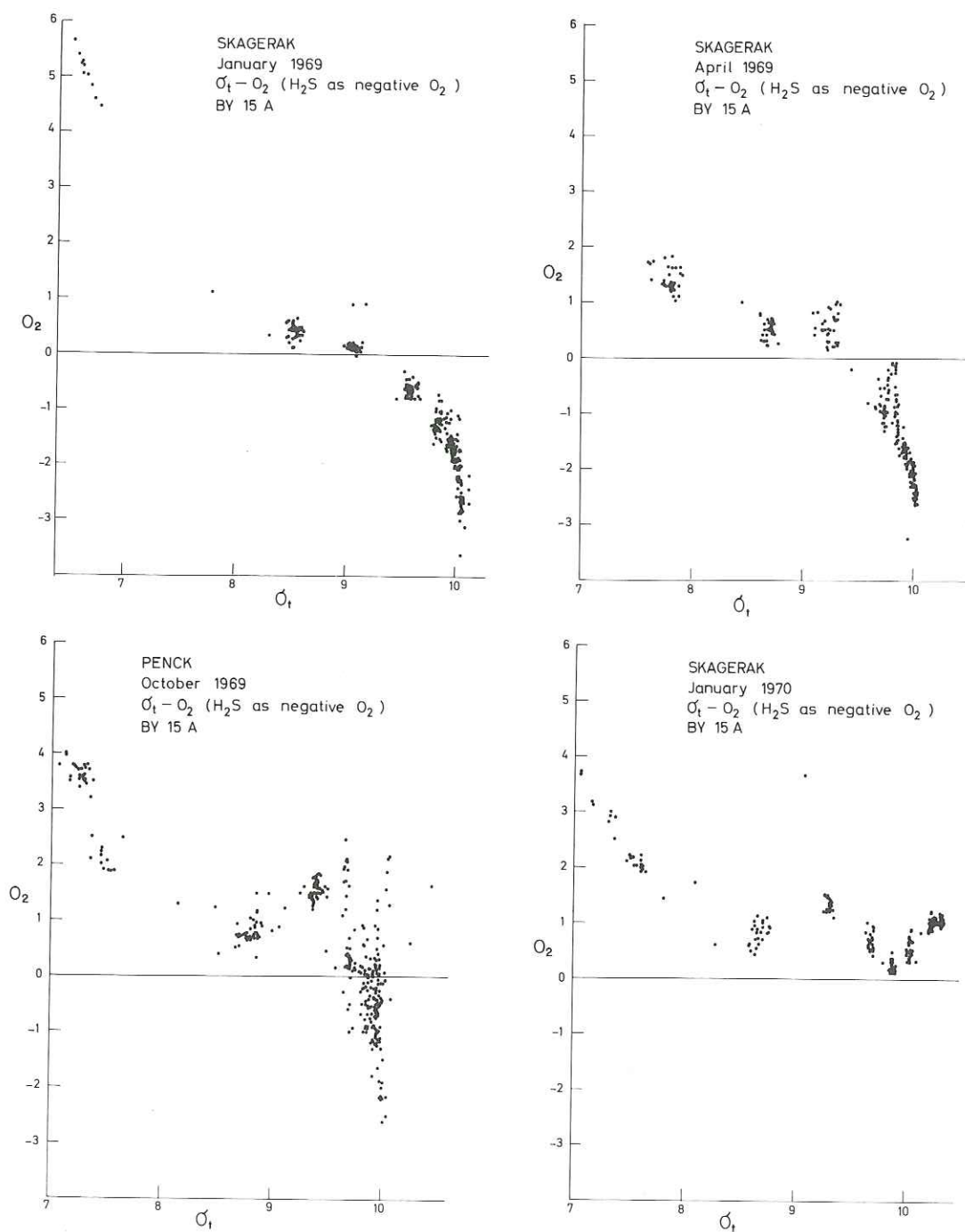
Fig. 9. Sigma-t / O_2 diagrams showing the relations between density and dissolved oxygen or hydrogen sulphide in the Gotland Deep. Oxygen is expressed in ml/l and hydrogen sulphide as "negative oxygen". (See explanation in the text. From Fonselius 1974).
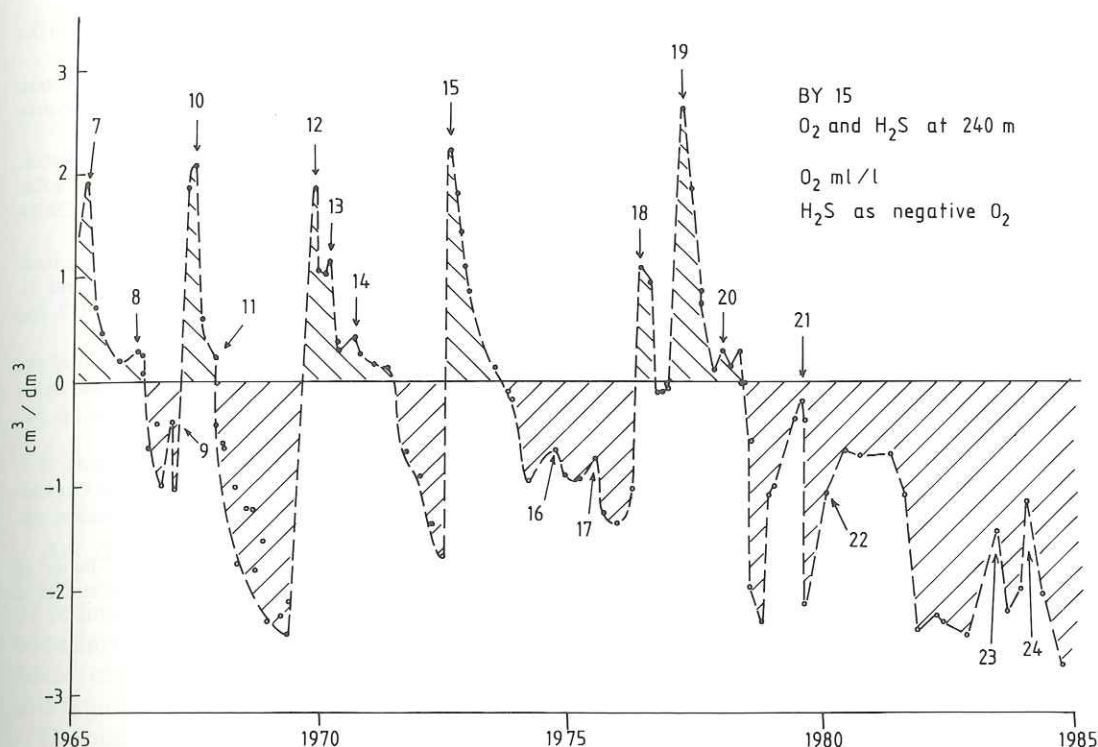
Fig. 10. Variations in oxygen (in ml/l) and hydrogen sulphide expressed as negative oxygen at 240 m in the Gotland Deep from 1965–1984. The arrows indicate inflows of new water. (Negative oxygen is explained in the text).

we can see how the hydrogen sulphide has completely disappeared.

The stagnation of water in deep basins is a natural phenomenon. Such stagnation periods have occurred many times during the development of the Baltic Sea. But stagnation does not necessarily lead to hydrogen sulphide formation. If the water is renewed before all oxygen has been utilized, no hydrogen sulphide will be found in the basin. In permanently stagnant basins, however, hydrogen sulphide is always formed, because there is no supply of new oxygen. Figure 10 shows the alternating periods with oxygen and hydrogen sulphide in the deep water of the Gotland Basin (cf. Fig. 3). The hydrogen sulphide in the figure is expressed as negative oxygen. Negative oxygen is the H_2S value in ml/l multiplied by 2. It expresses the amount of oxygen equal to the amount of H_2S produced through reduction of SO_4^{2-} (Fonselius 1969b).

If the primary production is increased in the surface layer of a semi-stagnant basin which owing to short stagnation periods does not normally contain hydrogen sulphide, the amount of dead matter produced will increase. This may lead to the depletion of all oxygen in the deep water and eventually to hydrogen sulphide formation. The primary production may be increased due to different factors, e.g. increased discharge of nutrients in sewage water from communities or in runoff from agricultural areas. The precipitation may also contain large amounts of nitrate, e.g. from industrial areas (Fonselius 1969a).

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