GÖTEBORGS UNIVERSITET

Ödsmål. Kville sn, Bohuslän

Hällristning   Rock carving
Fiskare från   Bronze age
bronsåldern   fishermen

MEDDELANDE från
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On the Oxygen Deficit in the Baltic Deep Water.
(Lecture given at the VI:th Conference of the
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by
Stig H. Fonselius

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Oceanographers with some experience of the Baltic have certainly observed that the oxygen values in the deep water below the halocline have been extremely low during the last decade. They must also have felt the smell of hydrogen sulfide in the bottom water of the Gotland basin. Students may easily get the impression that these conditions are normal in the Baltic deep water. It has been known for at least 80 years that there is an oxygen deficit in the deep water and that this water can only be renewed through inflows of Kattegat water through the Belts.

But if we take a look at some station profiles from different decades of this century, we will easily find remarkable differences in the oxygen concentration, especially in the northern part of the central basin. Fig. 1 shows the salinity, temperature and dissolved oxygen at station F 74 in the northern Baltic proper in May 1906. The depth is here more than 150 m and the station may well represent the conditions in the deep water of this area. The water has here a relatively homogenous composition below the halocline. The temperature is there around 4.2°C and the salinity at 150 m is 10.1‰. At the same depth there is 3.15 ml dissolved oxygen/1. Fig. 2 shows the same station in July 1939. The temperature is now nearly 1 C higher in the deep water, around 5.2°C. The salinity is 11.0 ‰ and there is only 1.5 ml dissolved oxygen/1 at 150 m. As can be seen the oxygen has decreased to half its value some 30 years earlier, in spite of the fact that the other factors have only undergone slight alterations. Fig. 3 shows 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 150m. The dissolved oxygen has, however, decreased alarmingly and is now only 0.4 ml/l. The same observations may be made at other deep stations in this area.

In order to find out if this decrease of the oxygen is continuous, I have put out all available oxygen saturation values for station F 74 between 150 and 170 m from 1900 to 1967 on Fig. 4. The oxygen saturation values show a steeply falling curve, which clearly indicates that all oxygen in few years will have been used up. Fig. 5 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 in the same area almost

in the middle of the basin. As can be seen, the oxygen curve shows
the same trend as at F 74. Fig. 6 shows the mean values for dissolved
oxygen below the halocline at station F 78 plotted in the same manner.
This station is the Landsort Deep, the deepest spot in the Baltic. Here
we observe again the same pattern for the oxygen curve. If this trend
will continue for some years, the oxygen will disappear completely from
the deep water. Then the formation of hydrogen sulfide will begin close
to the bottom and soon it will spread to the higher layers below the
halocline. The Gulf of Finland is not separated from the central basin
by any sills. Therefore it may be regarded as a part of the central basin.
Unfortunately it has not been possible for me to find any station in
the Gulf of Finland with a sufficient depth and continuous measurements
of oxygen from the beginning of the century to present time. Fig. 7
shows, however, the oxygen values at station F 54 in the deepest part
of the Gulf of Finland on the line Helsinki-Tallinn. The values are from
90-100 m depth, but the measurements end in 1939. Because the station
is not any more located on international water after the war, I have
not been able to find any later measurements in the literature. The
pattern of the oxygen values is however the same as for the other
stations in the central basin. It is therefore easy to extrapolate the
present condition. 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 that area. H_2S has been
found there at several occasions.

The Gulf of Bothnia is separated from the Baltic proper by a sill
with a silldepth of approximately 45 m, but there are indications of
the existence of a narrow 70 m passage to the Åland Sea (Palosuo 1964).
Because the halocline in the Baltic proper is located at around 60 m
depth, there will be 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 basin. Accordingly the oxygen supply should decrease
slightly in the deep water of the Åland Sea, due to the bad oxygen
conditions in the deep water north of Gotland. Fig. 8 shows the oxygen
values at 150-170 m on the station F 69 from 1899 to 1961. A decrease
of the oxygen values is detectable here. Fig. 9 shows the oxygen
saturation values computed for the same occasions at F 69. The Åland Sea
is divided into two basins through an approximately 80 m deep sill.
The deepest station in the northern Åland basin is F 64. Here only a very

small influence of the Baltic Deep Water may be detected. Fig. 10 shows
the oxygen values at F4 at 250-300 m depth from 1890 to 1967. The
Gulf of Bothnia has always been regarded as a sea with a very good
yearly aeration due to termohaline convection during the winter. Fig. 11
shows the oxygen values at station F 24 in the Gulf of Bothnia. The
values are from 175-200 m depth, plotted in the same manner as in the
previous figures. Here we get a clear decrease of the oxygen values
in the deep water from 1900 to 1961. F 24 is located near Ulvön at the
Swedisch coast. It is known to be the deepest spot of the Bothnian Sea.
The aeration of the deep water seems not to be as good here at present
as it was in the beginning of the century. Another possibility may be
that the consumption of oxygen in the deep water has inereased during
this time. No such effect could be detected in the shallow Bothnian Bay
north of the Quark.

It is a well established fact that the salinity of the Balitic
water has increased since the beginning of the 20th century. This
increase has been described by several authers as Granquist (1952),
Soskin (1963), Segerstråle (1953), Ahlnäs (1962), Lindquist (1959) etc.
This increase has occured both in the surface water and in the deep
water. It may best be followed in the deep water where the annual
variations of the river water discharge will not cause direct and fast
fluctuations of the salinity. Fig. 12 shows the salinity fluctuations
in the Gotland basin at station F 81 from the beginning of the century
until 1968. The values until 1960 are from Soskin (loc. cit.), the
latter values are mean values of the measurements carried out by the
Fishery Board of Sweden. There are no data for the time of the two
world wars, but juging from the condition before and after the wars,
one may draw the conclusion that no inportant changes have occured in
the Gotland basin during these periods. From the figure we can see the
decrease in salinity during the 1930 s described by Soskin (loc.cit.)
and others. This decrease occured both in the surface water and the
deep water. During 1938-39 there began an inflow of more saline water
in the bottom layers. Probably this process continued during the second
world war. As we can see from the figure the surface salinity has
remained above 7 ‰ since 1947 and the alinity below 150 m has not
decreased below 12 ‰ during the same time. The big salt water inflow
during 1951-52 raised the salinity above 13 ‰ up to 150 m. During the
following stagnation period the salinity decreased continuously from
1955 and reached the isohaline for 13.0 ‰ at 225 m dept in 1959. There
are no direct signs of a beginning general decrease of the salinity,

on the contrary, it may well continue to increase. The isohaline for 8 ‰ can be considered to be the upper limit for the halocline. From the figure it can be seen that the increased salinity of the deep water has forced the halocline to rise. During the first years of the century the halocline began at a depth of 80 m. Now in 1968 it begins at around 60 m. We also know that the temperature of the oceans has risen and that this increase has influenced the temperature of the Baltic water. This increase has been described by Soskin (loc. cit.). The density of sea water is a function of both temperature and salinity. An increase of 1 ‰ in salinity will, however, raise the density several times more than an increase of $1^{o}C$ will lower it. Therefore the density of the Baltic water has increased during the present century, and more in the deep water than in the surface water. Fig. 13 shows the increase of σ_t at 150-170 m depth on station F 74 from 1900 to 1968. The increase is almost 1 unit of σ_t. This increase is also observed in the Gulf of Bothnia. As an example I will show the salinity on station F 24 at 200 m depth from 1900 to 1960 (Fig. 14). This salinity increase observed in all parts of the Baltic will cause an increased stability in the halocline. The result of this increased stability will be that the exchange of oxygen through the halocline will decrease in all parts of the Baltic and that the winter convection in the Gulf of Bothnia will not as easily as before reach the deepest parts of the basin. This may be the reason for the decreasing oxygen values in the deep water of station F 24. Phosphorus is a nutrient and it is considered to be the limiting factor for the primary production in the Baltic (Fonselius 1967 a). Phosphorus occurs in sea water as organic and inorganic phosphorus. In both cases we distinguish between soluble and particulate phosphorus. Soluble inorganic phosphorus is measured as a routine on board research ships. With the analytical methods used by most laboratories ortho-phosphate is determined. Such analyses were carried out in the Baltic already during the 1930:ies by Buch (1934), Wattenberg (1940), Kalle (1932) and others. Unfortunately very few values have been published due to technical and analytical difficulties and the variations were great. On some occasions also the organic phosphorus was analyzed by boiling with sulphuric acid. After the second world war the methods have been considerably improved and phospate is now analyzed as a routine on all research ships in the Baltic. From the first analyses during the thirties it is known that phosphate was the main part of the total phosphorus in sea water. Now we have got adequate methods to analyze

total phosphorus as a routine analysis. In Sweden we have used Koroleffs (1968) method. Fig. 15 shows the result of such analyses in the Gotland basin on the stations F 81 and F 80. Total and inorganic P have been analyzed in the same sample on all standard depths. The difference between total P and 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 fractional part of the total P. The main part consists of inorganic P. It can also be seen that during stagnant conditions even organic P is accumulated in the deep water. The conditions were stagnant in the deep water at both stations during February 1968 when the analyses were carried out and H_2S was found in the deep water. Fig. 16 shows the phosphorus in the Landsort Deep during the same expedition. Even here the surface water contained more organic P than inorganic P and the deep water contained only a small fraction of organic P compared with the amount of inorganic P. Unfortunately we can not say if the amount of organic P has increased in the surface water due to the high amounts of sewage and industrial wastes disposed into the Baltic during the last decades or if this is the normal proportion between organic and inorganic P. The analyses of organic P are too scarce and the earlier methods too crude for such comparisons. The organic P in the deep water certainly originates mainly from dead organisms. We can, however, make some comparisons of the amounts of inorganic P in the   deep water during the last 15 years. There are fortunately enough data available for that. Fig. 17 shows the mean values for phosphate from 100, 200, 300 and 400 m depths in the Landsort Deep from 1954 to 1967. One value from 1938 is included. As can be seen the phosphate has increased continuously during this time from about 1 ug-at/l to nearly 3 ug-at/l. This means that the phosphate concentration is now three times higher than it was 15 years ago. Other stations show the same trend.

We know that phosphate is accumulated in the deep water of stagnant basins. This process has been described by Richards in several papers (Richards 1956, 1965, Richards et.al. 1965). According to Richards there should be a constant relation between the amount of accumulated phosphate and the oxygen utilization in stagnant basins. Dead organic matter sinks to the bottom of the basin. It is oxidized to simpler compounds and the final result is inorganic compounds as carbon dioxide, ammonia, nitrogen, phosphate etc. Richards also gives the relation AOU to P to be 276: 1 in atoms. This means that 276 atoms of oxygen are needed to oxidize organic

matter in order to set free 1 atom of P as phosphate. As I have described
in earlier papers (Fonselius 1962, 1967 a) this relation will not be true
for the Baltic. The oxigen utilization is here 550 atoms of oxygen for
one atom of P. Since P is the limiting trace element here this means that
the organisms in the Baltic probably get along with half the amount of P
normal for organisms in the oceans. During stagnant conditions the Baltic
bottom water, however, contains several times too much phosphorus compared
with the oxygen utilization. The relation is now 22:1. If we look at the
conditions in the central part of Skagerrack,we find this water contains
about 1 ug-at P/l at a salinity around 35 ‰. The water of the northern
Baltic contains below the halocline about 3 ug-at P/l, three times more
than the Skagerrack water.Theoretically it should contain 0.3 ug-at/l as
preformed phosphate at a salinity of 10 ‰. As we know, this water is
almost stagnant and the extra phosphate is accumulated there through the
decay of organic matter. On an average 465 km^3 water flows annually through
the Belts into the Baltic. This water has an average salinity of 17.5 ‰.
According to what has been said before, this water should contain about
0.5 ug-at P/l as preformed phosphate.   Thus 232.5 x 10^{12} g-at or 7207.5
tons of P are annually brought to the Baltic through the Belts. According to
Fedosov and Zaitsev (1959) 3472 tons of P are brought into the Baltic annually
with the river water. I have myself estimated the amount to about 3200 tons
(Fonselius 1967 a). 935 km^3 water flows annually out through the Belts from
the Baltic. This water contains about 0.2   g-at P/1, which may be a too high
estimation. This gives totally 187 x 10^{12} g-at or 6033 tons P annually. The
difference between incoming and outgoing P is 5147 tons. More P is brought in
than is brought out. The extra phosphorus is included in the biological life
cycle by being taken up by organisms, which as dead sink to the bottom. Partly
the P is transferred into inorganic form in the deep water and partly it is
deposited in the sediments. The phosphate accumulated in the deep water is
slowly transported up to the suface water. The accumulation rate depends on
the stagnation conditions in the deep water. The volume of the central basin
below the halocline is about 3500 km^3. The concentration of P in this water
was around 3   g-at/1. This gives totally 325 500 tons of P in the deep water
of the Baltic proper in the central basin.

  Normal sea water contains dissolved oxygen and is an oxidizing environment.
Sillén (1961) has ·in the oceanography introduced the conception pE, which is
an analogue to pH. It expresses the concentration of electrons in a solution
in the same manner as pH expresses the concentration of hydrogen ions. pE is
the negative logaritmus of the electron concentration. Sea water has usually
a pE around 12.5 and a pH around 8.2. The surface water of the Baltic is in

this respect like normal sea water. In the deep water the oxygen concentration decreases very much but the environment remains oxidizing as long as there is oxygen present in the water and no hydrogen sulfide has been formed. The pH of the Baltic deep water may decrease to 6.9 due to the increasing amount of carbon dioxide formed. Immediately when H_2S appears in the water and the last traces of oxygen disappear, there occurs a drastic change in the pE of the water. The environment now becomes reducing and the pE decreases to negative values around -3.8. The pH of the water changes only negligibly. It increases a little when the concentration of H_2S increases. The change may be 0.2 pH units probably due to the protolytic effect of H_2S.

The uppermost layers of the sediments may be reducing long before the overlying water has lost its oxygen. Sediment samples often smell of H_2S even when the overlying water contains oxygen. In this case hydrogen sulfide is oxidized at the sediment surface. Because the sediment itself is reducing, many sedimented substances may there be transformed into soluble form. In contact with water they will dissolve and through diffusion they will be brought up into the water above the sediment surface. This effect will increase if the water above the sediment also is reducing. Even the low pH of the water will contribute to the dissolution effect. It is well known from the limnology that iron phosphate is dissolved from the bottom sediments of lakes during reducing conditions. It has been suggested (Sillén loc. cit.) that calcium phosphate is dissolved from the sediments in the ocean bottom. The water of the Baltic is brackish and has therefore the properties of both lake water and sea water. Therefore it may be possible that both iron and calcium phosphate are dissolved from the sediments of the Baltic. Fig. 18 shows the relation between the phosphate concentration and the pH of the Baltic water. The values are from the Gotland basin in February 1967. In the figure the phosphate concentration on different stations has been plotted on a logarithmic scale against the corresponding pH on a linear scale. The open circles in the uppermost part of the figure indicate stagnant water containing H_2S. It can here be seen how the pH increases slightly due to the protolytic effect of the H_2S. Gripenberg (1937) has shown that Ca is dissolved in the deep water of the Baltic. Kwiecinski (1965) found that the Ca concentration of the water in the Gotland basin was higher during stagnant conditions than when oxygen was present. On the "Skagerak" we have analyzed the iron content of the water in the Baltic. During stagnant conditions we found very high amounts of dissolved iron in the water containing H_2S. Fig. 19 shows the concentration of reactive dissolved Fe at the stations F 81 and F 80 in the Gotland basin during May 1967. From the figure it can be seen that the iron concentration increases very much in the H_2S layer. Fe exists most probably in an oxidizing environment in sea water as $Fe(OH)_3$. This compound is very little soluble in water. In a reducing

environment the iron is transformed to divalent form. Ferrous sulfide is
formed. FeS is a much more soluble compound than the ferric hydroxide. Therefore
a part of the particulate iron hydroxide is transformed to soluble ferrous
sulfide in stagnant water. Insoluble ferric hydroxide will then be transformed
to soluble form and dissolved from the sediments into the water as FeS. From
the figure it can also be seen that during this occasion new oxygen rich water
had penetrated down into the Gotland basin below the stagnant layer. It had
not been able to reach over the sill to the Fårö Deep. This inflow has been
described closer by the author in a previous paper (Fonselius 1967 b).

A crude estimation of the amount of oxygen at present dissolved in the deep
water of the central basin, can easily be made. The volume of the central basin
below the halocline is as I mentioned earlier 3500 km^3. If we assume that the
water there as an average contains 0.5 ml oxygen/1, we will get totally 1.75 x
10^{15} ml oxygen or 2.5 x 10^6 tons. We have to assume that normally during
longer periods the oxygen which has been brought into the deep water, generally
has balanced the oxygen consumption there. In other case the deep water of the
Baltic would long ago have lost its oxygen. If one now by some means decreases
the oxygen supply or increases the oxygen consumption, this will cause a
decrease of the oxygen concentration in the water. This may happen through a
decrease of the oxygen supply with the inflowing water through the Belts or
through an increase of the stability of the permanent halocline or through an
increase of the primary production in the surface layers which increases the
amount of dead organic matter in the deep water or through direct supply of
organic matter to the deep water from disposal of sewage and wastes from
communities and industries.

When all oxygen of the deep water has been exhausted, hydrogen sulfide
will be formed and gradually the whole water mass below the halocline will
become poisoned. Hydrogen sulfide is a poisonous gas which kills all higher
life. The basin will be transformed to a lifeless oceanic desert. One may of
course ask oneself if this in any way will be of inconvenience for the
population around the Baltic. We know that the Black Sea contains enormous
amounts of H_2S below the halocline and nobody has complained about that. Here
in the Baltic the hydrographic conditions are, however, a little different.
The halocline is situated at around 60 m depth. As in the Black Sea, the surface
water of the Baltic is well aerated during the winter convection and there
seems to be very small risks for a contamination of the surface water. The
supply of oxygen from the atmosphere will certainly be sufficient to prevent
this. The worst risk is certainly that during such conditions a new big salt
inflow occurs, forcing the hydrogen sulfide contaminated water higher up and
over the sills into uncontaminated areas killing all life there.

in the future. We do not know enough about the fundamental processes which
regulate the oxygen supply to the deep water and the effects of waste disposal
into the Baltic. If we consider it necessary and worthwhile to take any steps
in order to improve the oxygen conditions, it will certainly be very expensive
and no country can carry out such a task alone. It has to be done as an inter-
national cooperation between the countries around the Baltic. But before such
steps can be seriosly discussed, the scientists have to answer the question
why the oxygen has begun to decrease during the present century. Therefore the
hydrographic research in the Baltic area has to be concentrated on that problem
in the future. The work has to be carried out in close cooperation between the
laboratories working in the Baltic.

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Fig. 1

Fig. 1

Fig. 2

F 74
JULY 8. 1939

Fig. 2

Fig. 3

F 74
JUNE 6. 1967

O₂ml/L   t°C   ‰S
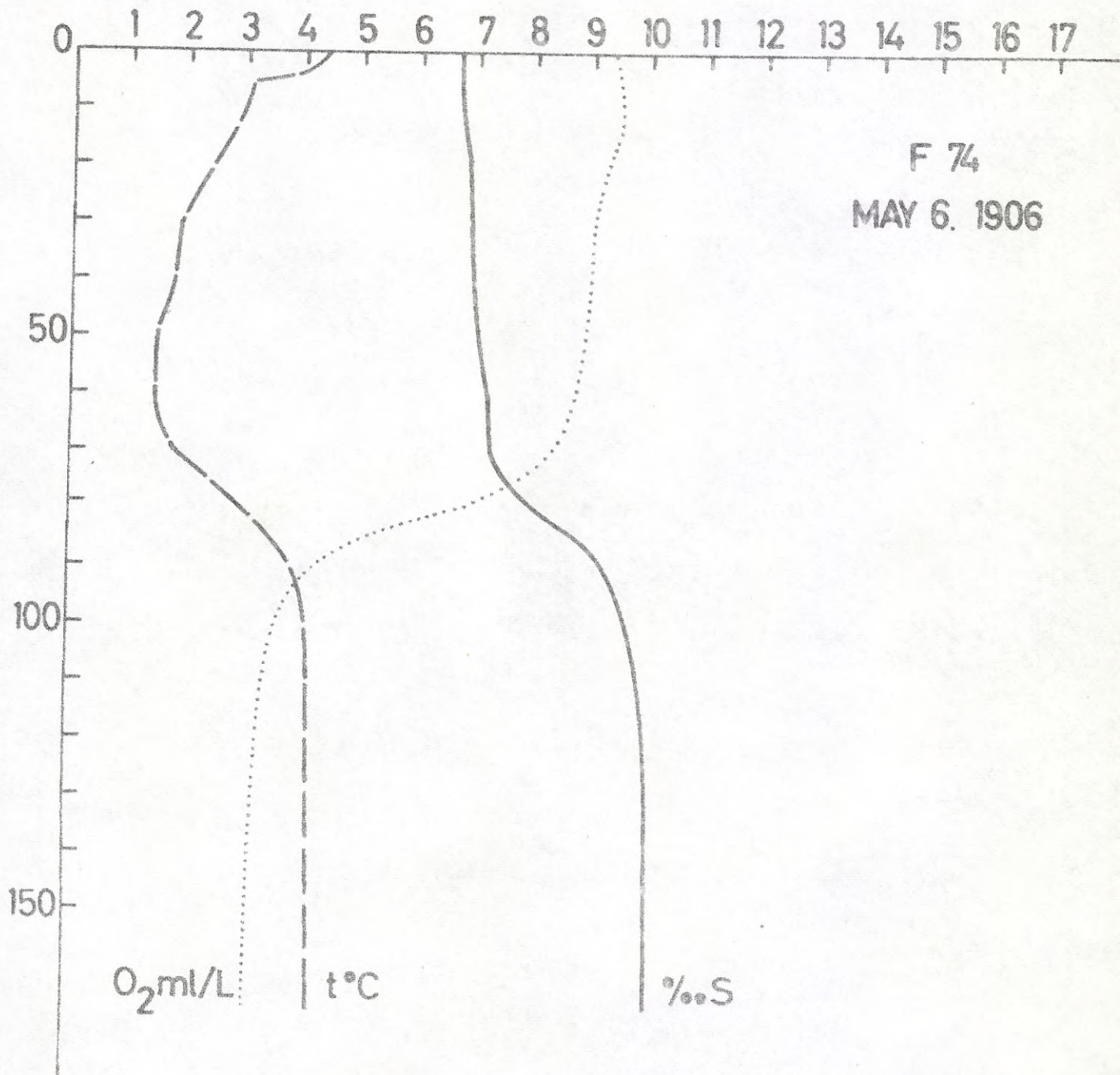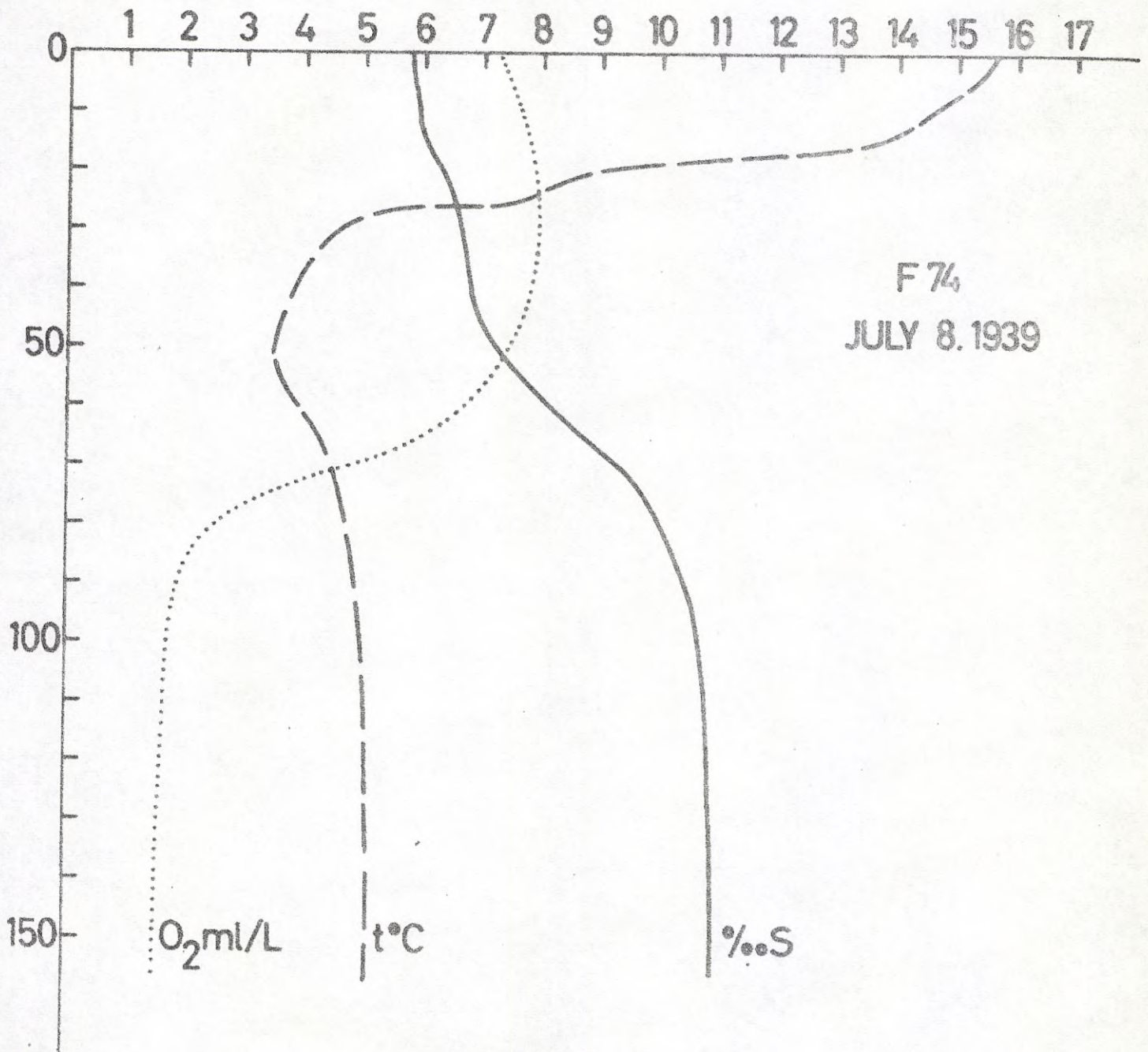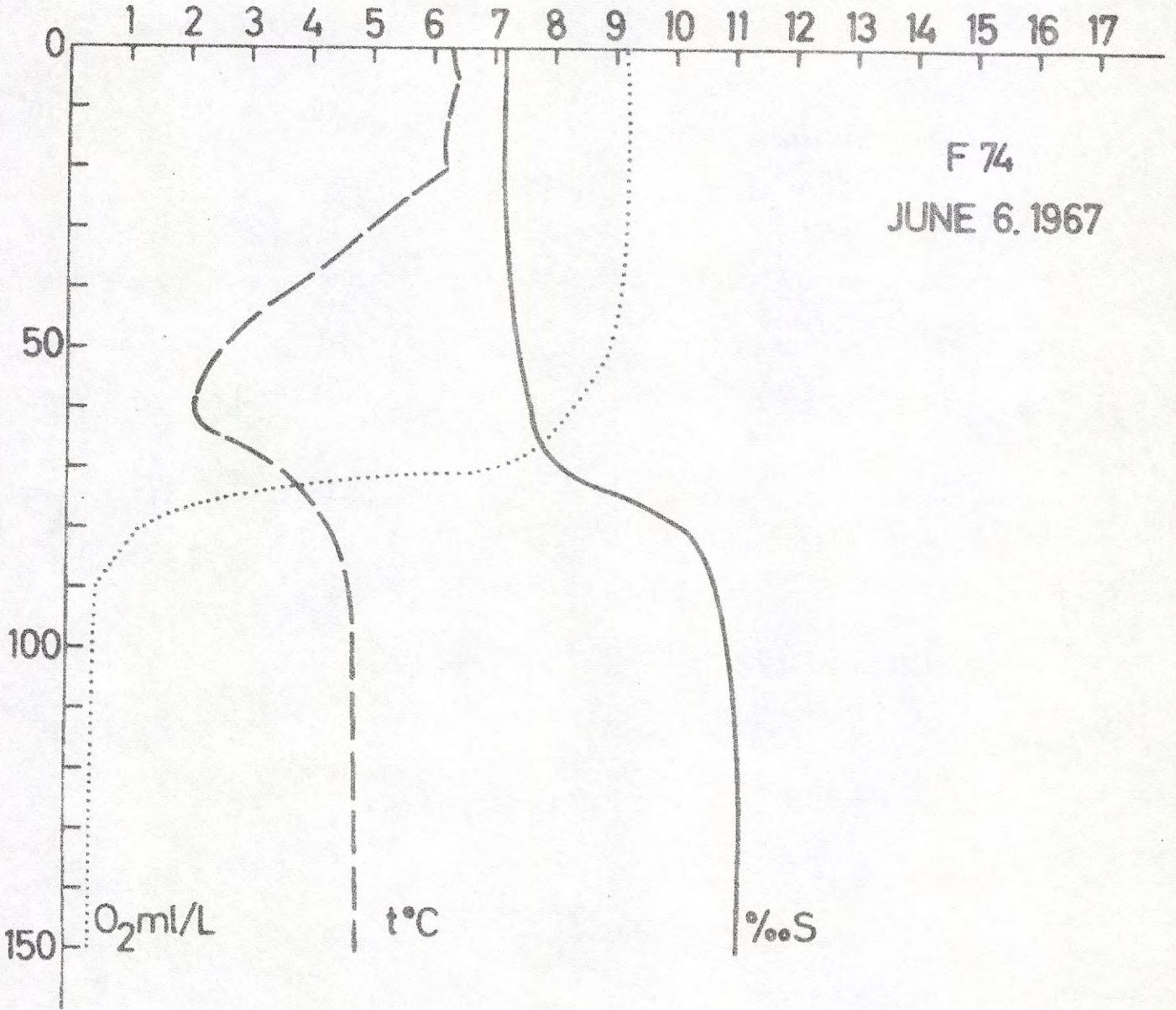
Fig. 3

Fig. 4

F 74

Oxygen Saturation %

150 - 170 m   1900 - 1967.
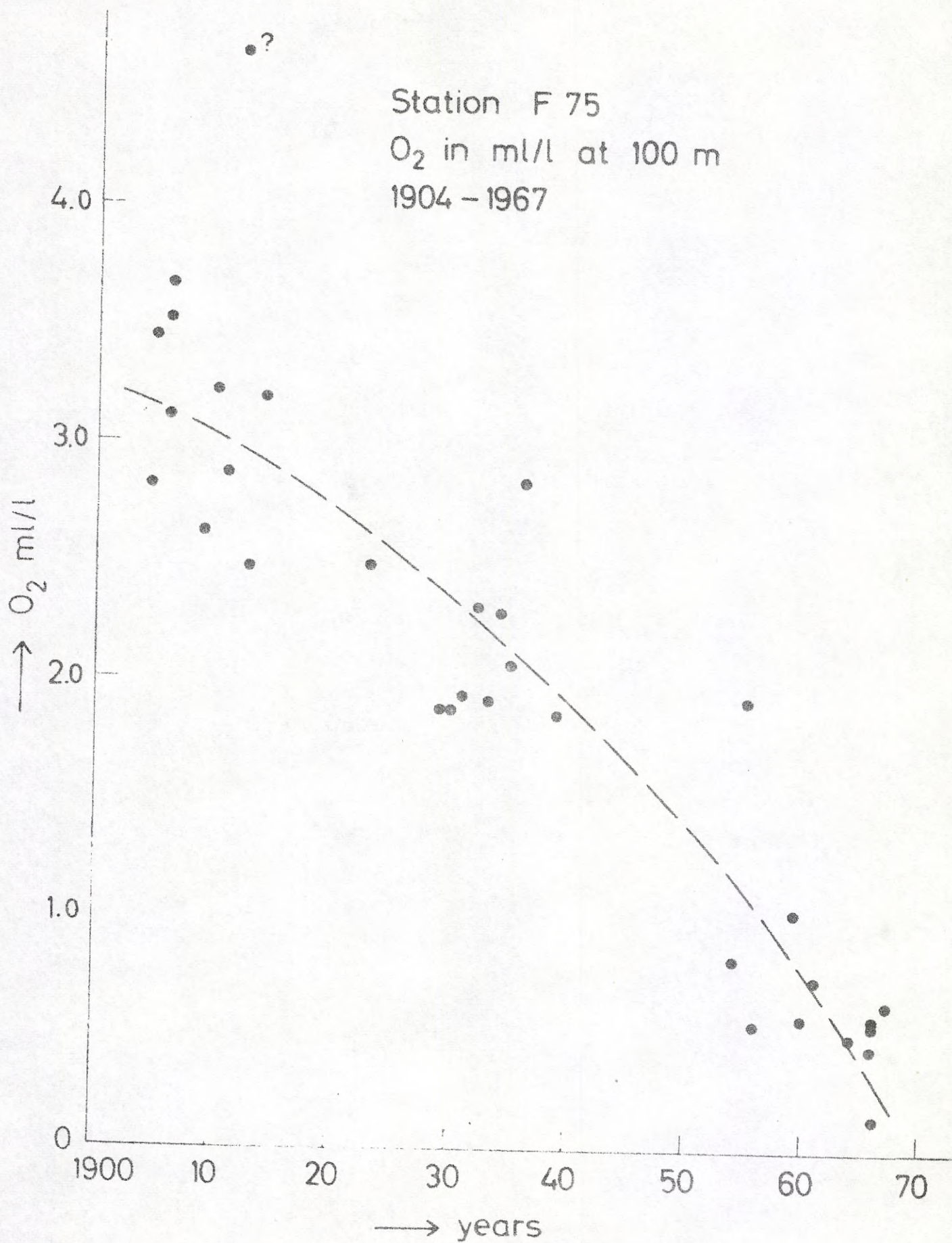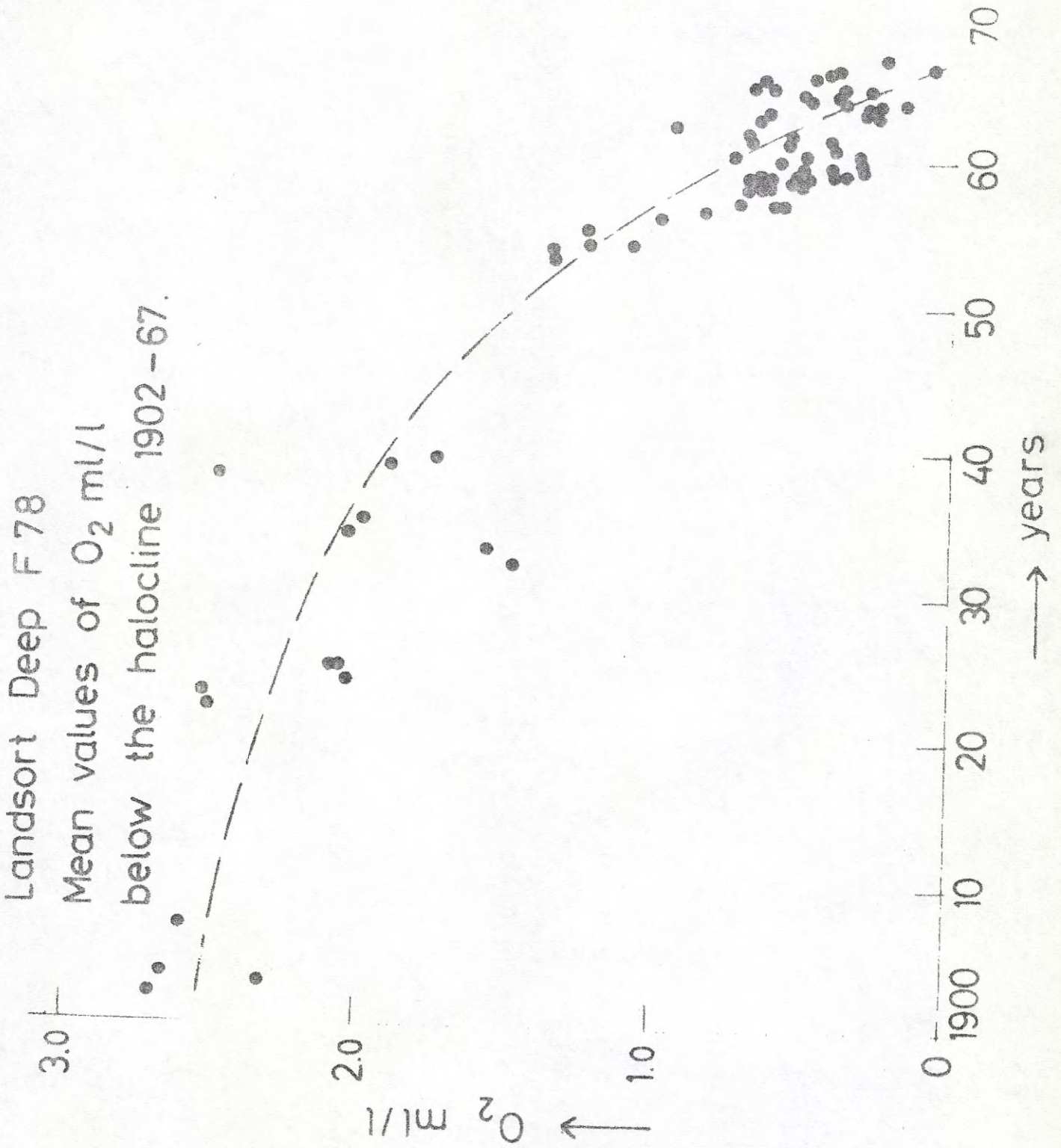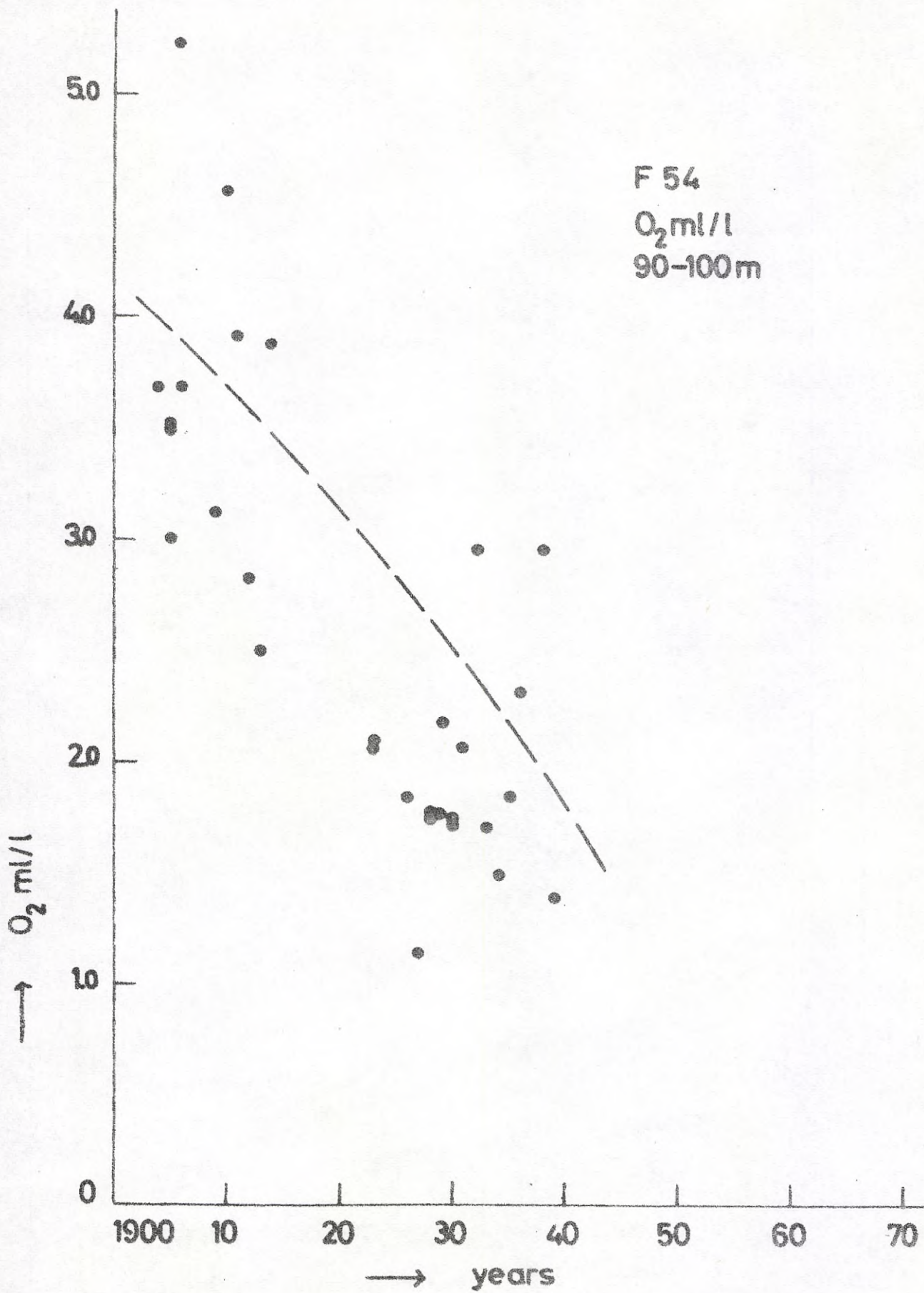

Fig. 4

Fig. 5

Station F 75
O_2 in ml/l at 100 m
1904 – 1967

Fig. 5

Fig. 6

Landsort Deep F 78
Mean values of O_2 ml/l
below the halocline 1902 – 67.

Fig. 6

Fig. 7

F 54
O_2 ml/l
90–100 m

Fig. 7

Fig. 8

F 69
O$_2$ ml/l
1899 – 1961
150 – 170 m

Fig. 9

F 69
Oxygen saturation
1899–1961
150–170 m

Fig. 10

Fig. 10

Fig. 11
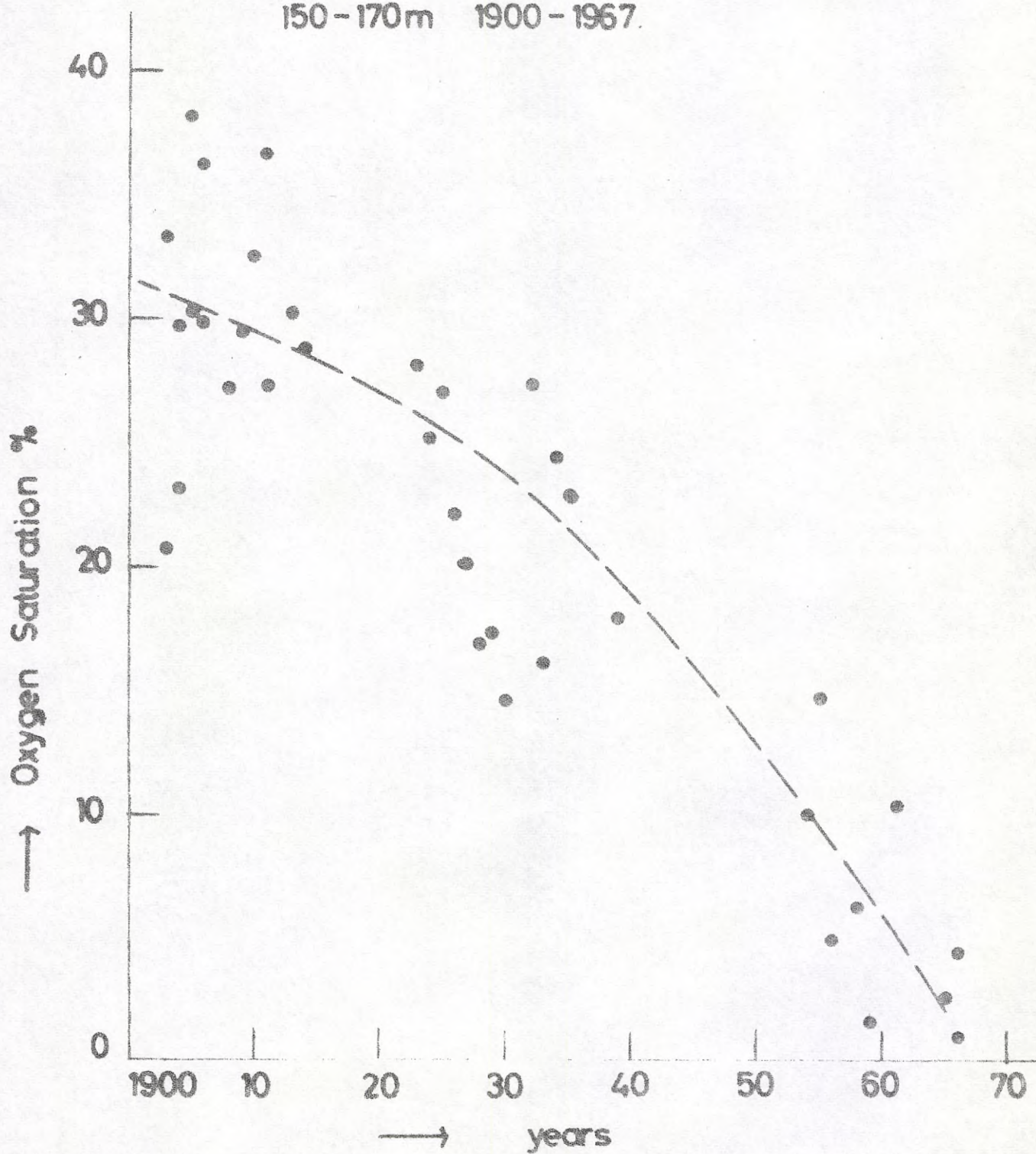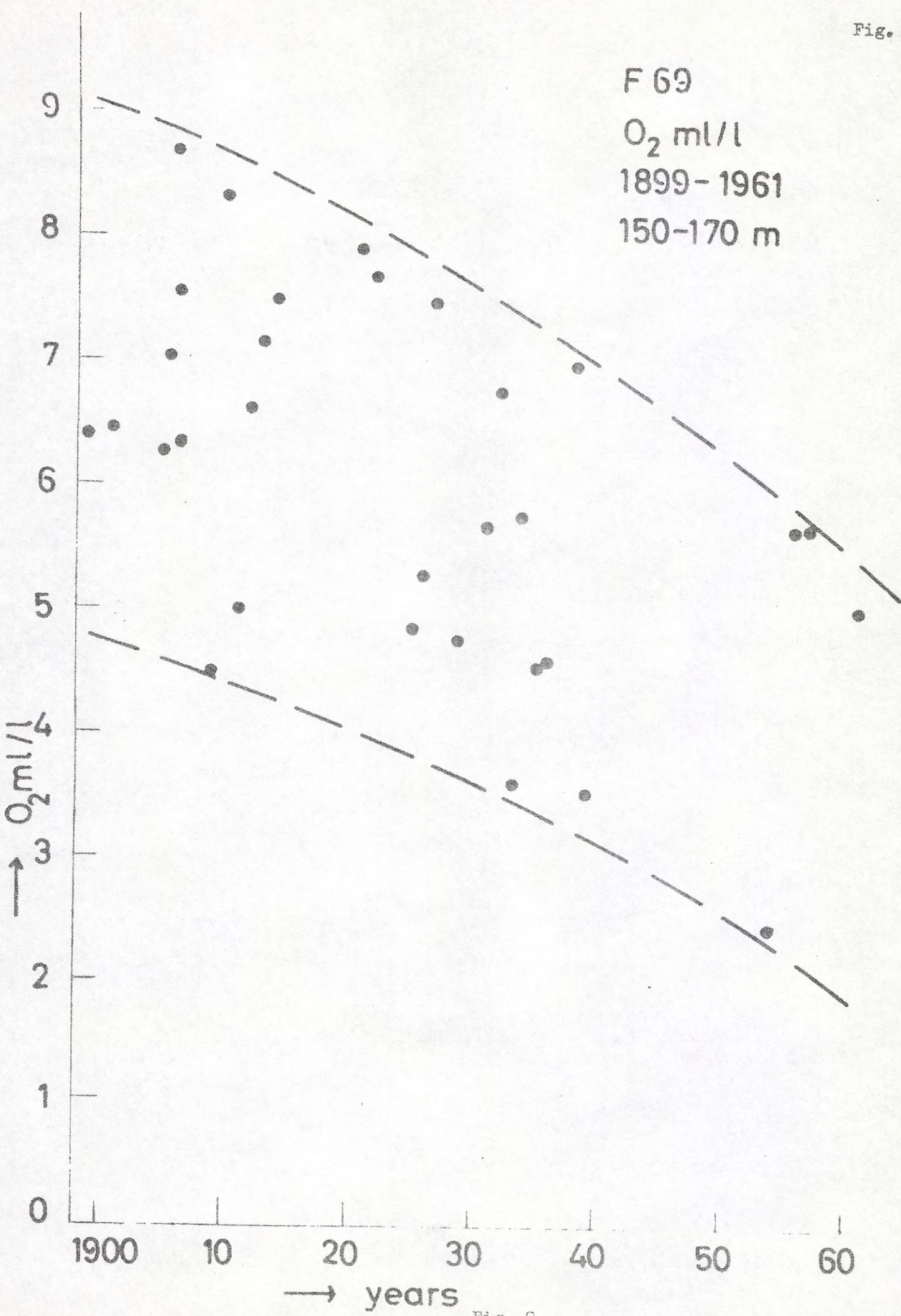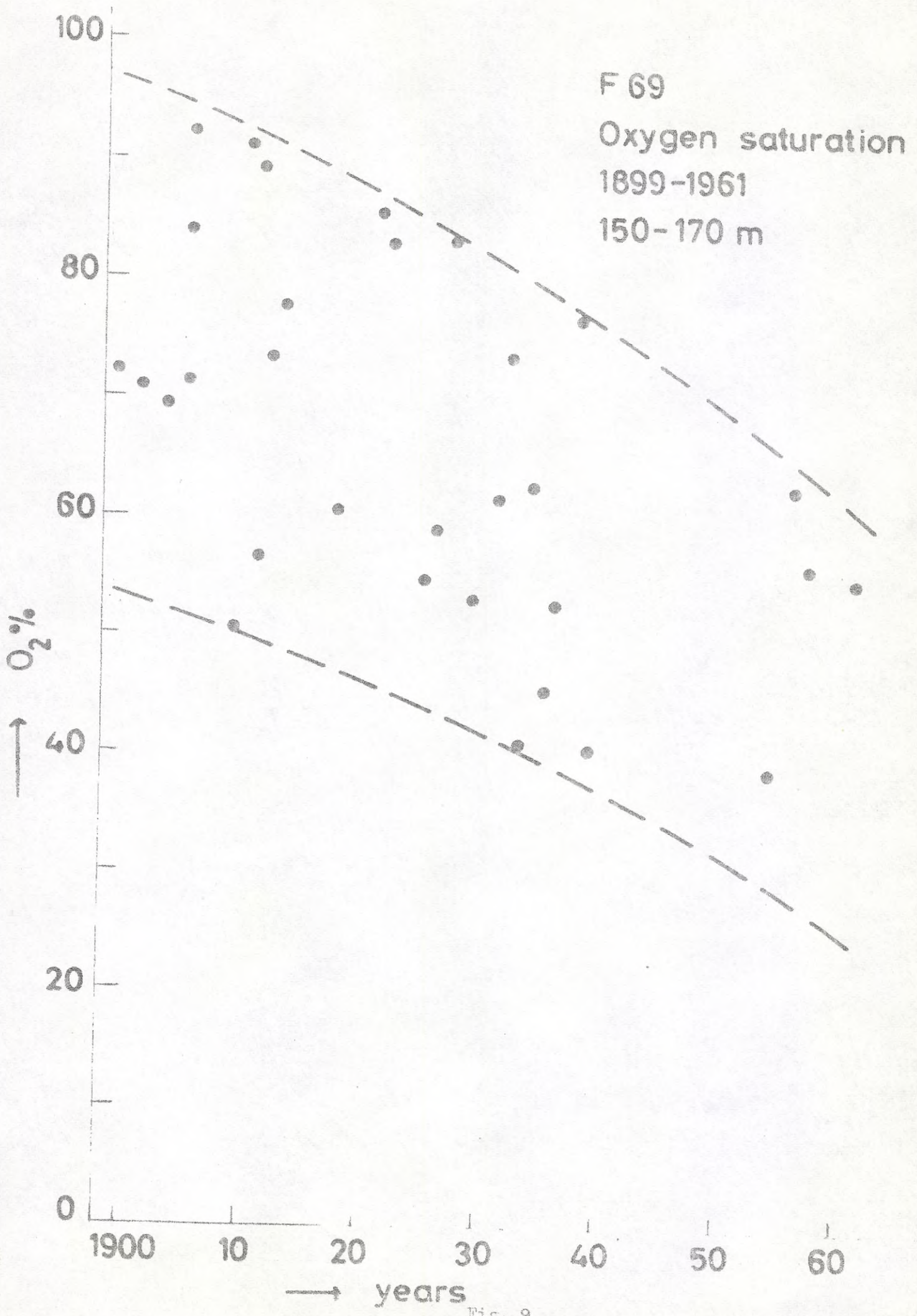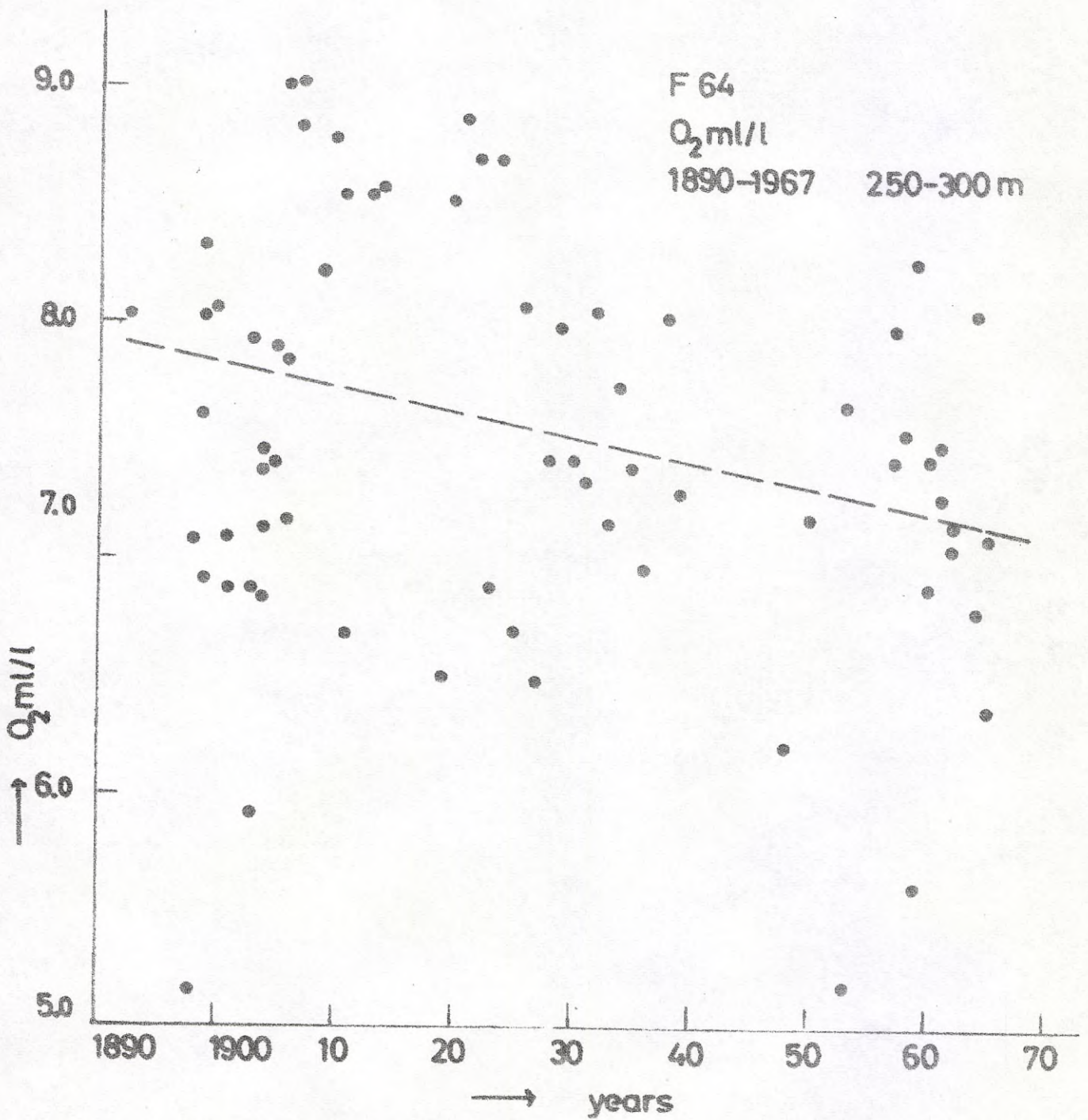
F 24
O_2 ml/l
175 – 200 m 1900–1967
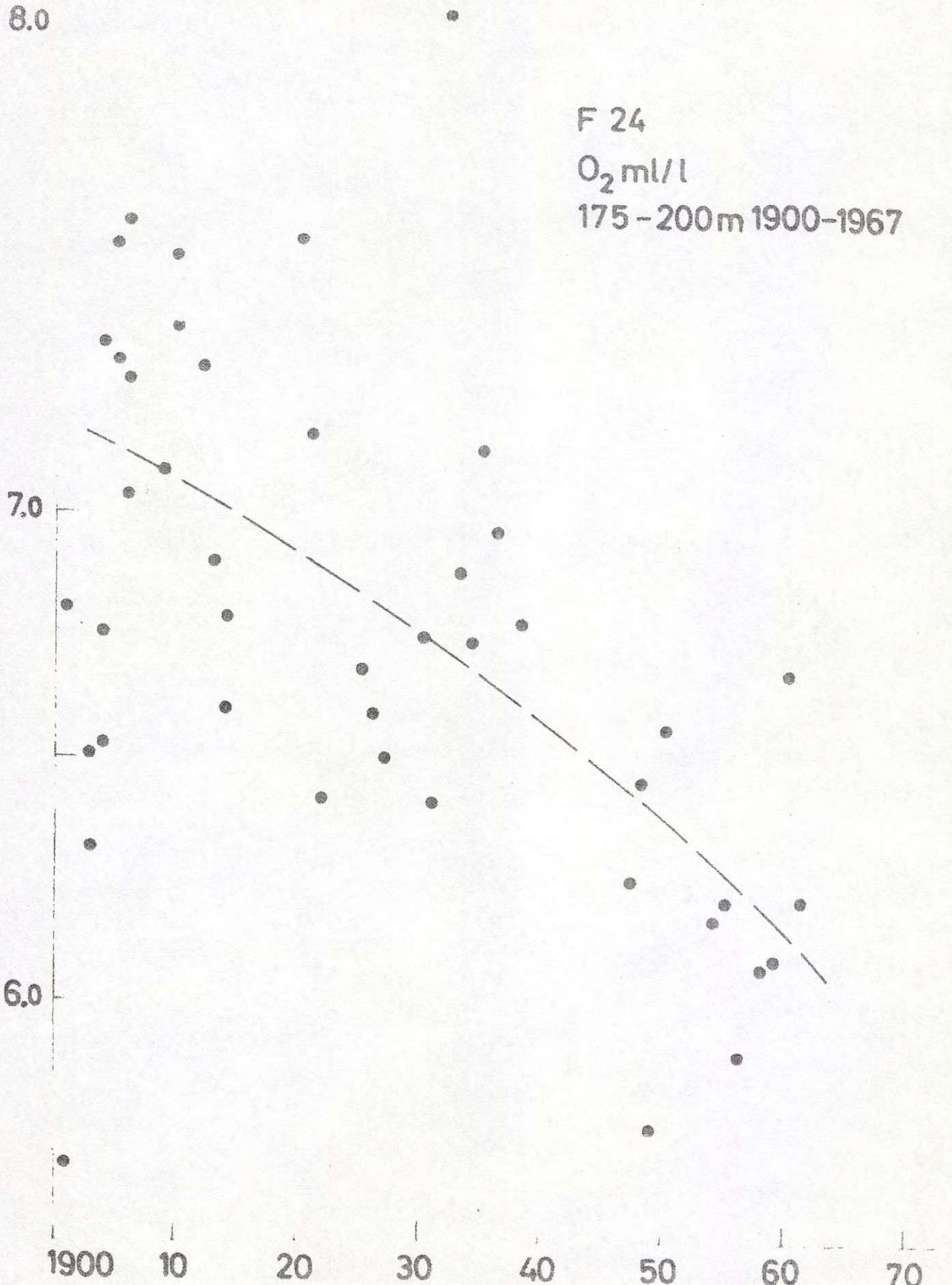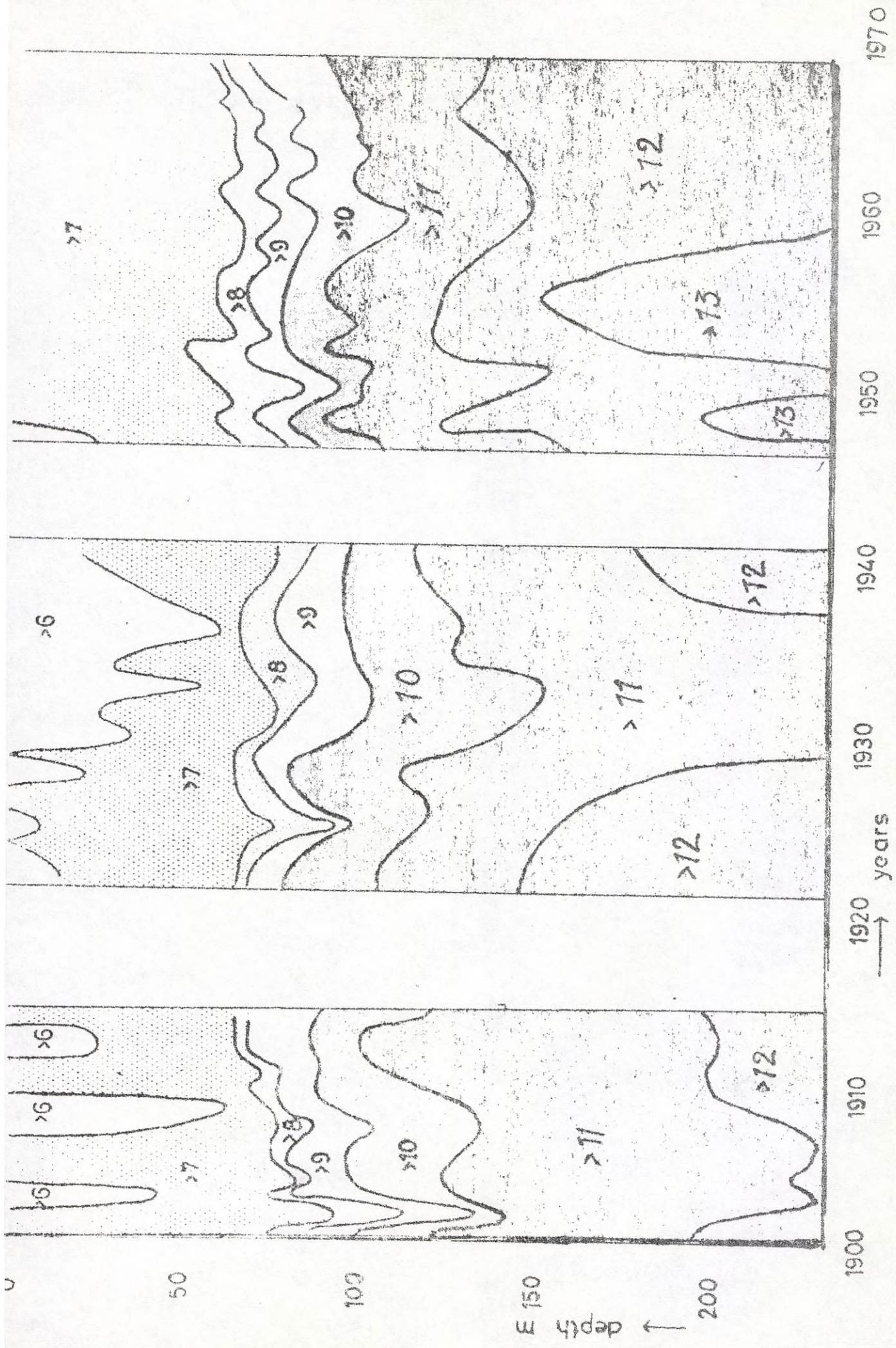
Fig. 12

F 81   S‰

Yearly mean values

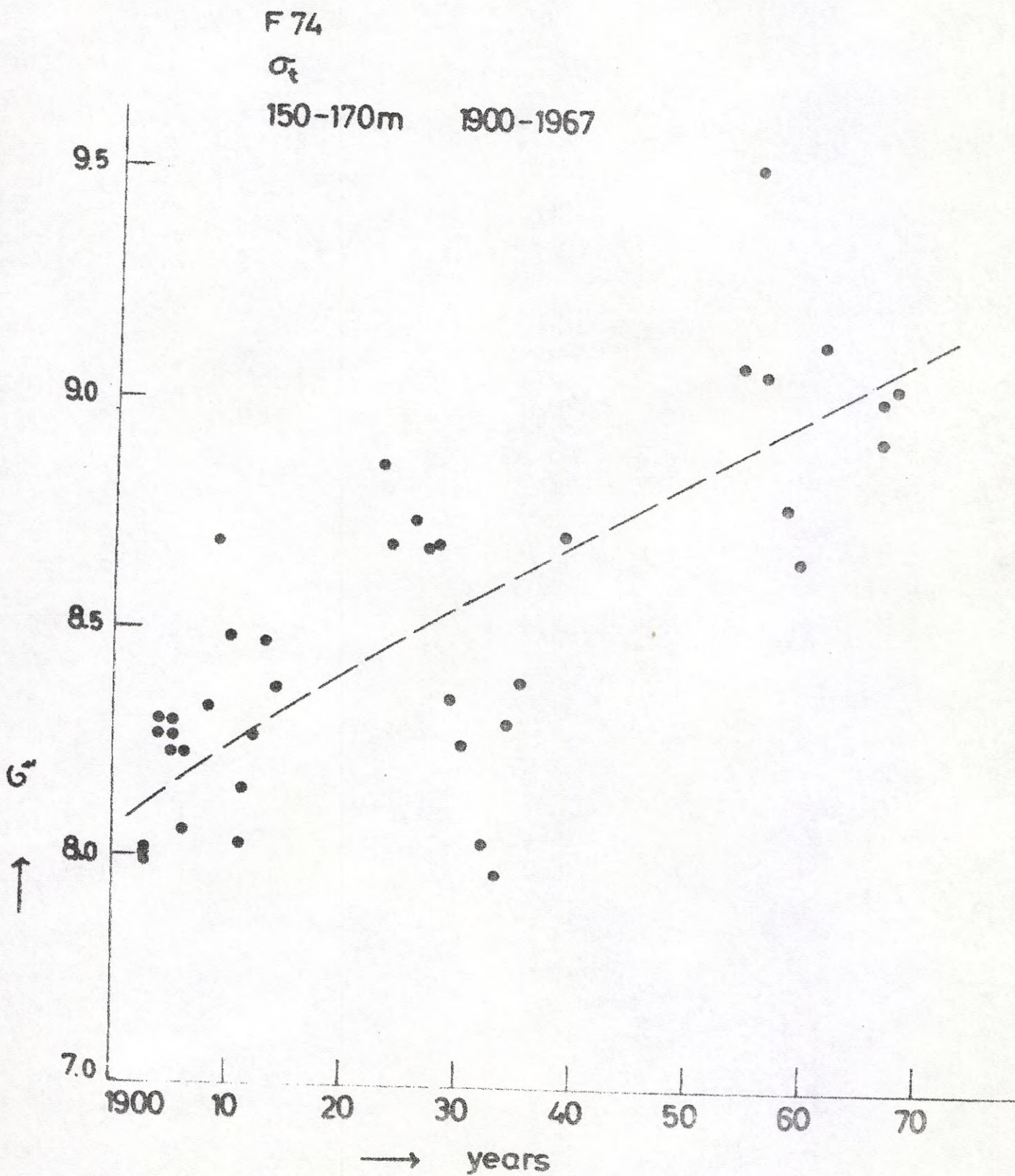Fig. 13

F 74
σ_t
150–170 m   1900–1967

Fig. 13

Fig. 14

F 24
Salinity S‰
200m 1900-1967

Fig. 14

Fig. 15

F 81
8.2.1968
Distribution
of
phosphorus

S‰

org. P.   PO₄-P   tot. P.

F 80
12.2.1968
Distribution
of
phosphorus

S‰

org P   PO₄-P.   tot. P.

Fig. 15

Fig. 16

F 78
15. 2. 1968
Distribution
of
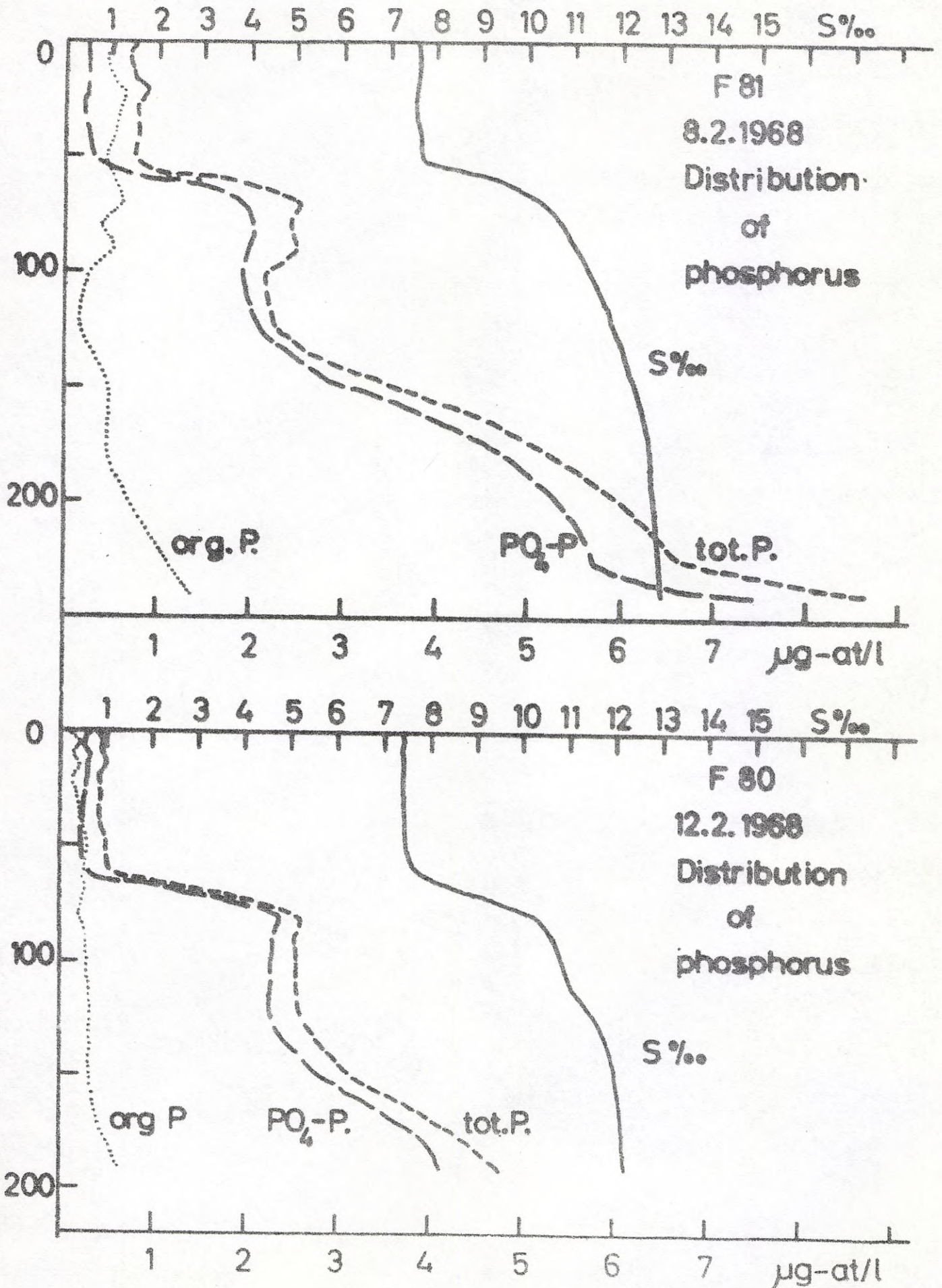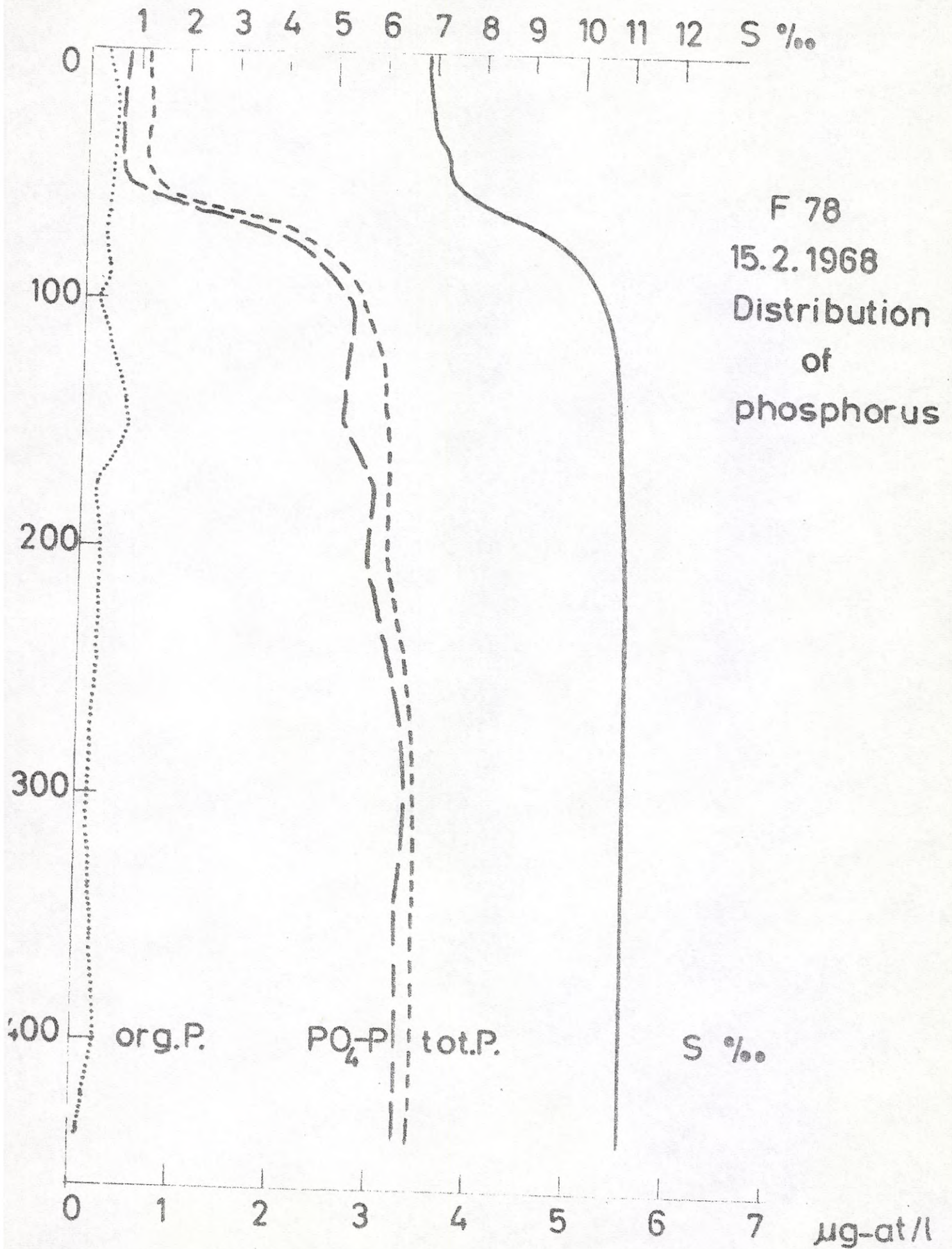phosphorus

org.P.   PO₄-P tot.P.   S ‰

Fig. 16
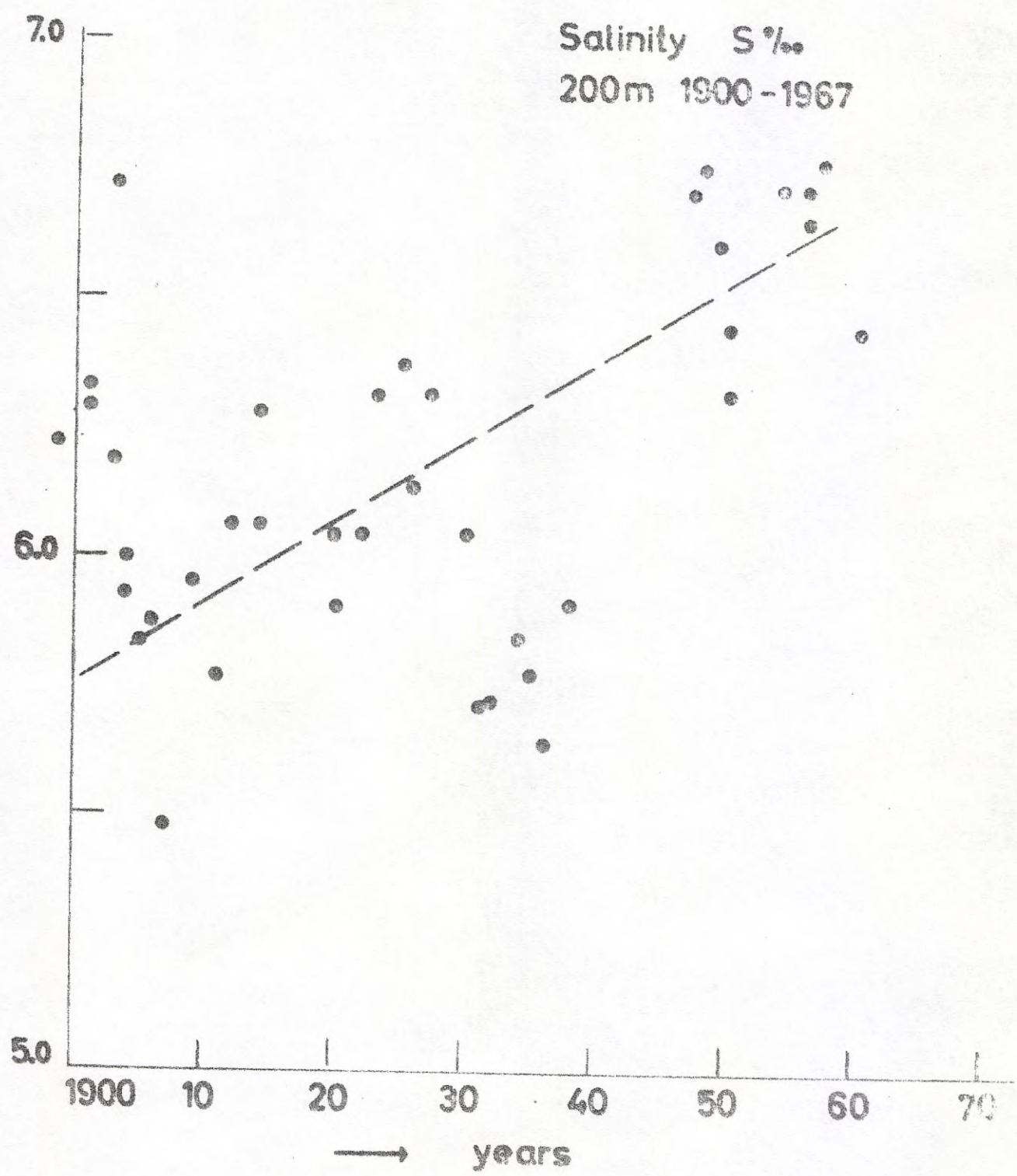
Fig. 17

F 78
PO_4^--P
Mean value
100-200-300-400 m
1938   1954-1968

Fig. 17

Fig. 18

Gotlandbasin
February 1967

Fig. 18

Fig. 19

GOTLAND DEEP
F 81
MAY 1967

O_2 ml/l

t°C

Fe µgat/l

H_2S-S µgat/l

O_2 ml/l

$PO_4^{\equiv}$-P µg at/l

FÅRÖ DEEP
F 80
MAY 1967

t°C

O_2 ml/l

$PO_4^{\equiv}$-P µgat/l

Fe µgat/l

H_2S-S µgat/l

Fig. 19