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Ödsmål, Kville sn, Bohuslän

Hällristning
Fiskare från
bronsåldern

Rock carving
Bronze age
fishermen



MEDDELANDE från
HAVSFISKELABORATORIET · LYSEKIL

nr
141

Hydrografiska avdelningen, Göteborg

A STUDY OF THE DISTRIBUTION OF ORGANIC CARBON
AND OXIDABILITY IN BALTIC WATERS

by Stig R. Carlberg

(The 8th Conference of the Baltic Oceanographers,
Copenhagen 1972)

December 1972

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Paper No. 25.

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by Stig R. Carlberg

Fishery Board of Sweden, Hydrographic Department, Göteborg.

Introduction

The study of organic compounds in sea water is well established in marine science. The approach is not only the purely scientific one such as in connection to studies of production and food webs, but also investigations of pollution involve determinations of organic compounds. Sea water as well as fresh water contain a great number of different organic components. In the pollution studies, where great numbers of samples have to be examined, it is by practical reasons not possible to determine the concentration of each component. In fact such detailed analyses are not necessary in most cases.

In fresh water analyses a method called oxidability, permanganate oxidation, chemical oxygen demand or oxygen absorbed has been employed for decades (Anonymous 1960, anonymous 1971). A modification of that method has been used earlier in sea water by Gillbricht (1957) and Szekiolda (1968). These procedures attack the compounds in bulk, instead of being specific for one component or group of components. Thus the method determines the ability of the compounds to be oxidized at specified conditions, rather than giving a direct measure of the concentration of them. This is a disadvantage, because the various molecules are attacked differently by the oxidant and hence they are oxidized to a greater or lesser extent, as has been shown by many authors (Holluta and Hochmüller, 1959, and others). The advantage of the method is that it is quick, simple to perform and requires no expensive equipment. In this study has been used a variant of the permanganate oxidation as described by Bouveng and Olsson (1965).

The reason for not using the method by Gillbricht - as Szekiolda did in his study in the Baltic in 1962 - is that the variant employed seemed

to give a higher degree of oxidation while being less sensitive to disturbance from chloride ions.

In fresh water analyses is nowadays frequently used another method for determination of the oxidability, using potassium dichromate as oxidant. Generally this results in a higher degree of oxidation of the organic substances, especially when using silver sulphate as catalyst. However, the procedure is a bit more time consuming than the permanganate method. Furthermore the disturbance from chloride ions is not easily corrected for and the sensitivity of the method is such that it can hardly be applied to samples with an oxygen consumption below 10 mg per litre.

In Swedish studies of pollution of fresh water areas the permanganate method has been used for decades and a lot of data has been collected. In these studies it is often of interest to compare the oxidability values of a river with those from its estuary and the neighbouring sea area. In order to judge the influence of the river on the estuary background values are needed.

The objectives of this study has been to produce such background values of oxidability from the open Baltic area and furthermore to investigate whether oxidability and organic carbon parameters could be used to follow the organic load or pollution in the different water masses of the Baltic. Due to the disadvantages of the described oxidability determinations, a new and growing interest has been shown for the determination of organic carbon in pollution studies of fresh water. As this determination is more objective than that of oxidability, it is commonly thought of as being the most important and relevant of the two for future studies. Thus it was of interest to determine the content of organic carbon in the same samples as was used for the oxidability studies.

The determination of total organic carbon is not only of interest for the pollution studies. The parameter may also be used for calculation of mass balance. Basing on the organic carbon values from this study and a lot of other data Fonselius (1972) was able to calculate a coarse model of the production and transport of organic matter in the Baltic.

Sampling Area and Period

The samples for oxidability have been collected during the period from August 1970 to June 1972 and the carbon samples during August 1970 to December 1971. During each cruise two stations in the Kattegatt (SW Vinga

and Lilla Middelgrund) and six or seven stations in the Baltic proper have been visited. In addition to that a number of stations in the Kattegatt and the Gulf of Bothnia have been visited once or twice. More details are found in Fig. 1 and Table 1. In all about 375 oxidability and 190 organic carbon samples have been investigated.

Regularly three samples were collected at each station; surface, 5 m and one sample below the halocline. At the Gotland Deep and the Landsort Deep further samples were collected.

Analytical Methods

For determination of oxidability a modification of the method by Bouveng and Olsson (1965) has been used. The only change in the procedure was that due to the comparatively low values of oxidability, all volumes were increased by a factor ten, Hence 100 ml sample was used instead of 10 ml. The details of the procedure are given in the New Baltic Manual. All samples were analysed aboard, within a few hours after sampling. It has to be pointed out, that all the oxidations were carried out in alkaline medium, thus avoiding the interference from the chloride ions.

The determination of the total content of organic carbon has been made using two different types of commercial instruments. The first one was a Beckman Carbon Analyzer. Into this instrument a small volume of the water sample, 20 - 50 μ l, was injected while passing in a stream of pure oxygen. The organic substances were burnt to carbon dioxide in an oven at 950 °C. The amount of the carbon dioxide thus evolved was measured in an infrared gas analyzer. Before injection the sample was acidified and nitrogen gas was bubbled through in order to remove all inorganic carbon. The results from this instrument seem to be higher than those obtained with the second one from Oceanography International Corporation. With that instrument, instead of using an oven, the sample is oxidized with peroxodisulphate in a closed ampoule in a pressure boiler. The ampoule is then opened in a closed system and the carbon dioxide is measured in a similar infrared gas analyzer. This latter way of oxidation follows the principles outlined by Menzel and Vaccaro (1964).

From the two sets of carbon data thus obtained it is not possible to say that one instrument produces data which are more correct than those from the other instrument. Therefore the data are here treated as being of equal quality.

The samples for determination of organic carbon were preserved with sulphuric acid and analysed ashore.

Results of oxidability and total organic carbon

In Fig. 2 is given a map, showing a representative distribution of the oxidability values for the surface samples. It is clearly seen that the values in the Baltic proper and the Gulf of Bothnia are about twice as high as those in the Kattegatt.

If the content of organic matter in a water mass is somewhat uniform it should be possible to obtain a relationship between the two parameters of oxidability and total organic carbon. Some authors have tried to do this. Lundstedt (1970) published a paper, showing the result from 929 determinations. 627 of these were made on fresh water from Swedish lakes and the remaining 302 determinations were made on Baltic water collected along the Swedish coast. The water were characterized as slightly to severely polluted by municipal and industrial sewage, mainly board or pulp and paper industry. The fresh water samples were oxidized in acidic medium and the sea water samples in alkaline medium. The organic carbon values were determined with the same Beckman instrument as in the present investigation. For the entire material Lundstedt got a correlation coefficient of 0.97 with respect to straight line. The equation for this line was not reported, but from his drawings it can be calculated as approximately: Organic carbon = $1.9 + \sim 0.139 \cdot \text{KMnO}_4$, where the value 1.9 was given in the text. This value indicates that a certain amount of the carbon is not oxidized by the permanganate.

Szekielda (1968) published a paper concerning a short investigation from the Baltic proper in May 1962. He had used the permanganate method reported by Gillbricht. The determination of organic carbon was made by a hot wet oxidation with silver dichromate and potassium dichromate in sulphuric acid according to a procedure by Kay (1954). The 56 values by Szekielda are reproduced in Fig. 3. From his data I have calculated a correlation coefficient of 0.30 and the equation for the straight line as: Organic carbon₅₆ = $2.40 + 0.150 \cdot \text{KMnO}_4$. This correlation is not very good, but it is based on too few data to be significant.

In Fig. 4 and 5 are presented the corresponding data obtained in the present investigation. Fig. 4 shows the total organic carbon from the Beckman instrument versus oxidability. Some of the 106 values could be regarded as extremes. Therefore calculation has been made on 106 as well as 97 values. The correlation coefficients were 0.41 and 0.58 and the equations: Organic carbon₁₀₆ = $2.67 + 0.144 \cdot \text{KMnO}_4$ and Organic carbon₉₇ = $2.24 + 0.158 \cdot \text{KMnO}_4$. The resulting lines are quite similar. In Fig. 5 are shown the values obtained with the other instrument (Oceanography International).

The carbon values are not as widely scattered as in Fig. 4. The correlation coefficient was calculated as 0.74 and the equation: Organic carbon₈₀ = $1.84 + 0.112 \cdot \text{KMnO}_4$. Maybe this is the best correlation so far for the Baltic waters, but when the lines are compared as in Fig. 6 it can be seen that within certain limits they all are quite similar. The angles of the five lines are not too different and they all indicate that a certain amount of organic carbon (1.8 - 2.7 mg/l) is not oxidized with the permanganate.

Discussion

It might be of interest to see if there is any direct relationship between the total organic carbon content and the total organic phosphorus content. In this case the word total means the sum of dissolved and particulate material. In Fig. 7 is shown a plot of these two parameters. Organic phosphorus was calculated as the difference between total phosphorus and phosphate phosphorus. From the figure it is evident that no direct relation exist. If the numerical magnitudes of the two elements in Fig. 7 are compared we find that to a phosphorus content of 0.25 $\mu\text{gat/l}$ (ca 7.75 $\mu\text{g/l}$) correspond carbon concentrations of 1.3 mg/l to 6.0 mg/l. This means a weight ratio for C/P of $\frac{1300}{7.75} = 168$ to $\frac{6000}{7.75} = 774$. This is very different from the figures for the relation in plankton as cited by Fleming (1940). His figures are 106:16:1 as relation for the atoms of C:N:P, or a weight relation for C/P of $1272/31 = 41$.

If the Baltic plankton is not extremely poor in phosphorus, maybe this difference can be taken as an indication that either a great part of the organic carbon comes from dead cells subjected to mineralization or that a major part of the organic carbon is not of marine origin.

A plot of organic carbon versus salinity (Fig. 8) does not reveal any direct relation and hence no indirect geographical difference of the carbon content. To almost any salinity corresponds a great range of carbon concentrations.

If however the oxidability is plotted versus salinity quite another picture appears (Fig. 9). There is a clear tendency to inverse relation. This resembles very much of what is found when yellow substance is plotted versus salinity. This is shown in Fig. 10, which is taken from the investigation by Bladh (1972), presented at this conference. This rises the question whether the measurements of oxidability and yellow substance to their greatest extent concentrate on the same substances. In Fig. 11 some oxidability values from this investigation have been plotted together with the corresponding values for yellow substance as obtained by Bladh, (1972).

Even if the values are somewhat scattered it is obvious that the two parameters are directly related. As can be seen in Table 3, the regression line is expressed with the equation; $\text{Oxidability}_{104} = 2.37 + 11.06 \cdot \text{yellow substance}$, with a correlation coefficient of 0.71.

In Fig. 8 and 9 indirectly can be seen that the organic carbon shows no geographic variation whereas the oxidability did. In Fig. 12, finally, this is shown in a more clear way. The figure consists of histograms for organic carbon and oxidability for two Kattegatt stations (SW Vinga and Lilla Middelgrund) and six BY-stations from the Baltic proper. Through all histograms the highest and the lowest value of each parameter, as found in the Kattegatt, are marked as broken lines. The histograms represent three or more depths as indicated by numbers below the station codes. Above each histogram are finally some numbers (N = 7, N = 6.5.6.1 etc) showing from which number of observations the mean value was calculated. It seems obvious that the carbon content in the Baltic is the same or slightly higher than that in the Kattegatt, while the oxidability values in the Baltic are about twice or three times those in the Kattegatt.

As was pointed out in the introduction it is a well known fact that different types of organic substances are oxidized to a greater or smaller extent by permanganate. Thus it may be allowed to conclude that a major part of the organic matter in the Baltic is of another type and perhaps of other origin than a major part of the organic matter in the Kattegatt.

Of course it should be of great interest to recalculate the data of oxidability and yellow substance into weight amounts of organic matter in order to make better comparisons. However, as the methods for these two parameters measure not in absolute units but in relative units, no such calculations have been made yet. Maybe this can be done in the future, when more data and experience have been achieved.

Acknowledgements

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Table 1. Sampling stations for oxidability and organic carbon

| Station code | Position | | Number of samplings | |
|-------------------|--------------|-------------|---------------------|-------------|
| | | | Oxidability | Org. carbon |
| SW Vinga | N 57° 38.5' | E 11° 26.6' | 8 | 6 |
| Djupa rännan | N 57° 33' | E 11° 31' | 1 | 0 |
| N Läsö | N 57° 30.3' | E 11° 08.5' | 1 | 0 |
| E Fredrikshamn | N 57° 26' | E 10° 42.5' | 1 | 0 |
| Läsö ränna | N 57° 12' | E 10° 44' | 1 | 0 |
| Ålborg bukt | N 56° 51' | E 10° 48.5' | 1 | 0 |
| W Anholt | N 56° 39' | E 11° 18.5' | 1 | 0 |
| Grenå II | N 56° 29' | E 11° 19' | 1 | 0 |
| Kattegatt SW | N 56° 07' | E 11° 10' | 1 | 0 |
| SE Hesselö | N 56° 10' | E 11° 48' | 1 | 0 |
| Kullen | N 56° 15' | E 12° 24.5' | 1 | 0 |
| W Tylön | N 56° 37' | E 12° 34' | 1 | 0 |
| SW Varberg | N 57° 01' | E 12° 12.5' | 1 | 0 |
| E Fladen | N 57° 12.5' | E 11° 58' | 1 | 0 |
| SW Tistlarna | N 57° 26.5' | E 11° 41' | 1 | 0 |
| Lilla Middelgrund | N 56° 57.5' | E 11° 45.5' | 8 | 6 |
| BY 5 | N 55° 15' | E 15° 59' | 9 | 6 |
| Hanö Bight | N 55° 37' | E 14° 52' | 3 | 1 |
| BY 8 | N 55° 38' | E 18° 36' | 1 | 0 |
| BY 9 | N 56° 05' | E 19° 10' | 8 | 4 |
| BY 15 | N 57° 20' | E 20° 03' | 8 | 7 |
| BY 22 | N 59° 55' | E 25° 36' | 2 | 2 |
| BY 25 | N 59° 35' | E 23° 18' | 1 | 0 |
| BY 27 | N 59° 17.80' | E 21° 34' | 7 | 5 |
| BY 29 | N 58° 53' | E 20° 19' | 1 | 0 |
| BY 31 | N 58° 35' | E 18° 14' | 8 | 5 |
| BY 38 | N 57° 07' | E 17° 40' | 7 | 4 |
| F 64 | N 60° 13' | E 19° 04' | 3 | 2 |
| F 28b | N 61° 07.2' | E 20° 37' | 1 | 0 |
| F 29a | N 61° 06.5' | E 20° 16' | 2 | 0 |
| F 29b | N 61° 06' | E 19° 57' | 2 | 2 |
| F 30a | N 61° 05' | E 19° 35' | 2 | 0 |
| F 31a | N 61° 04.5' | E 18° 37' | 1 | 0 |
| F 32a | N 61° 12' | E 17° 52' | 2 | 0 |
| F 32b | N 61° 15.5' | E 17° 28' | 1 | 0 |
| MS 2 | N 61° 08' | E 17° 51.5' | 1 | 0 |
| MS 4 | N 62° 06' | E 18° 32.5' | 2 | 0 |
| MS 10 | N 61° 41' | E 21° 00' | 1 | 0 |
| F 26 | N 61° 59' | E 20° 04' | 2 | 1 |
| F 24 | N 62° 51' | E 18° 52' | 2 | 0 |
| F 8 | N 64° 40.5' | E 22° 44' | 2 | 1 |
| F 9 | N 64° 42' | E 22° 03' | 2 | 0 |
| F 3 | N 65° 10' | E 23° 14' | 1 | 0 |

| Investigation | Regression equation | Correln. coeff. | Mean error | Oxidability (=X) | | | Total Organic Carbon (=Y) | | |
|--------------------------|------------------------------------|-----------------|------------|------------------|---------------|------------|---------------------------|---------------|------------|
| | | | | mean of X | std.dev. of X | range of X | mean of Y | std.dev. of Y | range of Y |
| Szekielda ₅₆ | Org C=2.40+0.150·KMnO ₄ | 0.3047 | 0.1212 | 5.24 | 2.69 | 0.12-11.38 | 3.19 | 1.30 | 1.17-6.26 |
| Beckman ₁₀₆ | Org C=2.67+0.144·KMnO ₄ | 0.4097 | 0.0808 | 11.5 | 4.27 | 1 - 23 | 4.32 | 1.45 | 0.9 - 8.3 |
| Beckman ₉₇ | Org C=2.24+0.158·KMnO ₄ | 0.5783 | 0.0676 | 11.5 | 4.45 | 1 - 23 | 4.06 | 1.21 | 0.9 - 6.2 |
| OI ₈₀ | Org C=1.84+0.112·KMnO ₄ | 0.7354 | 0.0523 | 11.2 | 4.48 | 1 - 19 | 3.10 | 0.69 | 1.2 - 4.5 |
| Lundstedt ₉₂₉ | Org C=1.9+~0.139·KMnO ₄ | 0.97 | ? | ? | ? | ~10 - ~400 | ? | ? | ~2 - ~70 |

Table 3

| Investigation | Regression equation | Correln. coeff. | Mean error | Yellow substance (=X) | | | Oxidability (=Y) | | |
|-------------------------------------|--|-----------------|------------|-----------------------|---------------|------------|------------------|---------------|------------|
| | | | | mean of X | std.dev. of X | range of X | mean of Y | std.dev. of Y | range of Y |
| (Bladh and Carlberg) ₁₀₄ | KMnO ₄ = 2.37 + + 11.06·Yellow substance | 0.7131 | 0.0480 | 0.70 | 0.28 | 0.04-1.47 | 10.14 | 4.12 | 1 - 19 |

10°

15°

20°

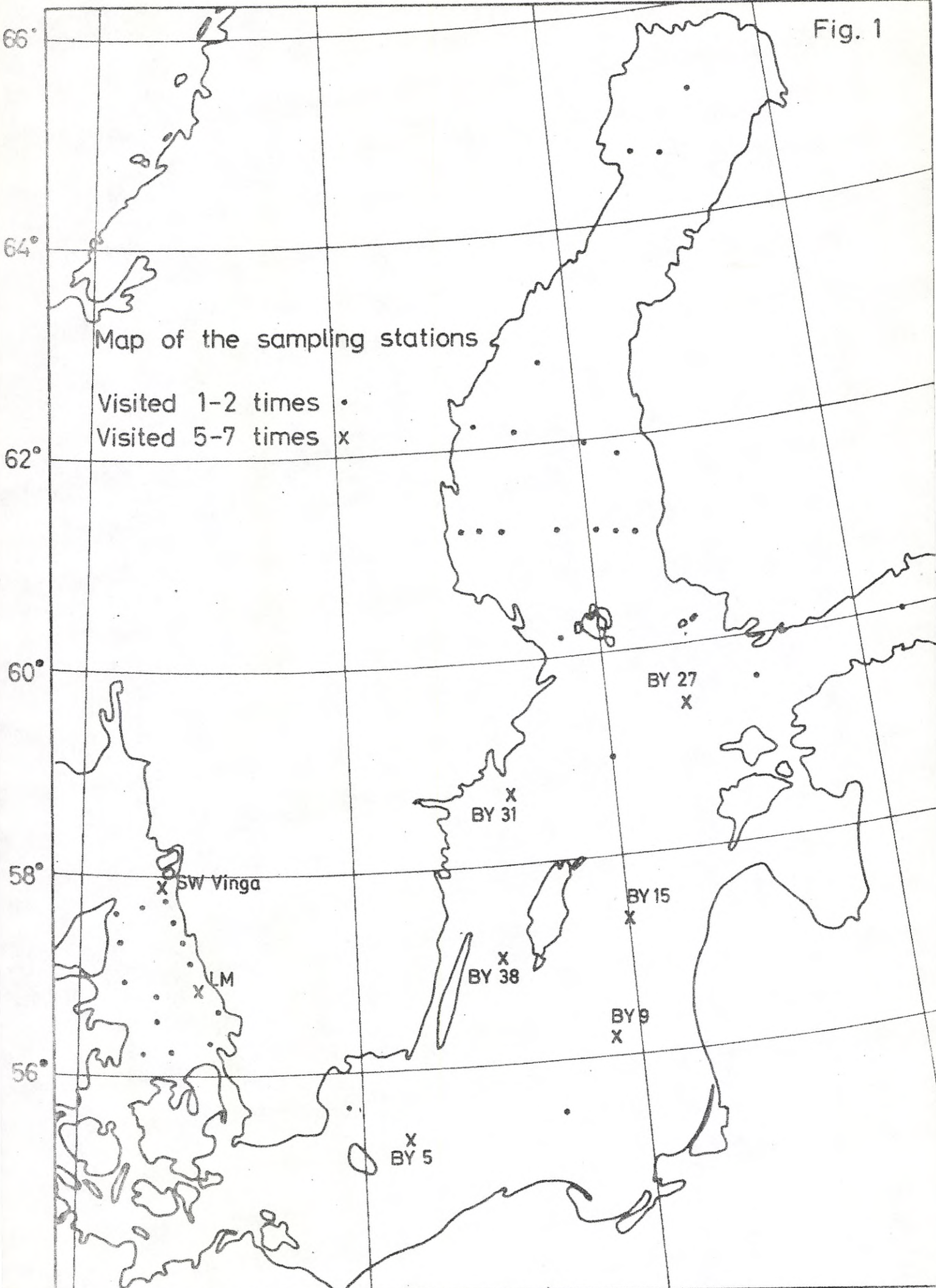
25°

Fig. 1

Map of the sampling stations

Visited 1-2 times •

Visited 5-7 times x



10°

15°

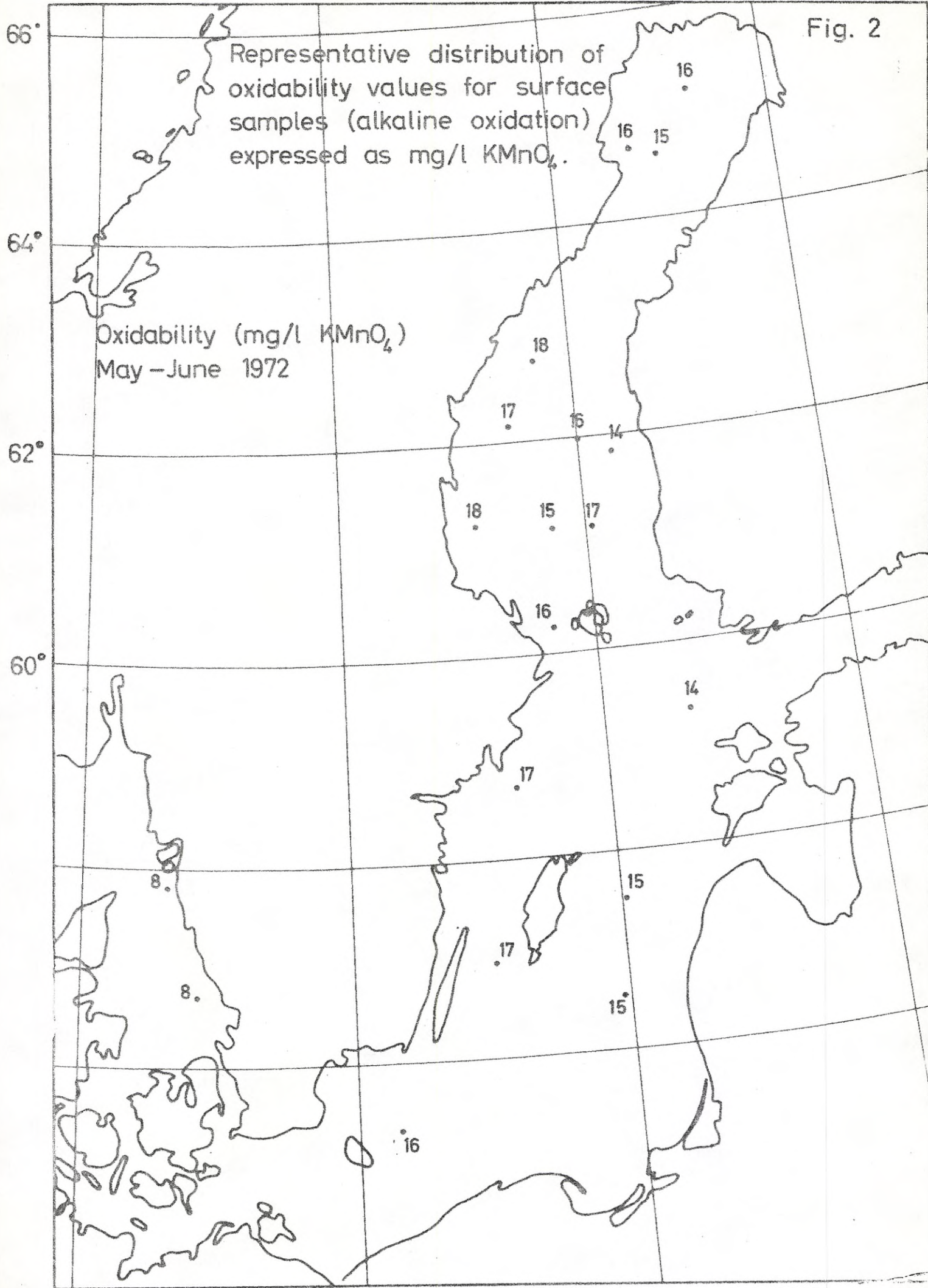
20°

25°

Fig. 2

Representative distribution of oxidability values for surface samples (alkaline oxidation) expressed as mg/l KMnO_4 .

Oxidability (mg/l KMnO_4)
May - June 1972



Organic carbon (mg/l) versus oxidability (mg/l KMnO_4).
Material from Szekiolda (1968).

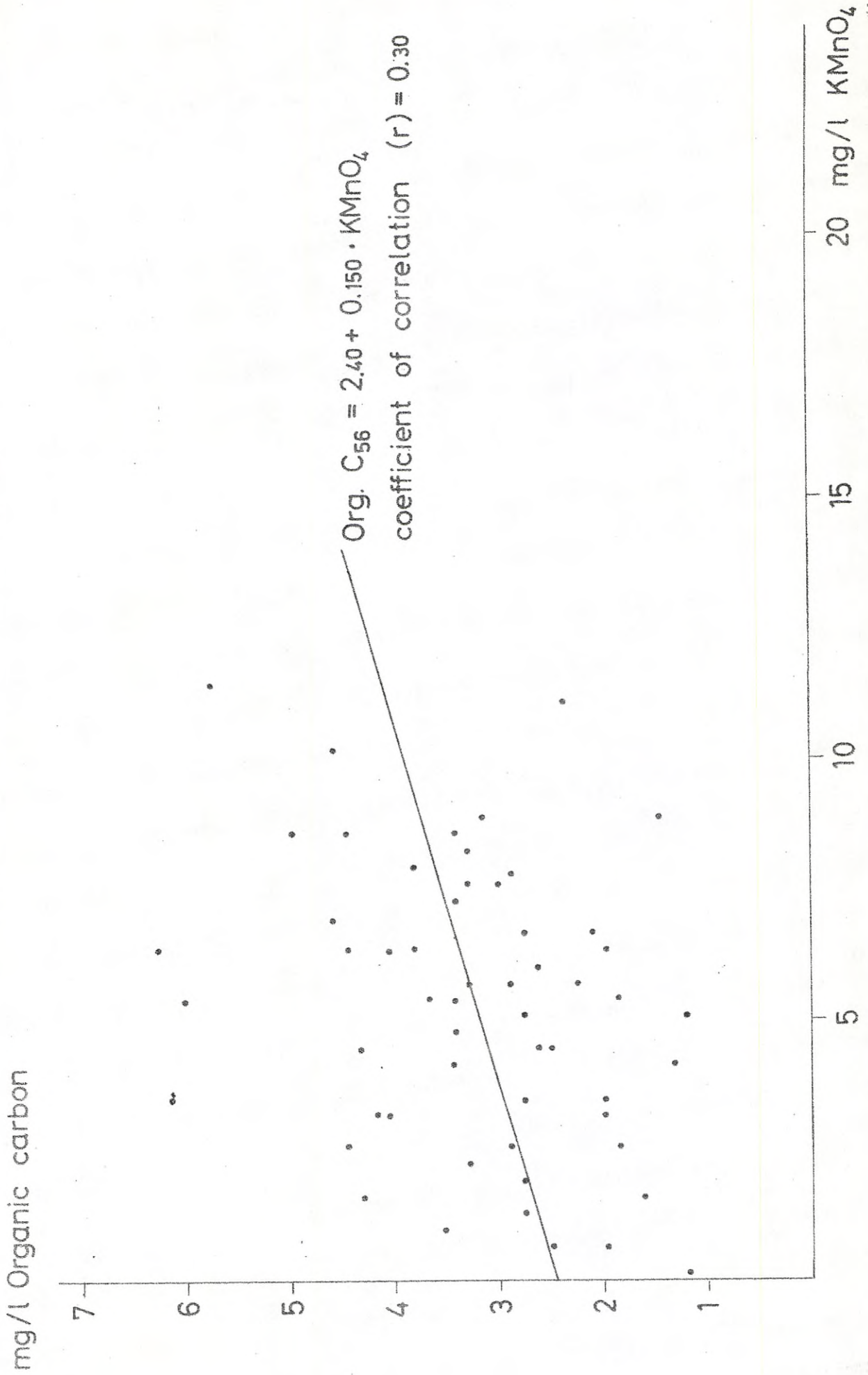


Fig. 3

Organic carbon (mg/l) versus oxidability (mg/l KMnO_4).

Beckman instrument.

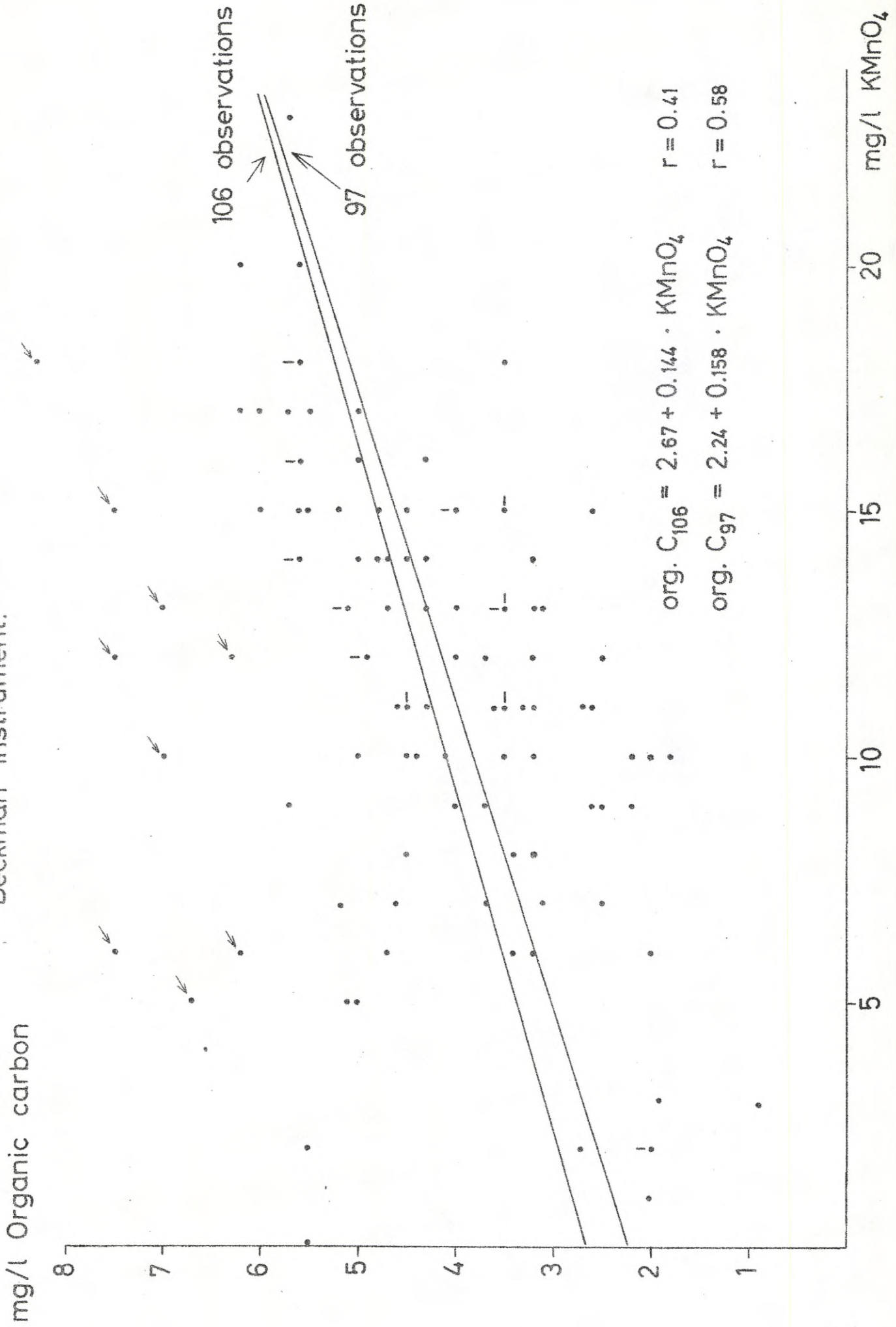


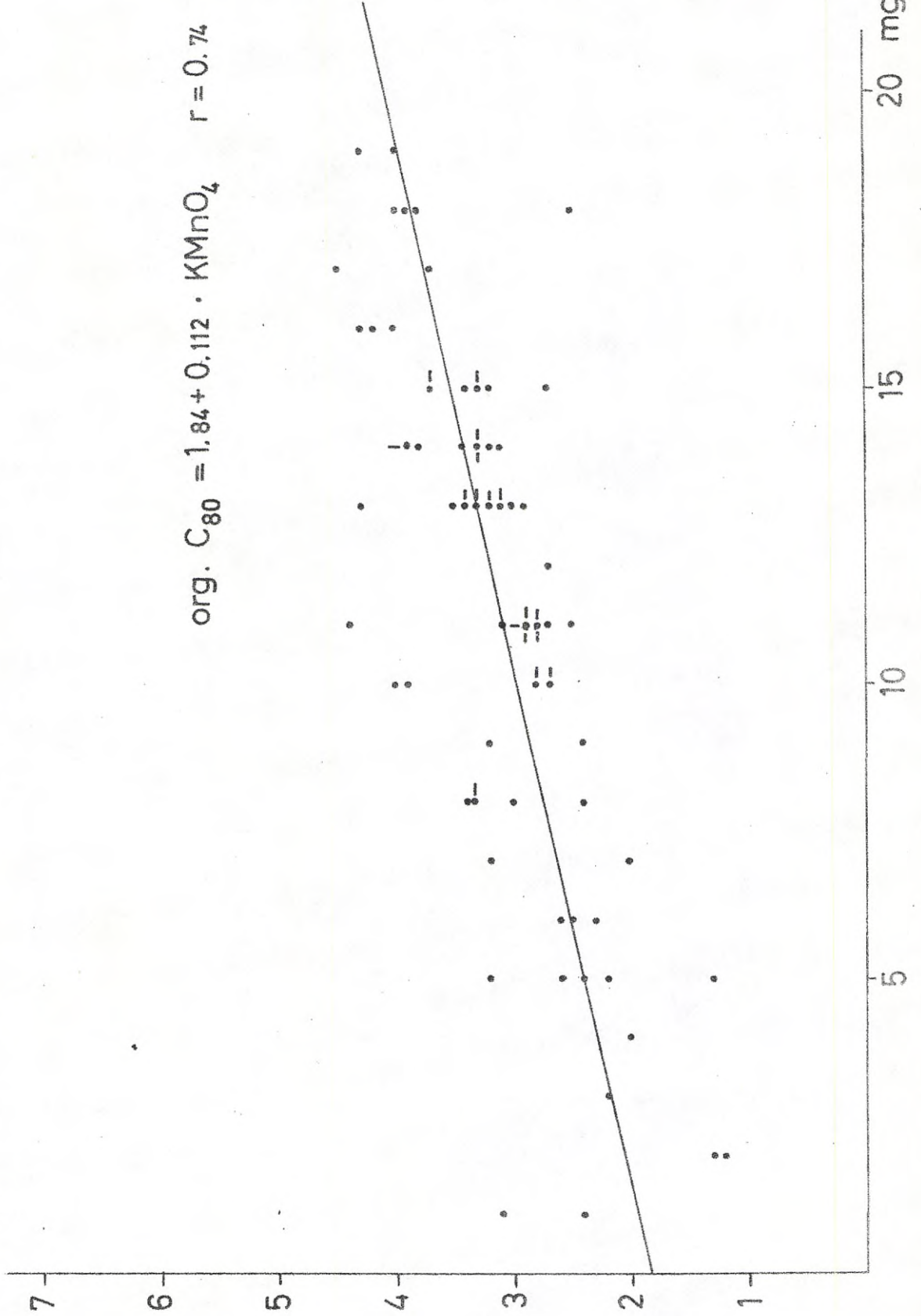
Fig. 4

Organic carbon (mg/l) versus oxidability (mg/l KMnO_4).

Oceanography International instrument.

mg/l Organic carbon

$$\text{org. C}_{80} = 1.84 + 0.112 \cdot \text{KMnO}_4 \quad r = 0.74$$



Comparison of the different regression lines for the relation between organic carbon and oxidability.

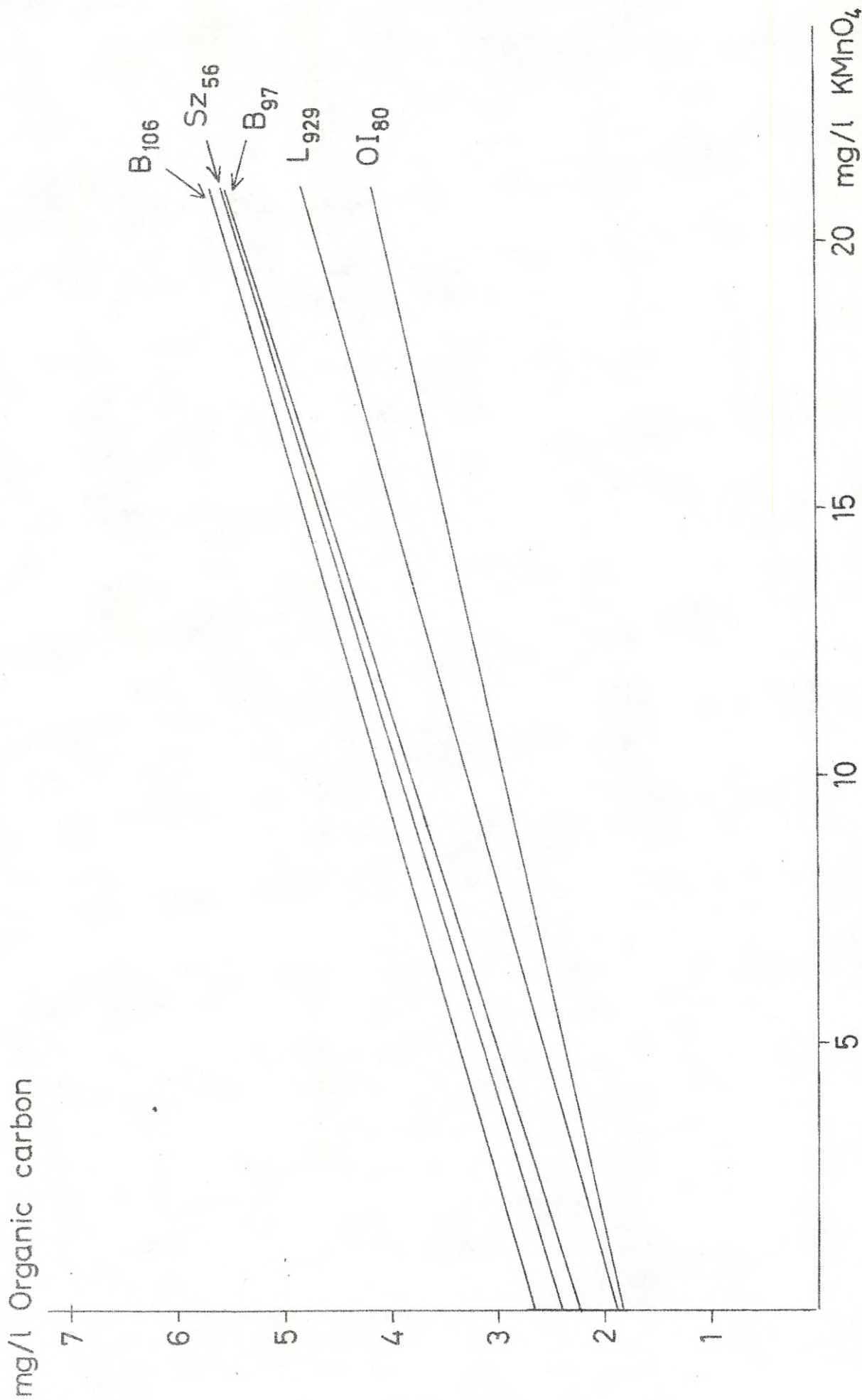


Fig. 6

mg/l Organic carbon

Organic carbon versus organic phosphorus.

Beckman instrument (•)

Oceanography International instr. (+)

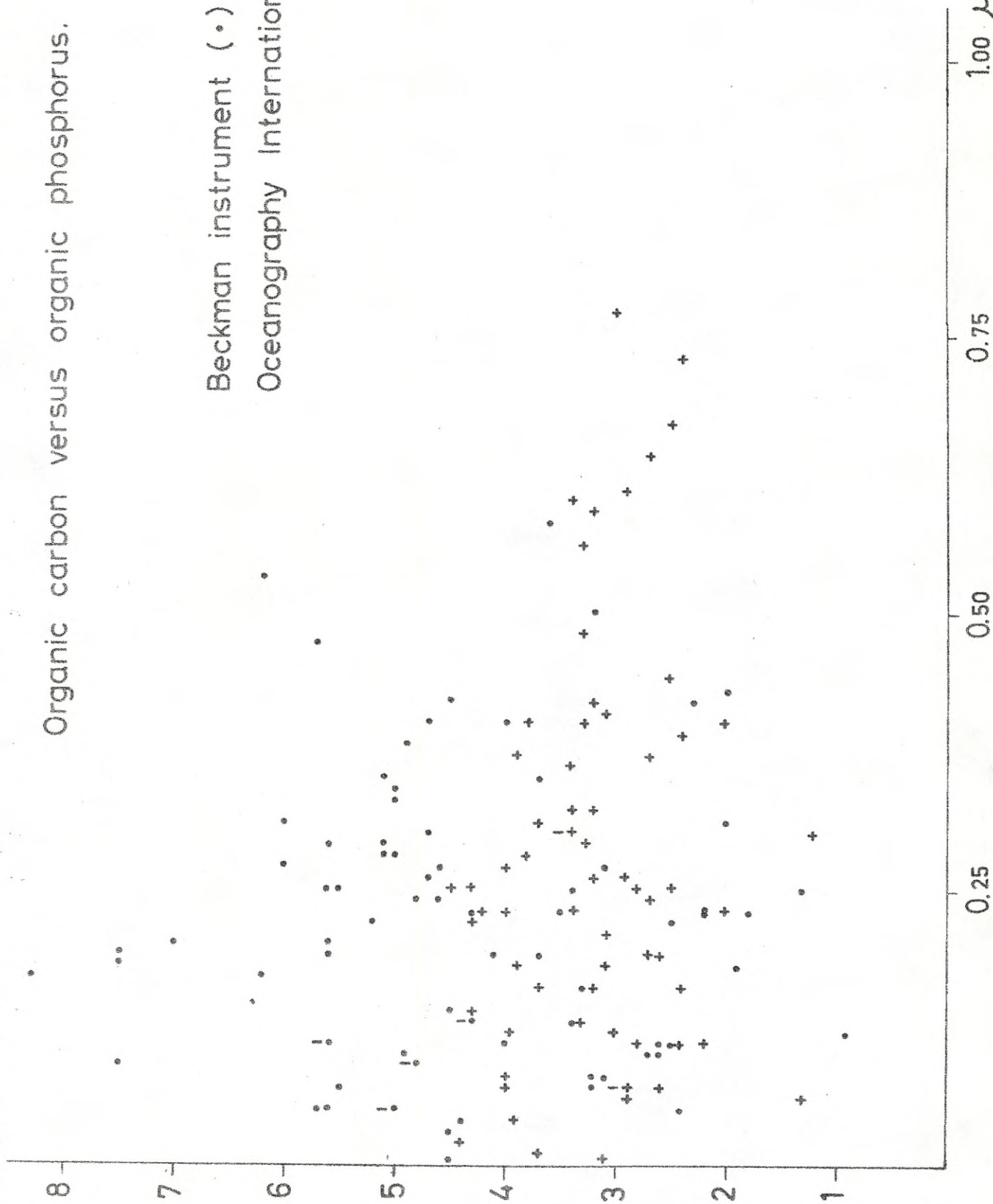


Fig. 7

Total organic carbon plotted versus salinity
184 samples

Beckman apparatus (·)

Oceanography International apparatus (+)

mg/l Organic Carbon

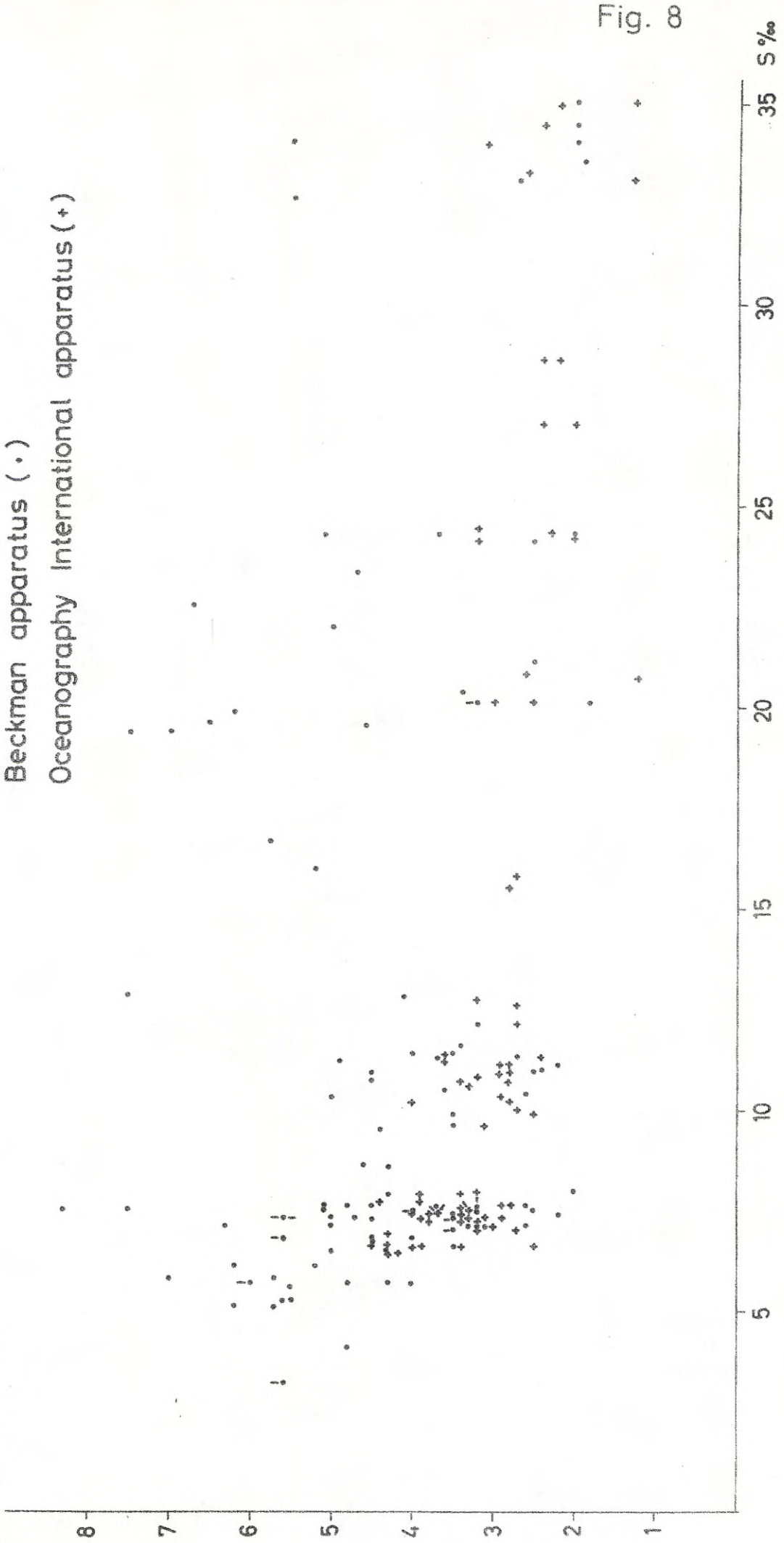
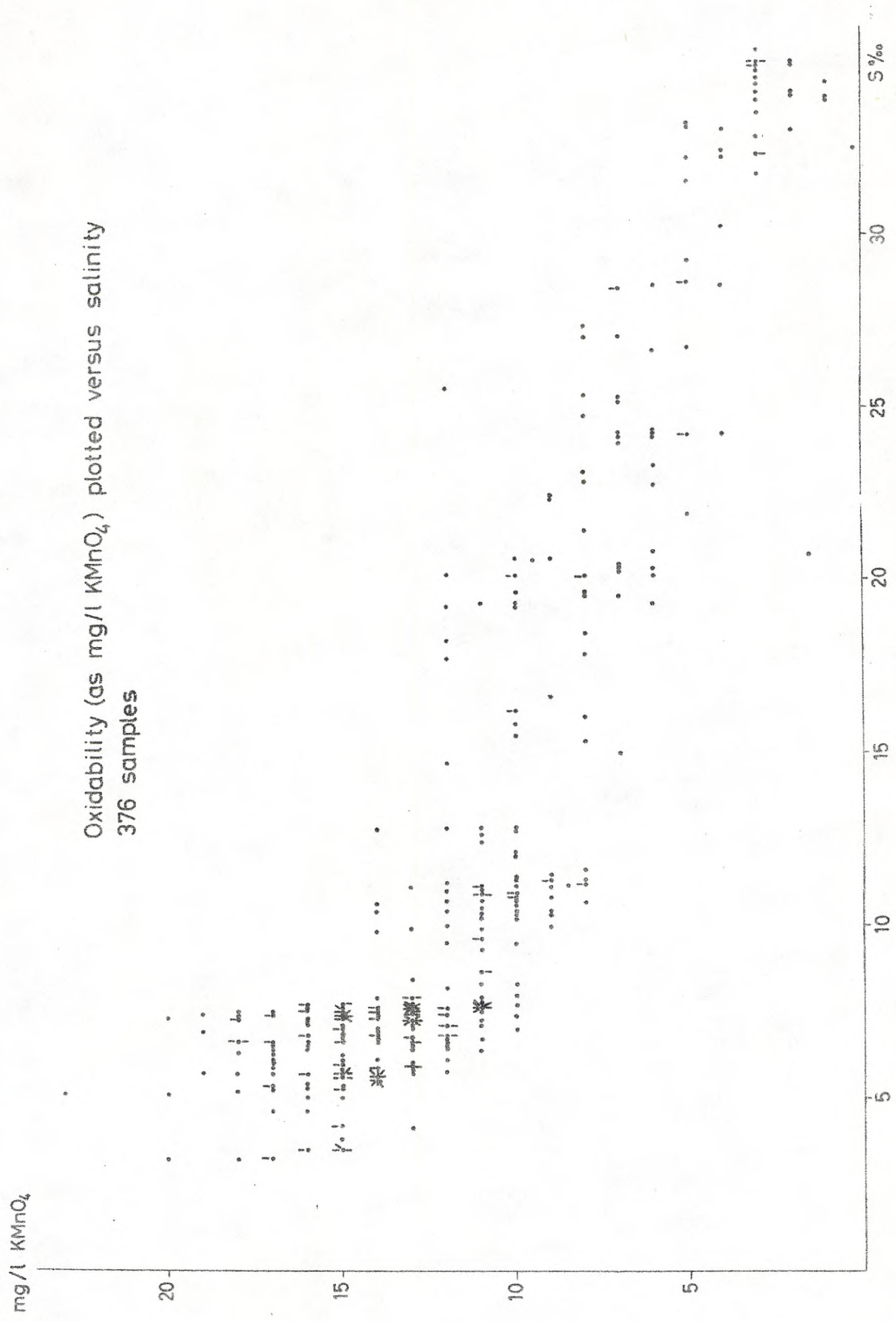


Fig. 8

Fig. 9



Yellow substance (as m^{-1}) versus salinity

MAY - JUNE 1972

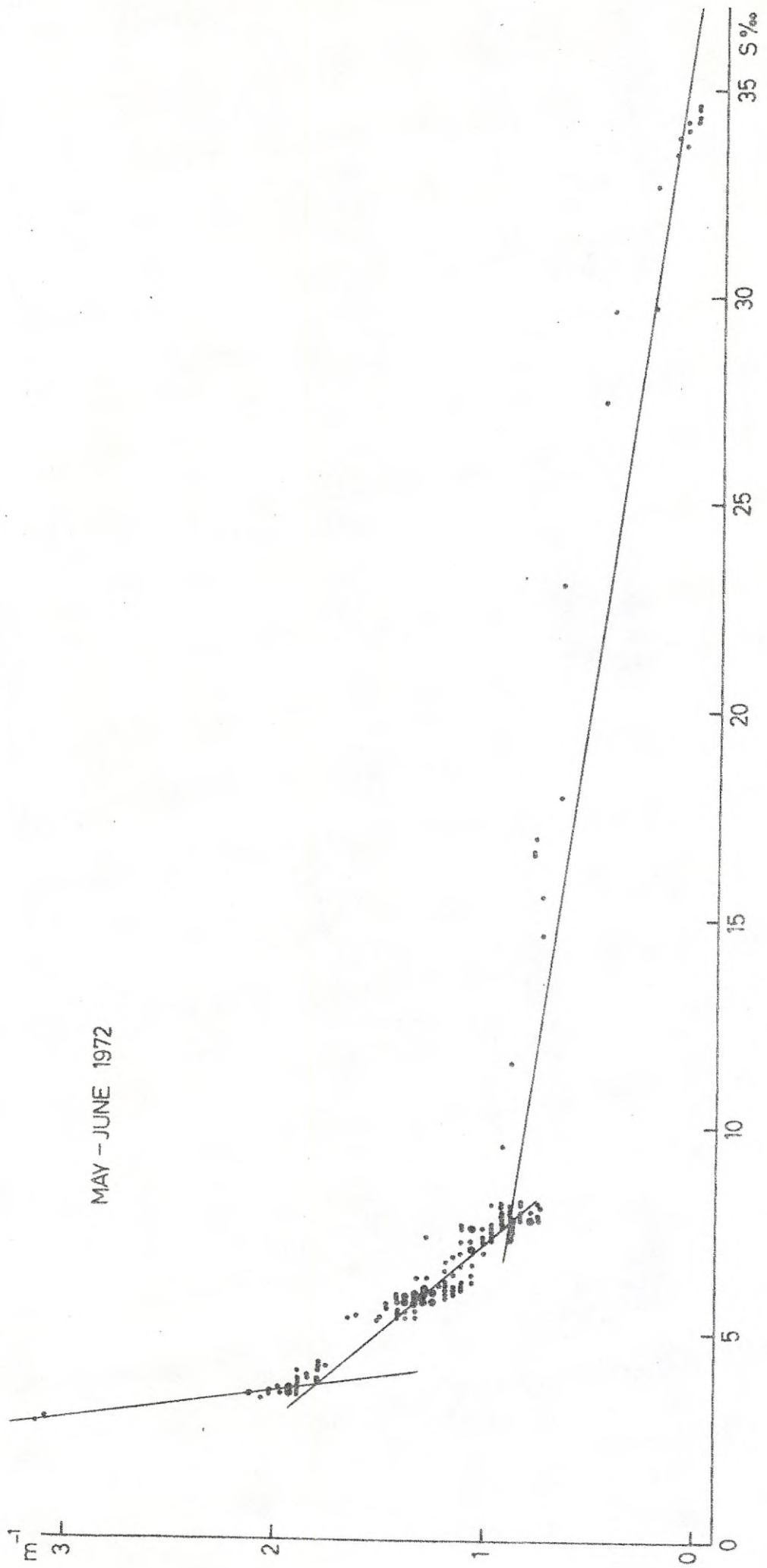


Fig.10

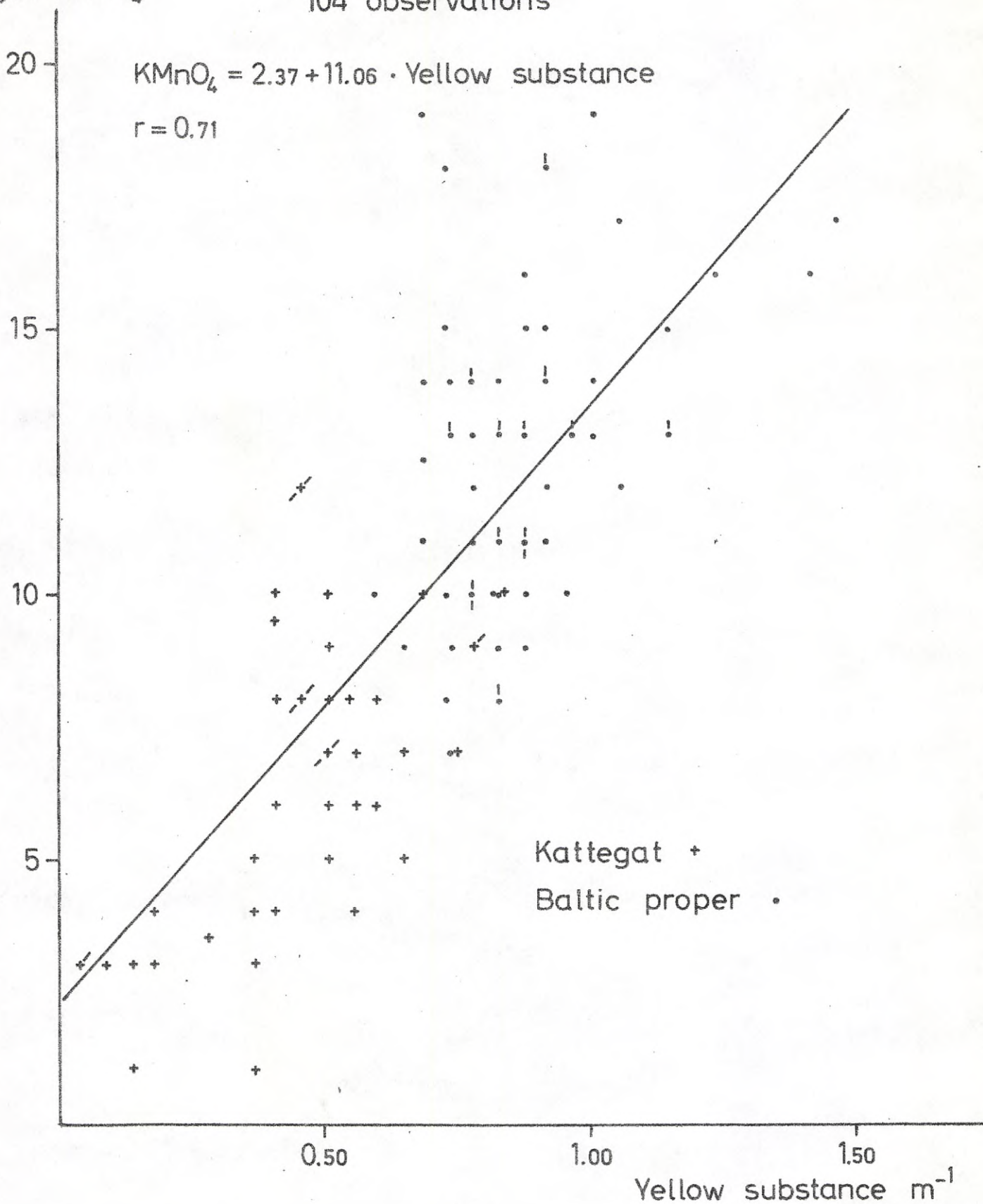
Oxidability (as mg/l KMnO_4) versus
yellow substance

104 observations

mg/l KMnO_4

$$\text{KMnO}_4 = 2.37 + 11.06 \cdot \text{Yellow substance}$$

$$r = 0.71$$



Organic carbon and oxidability. Kattegat compared with the Baltic proper.

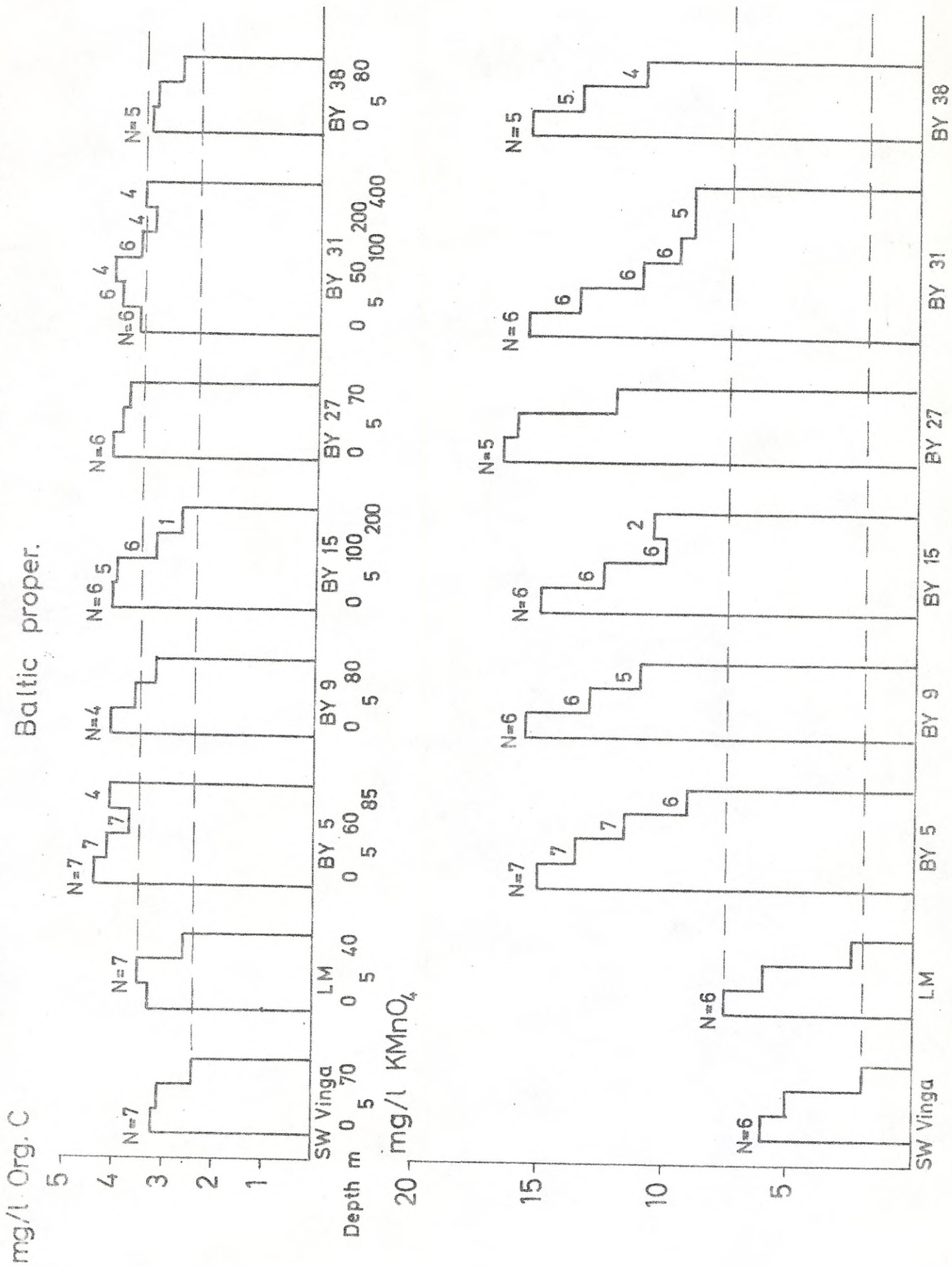


Fig. 12

