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The results of bichromate and permanganate methods application in analytical investigations of the Baltic Sea water.

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Carbon-main element of organic molecules,is widely used in hydrochemical characteristics of regimes.The fact that the value of $C_{org.}$,summerizing the quantity of a given skeletal element of organic compounds different by origin and classification in natural waters,is analytically easier stated in comparison with quantitative identification of different classes of organic matters is of no small importance.

Hydrochemical category "$C_{org.diss.}$" includes the essential part of organic matter dispersed in natural waters.Used in absolute analytical method,it takes into account metabolits of organisms,substances of transformation of vital activity products of hydrobionts(water humus),organic matters of soil and industrial origin.The spectrum of organic compounds must be highly extensive and dynamic in the Baltic Sea where the role of river flow is very great and surrounding countries are highly developed,with considerable density of population.In such a situation information obtained through the determination of integral value of "$C_{org.diss.}$" has limited and generalizing character.The latter is valuable when given ingradient is used as control parameter in conditions of increasing pollution of natural waters.

The regime of organic matter,especially its dissolved part,(by $C_{org.}$) in the Baltic has been studied relatively poorly. Concerned with a concrete region of the sea,investigations were carried out in a short period of time(2,6)that prevented from making common view about the regime of organic substance and its peculiarities in the Baltic Sea.

Materials and methods

The content of dissolved organic matter in the Baltic Sea

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was studied in I971-I973. Material was collected at standard horizons of bench-marked stations of "Baltic Year-69" program: 2A, 5A, 9A, I5A, 20A, 28B, 32B-characterizing 6 Deeps of the sea (fig.I). Samples of water were filtered through preliminary treated membrane filters with pore size-0,9mk; filtrate was fixed by metalic mercury, and then it was analysed under coastal conditions. $C_{org.diss.}$ concentration was determined by bichromate(4) and permanganate(I) micromethods.

In bichromate method test-tubes of volume of about 35ml were filled in with samples of water (halogen-ion concentration≤ IIOmg and organically bound carbon≤I15mg) by pipette, then 2-3 drops of 0,6N Na_2CO_3 were added to the samples up to pH equal to 9 and the solution was evaporated at temperature of about 70°C in drying cabinet. I ml of I,IN solution of $HgSO_4$ in 6N H_2SO_4 and then 0,5N solution of $K_2Cr_2O_7$ and 0,55N solution of $HgSO_4$ in 6N H_2SO_4 by 5ml were added to the evaporated samples and in the test-tubes, assigned for the control testing, by automatic pipette with fixed, for series, angle of inclination. Samples were intermixed and 4ml of 0,05N solution of Ag_2SO_4 in concentrated H_2SO_4 were added to them. The test-tubes were shut to with reflux condensers and then were put into already heated thermostat to carry out oxidation process. Not influencing the results, reflux condensers may be substituted by Kjeldhal nozzle-condensers. Temperature of oxidation mixture (IOO°C) was fixed 30 minutes before and was kept on this level (±2°C) during subsequent I hour period.

Samples were cooled off in 30 minutes, then by turns they were quantitatively placed into IOOml flasks where residual bichromate was titrimetrically determined by 0,IN solution of ferrous ammonium sulphate in presence of phenylanthranilic acid. The value of burette scale division-0,OIml, the volume of a drop-0,OI5 ml. $C_{org.diss.}$ content in samples was counted by COD value according to the equation of burning-carbon oxidation reaction in excess oxygen conditions. Amendment on $K_2Cr_2O_7$ consumption in halogen-ion oxidation, complexed with mercury, was calculated by the curve fitted upon the solutions of "sea salt" made free from organic matter.

Precision of the analysis is 0,I5mg/l, reproduction of results-3-5%, method sensitiveness-2mgC/l. Draughts of applied apparatus, burettes and test-tubes are published.(4) Conditions of the method promote practically complete oxidation of such, stable to decomposition,organic compounds,as aminoacids-asparagin and glycin.

Simultaneously permanganate oxidizability of organic matter in neutral medium(I) was determined.Microvariant of the method was used.

Different ability of humic compounds and substances of plankton humus for oxidation by permanganate in neutral medium was used for differentiation of dissolved organic matter of the Baltic Sea into terrigenous-soil and autochtonous-plankton fractions.Based upon experimental data(3,5) and confirmed by the results of analytical study of natural samples of oceanic and fresh water(3),an equation was worked out to estimate,with some approximateness,concentration of natural organic matter:

$A=0,045(C-B)+0,275B$,

where

$B=4,35A-0,20C$;

A-neutral permaganate oxidizability value,mgC/l;

B-humic substance quantity,mgC/l;

C-bichromate oxidizability value,mgC/l.

Calculation error did not exceed IO%;only analytical error of methods and fixed variations of oxidation coefficients were taken into account.

Proceeding from the above cited equation,it was found that in ratio of autochtonous and allochtonous fractions in dissolved organic matter as I:I,the share of terrigenous substance in the value of permanganate oxidizability is equal to 86%.Even increasing the ratio up to 3:I,given value is comparatively high-67%.

Thus,the value of neutral permanganate oxidizability,taken separately,may be regarded as highly specific,but of relative character,index of humic substance content.

Results

Concentration of dissolved organic matter in the Baltic Sea in I97I-I973 fluctuated in 2,0-II,3mgC/l diapason.Certain seasonal dynamics of "$C_{org.diss.}$" value(fig.2,3,4) and its dependence upon the location of measurement point and the depth of sampling(fig.3,4) is determined.The decrease of organic matter content over all area of the Baltic in I973 should be pointed out.

Relatively frequent hydrochemical observations in I972 made it possible to reveal spring maximum value of organically bound carbon in Gotland Deep and observe its development in February-May(5). Concrete peak remained during April(fig.2). Biochemical and physiological processes, causing it, served as a source of increase of organic matter abundance in deep layer.

In deep thickness of the Gotland Basin peaks of organic matter concentrations were observed. The depth of their location is hypothetically associated with oxidation-reduction conditions in the Deep, with upper boundary of hydrogen sulphide zone extention(fig.5). It is supposed that determined $C_{org.diss}$ maximum values are inderectly connected with activity of autotrophic microorganisms-chemosynthetics.

Terrigenous organic matter is medium natural factor effecting production process in the Baltic. The abundance of humic substances in 0-40m layer of the sea in 1972 changed within the limits of I,6-3,0mgC/l;20-50% of $C_{org.diss.}$ falls to their share. With a purpose of comparison it should be mentioned that in May of the same year in southern part of the Gulf of Riga(layer 0-I0m) stated values reached 5,8mgC/l and 70%. Soil substance content decreased with depth. We consider that a significant part is played by halocline existing in the sea. The break of stability of humic-iron colloid system, their partial coagulation and sedimentation, caused by sharp increase of electrolyte concentration in halocline, may take place. Particular conception is confirmed by the results of investigations of suspended phase of substances in deep-water regions of the Baltic. Experiments on the samples from different regions of the Baltic Sea(0-40 layer)showed that in August I971 organic matter fraction, precipitated by aluminium hydroxide, made up 20-40%. Thus, method, practically taking into account substances of colloid degree of dispersion, gave the results close to the values obtained by calculation mathod based upon measurements of bichromate and permanganate oxidizability of organic matter dissolved in water.

Conclusions

Obtained results of investigation should be estimated as a certain step in enrichment of Baltic Sea knowledge:

I)of regularities of space-time dynamics of organic matter concentration, its casual connections with changes in biological, physical and chemical parameters of medium;

2) of components of organic compounds system, significant from the point of view of their effect on biohydrochemical regime of the sea.

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Figures

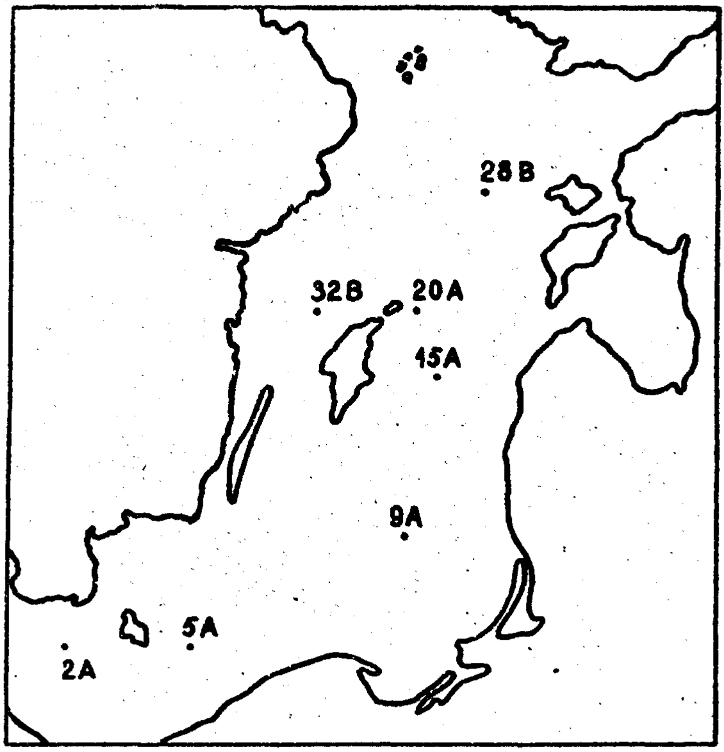
I)Scheme of stations location in the Baltic Sea.

2)Changes of average weighted value of $C_{org.diss.}$ in water thickness(0-230m) during the year(station I5A).

3)Distribution of $C_{org.diss.}$ concentration (mg/l) in the Baltic Sea in I972:I-February,2-May.

4)Distribution of $C_{org.diss.}$ concentrations(mg/l) in the Baltic Sea in I972:I-August,2-October.

5)Dynamics of bedding depth of izooxen 0,3;0,2;0,I;0ml/l and vertical distribution of $C_{org.diss.}$ concentration peaks by Years(station I5A).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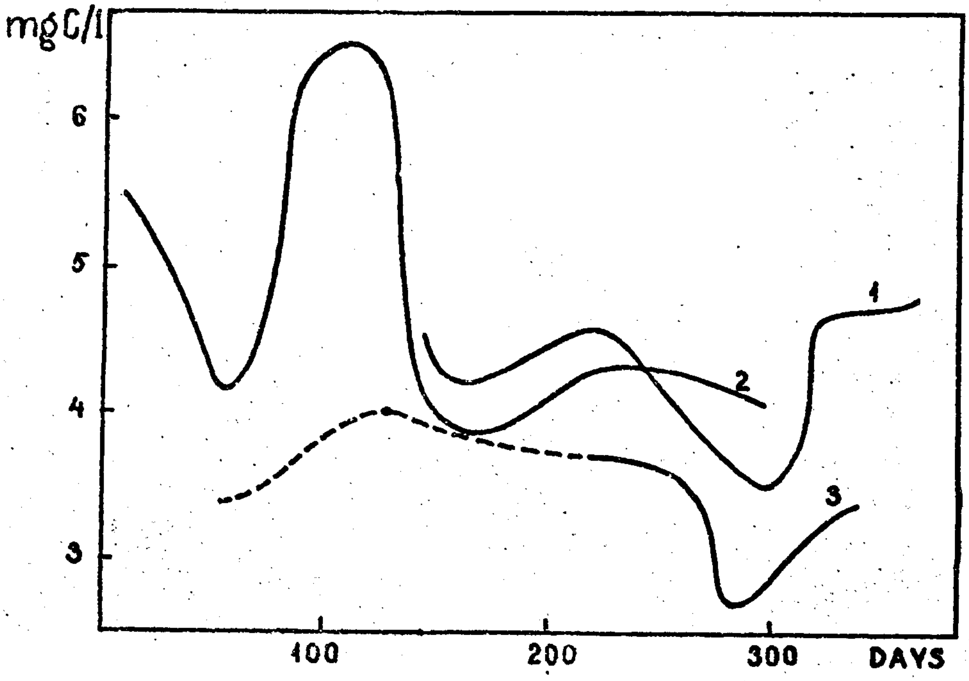
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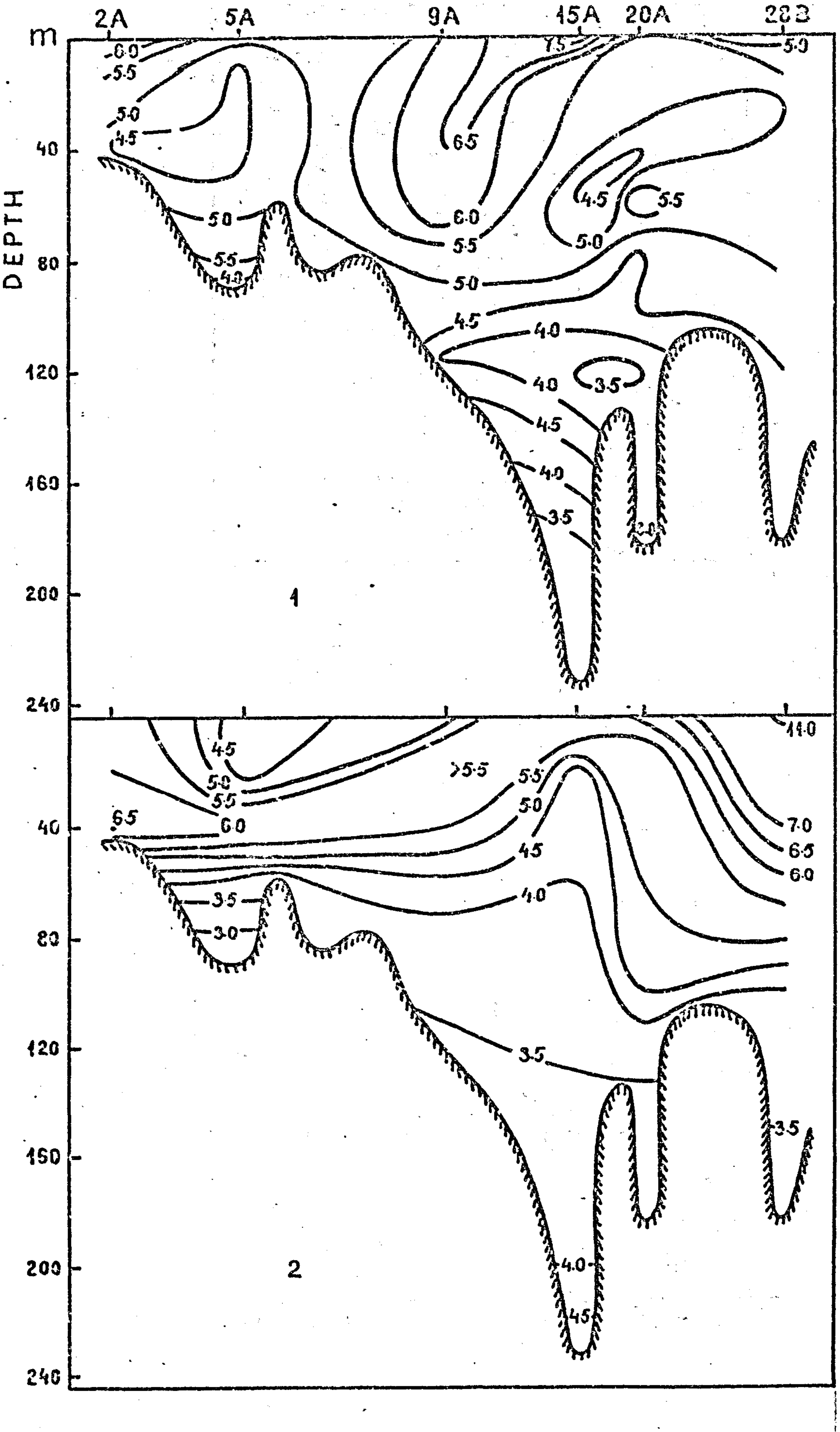
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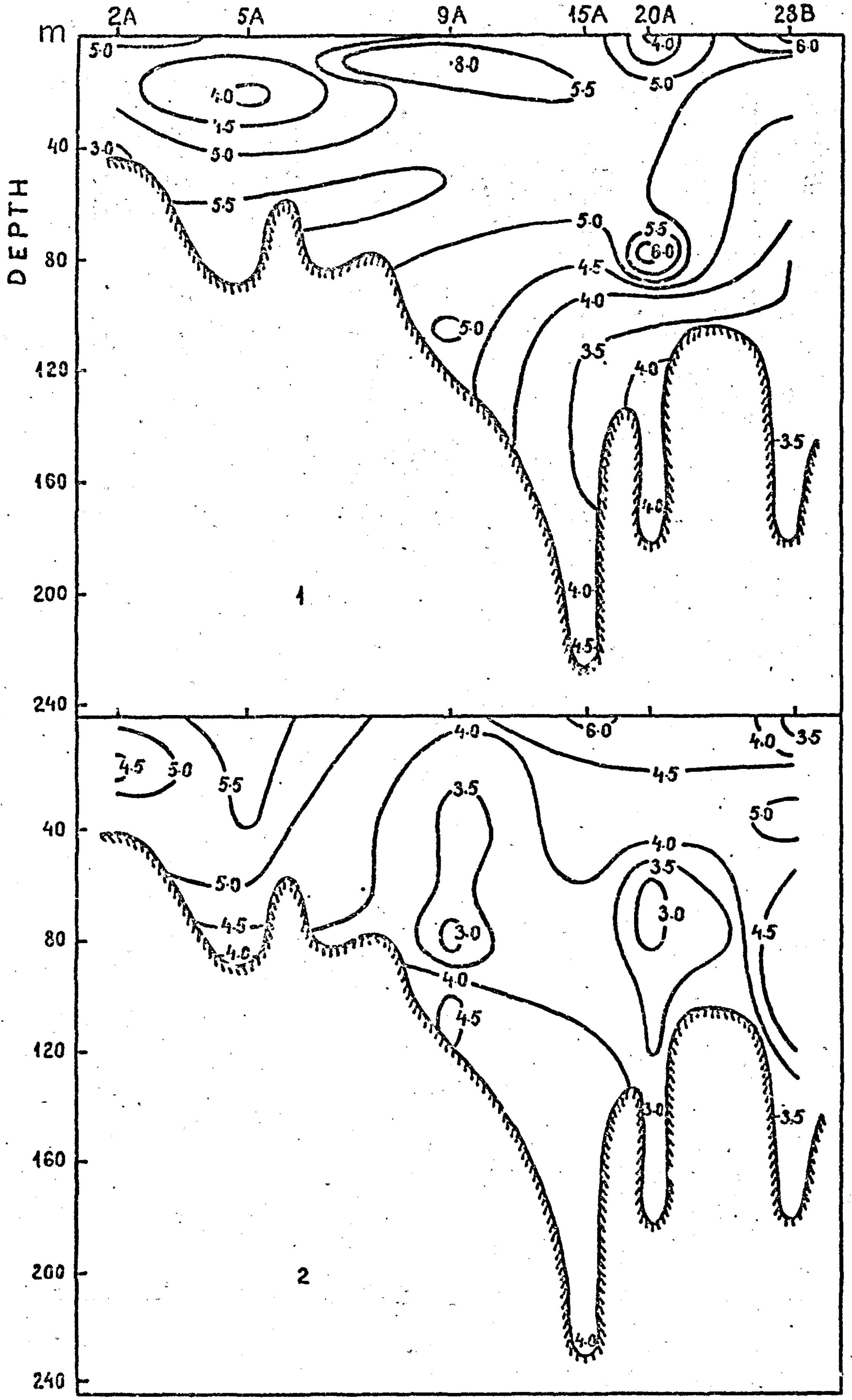
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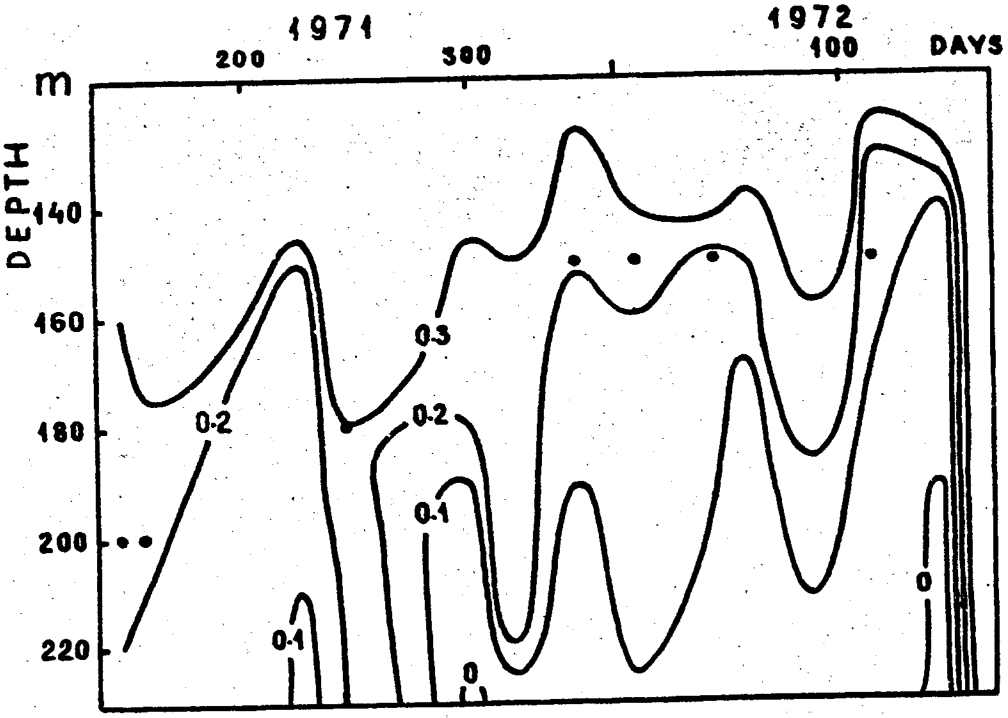

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