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CHLORINATED BYPRODUCTS FROM VINYL CHLORIDE PRODUCTION – A NEW SOURCE OF MARINE POLLUTION

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by

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CONTENTS

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Abstract

When chlorinating aliphatic hydrocarbons, numerous unwanted chlorinated aliphatic hydrocarbons (C-Cl) are formed. These byproducts amounting at least 75 000 tons per year in Northern Europe alone, are commonly burned at sea in special vessels or dumped into the sea.

The rate of accumulation of C-Cl to living organisms, as well as the degradation and solubility in sea water have been studied. Estimations of the C-Cl have been done on samples of sea water and marine organisms collected during cruises, and from land stations in the North Sea, along the Norwegian coast and in the Barents Sea.

In attempts to establish data to be used in assessments of the possible harmful effects of C-Cl, some laboratory experiments dealing with acute effects of these substances have been performed on algae, invertebrates and fish.

The preliminary data indicate that the highest concentration of C-Cl found in the open sea is about one tenth of the lowest value found to cause an unequivocal acute biological effect.

1 INTRODUCTION

Unwanted chlorinated aliphatic hydrocarbons (C-Cl) are formed as by-products in for example vinyl chloride production. Reports in May 1970 on dumping of large quantities of C-Cl into the sea, and the lack of knowledge as to possible effects on marine organisms, initiated a joint Norwegian/Swedish research programme. This includes field studies and laboratory experimants.

The first report from one of the research vessels engaged, "Johan Hjort", indicated that C-Cl is an even more serious problem than originally assumed. The report stated (translated):".... high densities of particles were observed, and within some areas the sea was coloured red-white by the particles. Samples were taken from station 710 (57°00' NB, 4°18' EL). Fish in bad condition were observed in the surface water and the particles could be seen down to a depth of about 2-3 m. They looked like dead plankton. The weather conditions were good during the two days the particles were observed" (cruise distance 70 nautic miles, indicated by the arrow in fig. 1). Subsequent analysis have verified the assumption that the particles were dead plankton (mainly Calanus finmarkicus, stage IV and V), and has also shown that the plankton, fish(cod of 3 cm length) and water sampled contained C-Cl.

The purpose of the present paper is to draw attention to the pollution problem arisen from chlorinated compounds other than DDT and PCB by giving short descriptions of the results obtained so far.

2 MATERIALS AND METHODS

Sea water and biological material have been sampled at stations covering a large part of the North Atlantic waters (fig. 1) during the period June 18th to Sept. 28th 1970. This was made possible mainly by the kind cooperation of the leaders of already scheduled cruises for R/V "Johan Hjort" and R/V "G.O. Sars" and also by specially designed cruises with the smaller vessels "Peder Rönnestad", "G.M. Dannevig" and "Gunnar Knudsen". Most of the biological material, however, was sampled by other means along the Norwegian coast. Water was collected by means of conventional Hansen bottles, tapped and stored in glass bottles stoppered with screw caps (insulated from the water by a double layer of Al-foil) until analysed. Fifty species of animals have been collected (invertebrates,

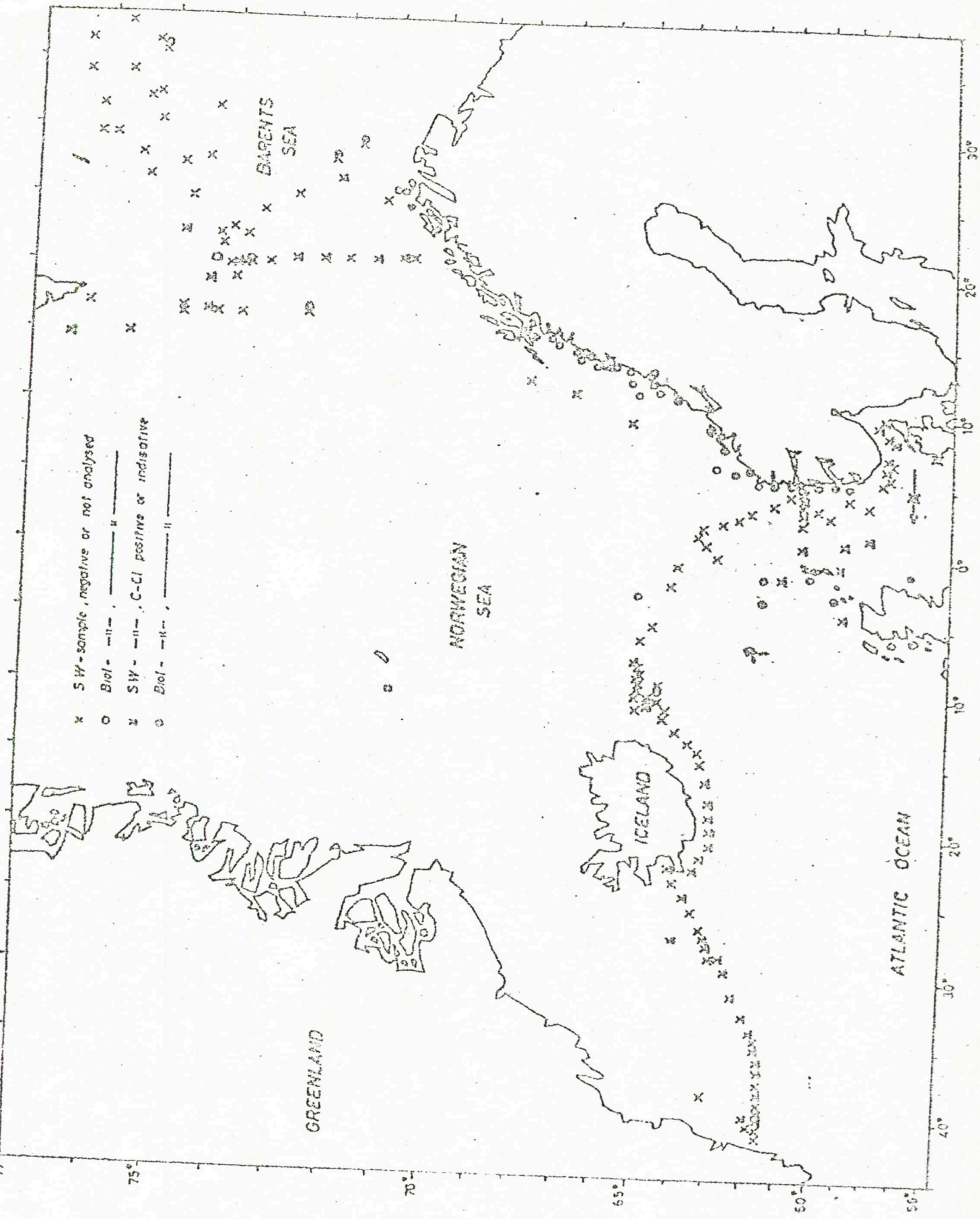

Fig. 1 On the map positions of sampling are given

elasmobranchs, teleosts, birds and grey seal). Samples of about 10 g were collected, wrapped in Al-foil, quickly deep frozen and stored at - 40°. So far mainly fish (epaxial muscle) have been analysed.

Toxicity tests. The primary production has been measured at room temperature according to the method by Steemann Nielsen (1952) using C^{14}-bicarbonate ("Isotope Laboratory", Charlottenlund Slot, Denmark. 1 uCi/ampulla). Aqueous solutions of the byproducts (C-Cl) were prepared by mixing the tar with synthetic sea water (Andersen and Föyn, 1969) for 3 hr. This solution (80 ul/l S.W.) was added to the reaction vessels (125 ml) in amounts giving the desired final concentration. One ml of an algae suspension 1 ampulla C^{14}-bicarbonate was added to each vessel. These were shaken, well illuminated, for the whole period, i.e. preincubation + 3 hr reaction time. A pure culture of Dunaliella sp. has been used in most of the experiments, whereas in others, the algae (Chlorella stigmatophora and Porphyridium violaceum + some dead diatoms) present in surface water (S= 22,22 o/oo, t= 17,8°C.) collected at the mouth of the Oslo fjord were used.

Tests on the acute toxicity were performed on cod (Gadus morrhua), plaice (Pleuronectes platessa) and the invertebrates Leander adspercus (Crustacea), Mytilus edulis (Mollusca) and Ophiura texturata (Echinodermata according to methods described by Litchfield and Wilcoxon (1949). The test populations were also analysed for heterogenity regarding sensibility to C-Cl by X^2 (chi-square)-test in accordance with the observed values to straight dose/effect line. The tests were done in 60 l glass aquaria at a temperature of 13-18°C. and a salinity of 30-35 o/oo. The LC_{50}-values obtained were plotted against time (fig. 3). The common mussel exhibited a pronounced latent period before reacting upon C-Cl. They were exposed during a maximum of 96 hr and thereafter transferred to pure sea water and observed for 11 days.

Chemical analysis of C-Cl. The following method has been developed for estimation of C-Cl: The isolation of C-Cl was achieved by means of co-distillation with water and cyclohexane. The procedure for biological samples was: Ten grams of homogenized animal tissue in 250 ml distilled water, three ml cyclohexane and one ml antifoaming agent were set up for downward distillation in a one litre round bottomed flask. The distillation was ended when the three ml of cyclohexane and 25 ml of water had passed over and into a 25 ml volumetric flask. The procedure for sea water samples was:

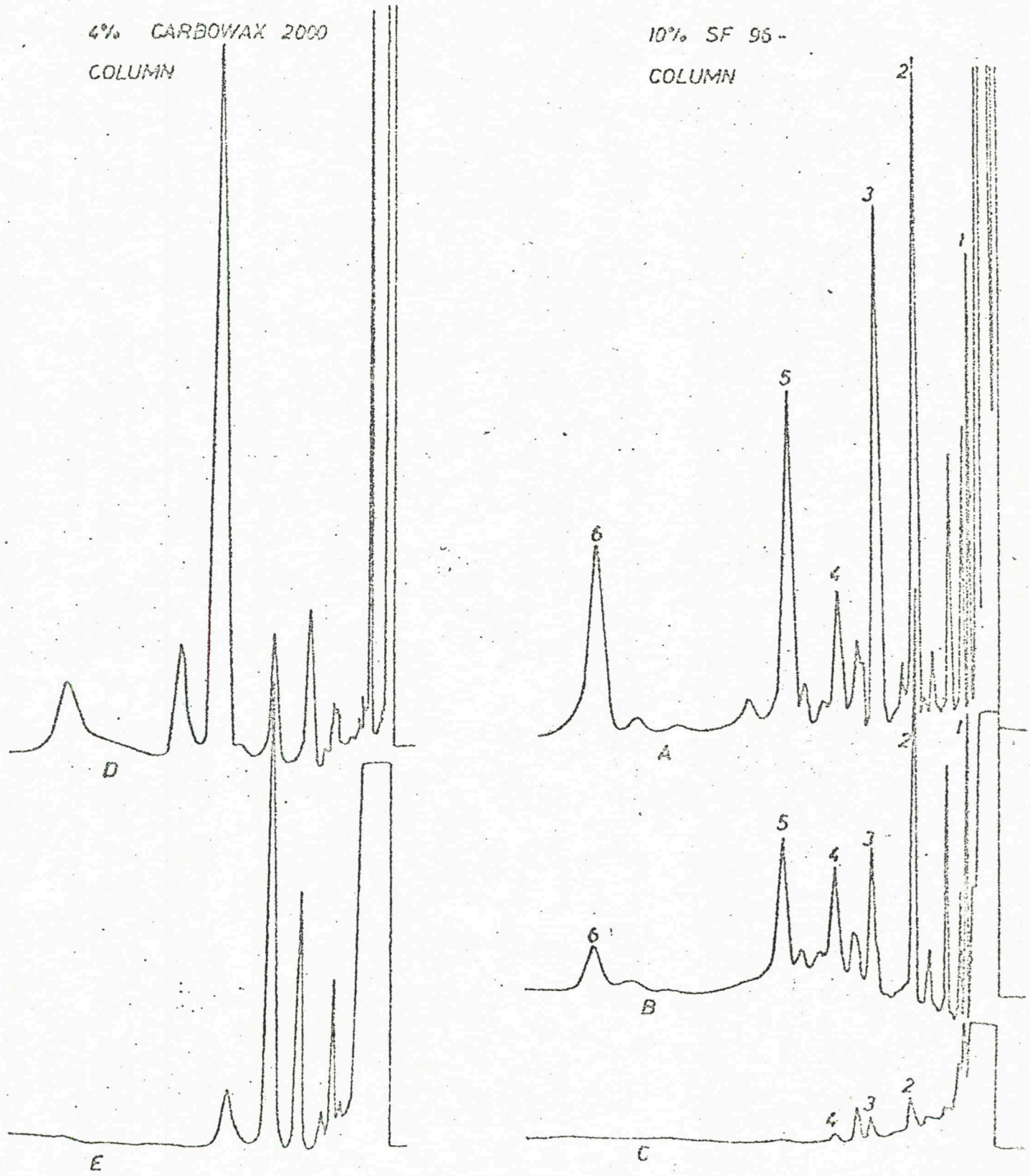

Fig. 2 The chromatograms show:
A: Standard solution
B: Water sample, equal to 0.6 ng/g (ppb), taken close to Iceland
C: Distilled water (one litre)
D: Equal to A
E: 10 g fish sample (Saith sampled at NB 64°20' EL 10°25')

One litre unfiltered sea water was distilled with three ml cyclohexane, antifoam agent not needed. The separation of the C-Cl components, now quantitatively dissolved in the cyclohexane layer, was achieved by means of gas liquid chromatography. Ten ul of the cyclohexane distillate was injected on a gas chromatograph fitted with an electron capture detector. The chromatograms were refered to that obtained using a standard solution made from samples of the byproduct of the production of vinyl chloride according to the oxychlorination method. (The composition of the byproduct is given in Table I). An analytical result (fig. 2 B) is taken as a positive iden-

Table I

Composition of byproducts from vinyl chloride production using the oxychlorination process. (Analysis made by a petrochemical factory at Lake Charles, U.S.A.)

		Mv.	Bp.	Weight %
1.2-Dichloroethane (EDC)	CH_2Cl-CH_2Cl	99.0	83.6°C	20
Trichloroethene	$CHCl=CCl_2$	131.4	87	1
1.1.2-Trichloroethane	$CHCl_2-CHCl_2$	133.4	113.5	67
1.2-Dichlorobutane	$CH_3-CH_2-CHCl-CH_2Cl$	127.0	124	2
1.3-Dichlorobutane	$CH_3-CHCl-CH_2CH_2Cl$	127.0	131	3
asym. Tetrachloroethane	ClC_3CH_2Cl	167.9	130.5	1
Monochlorobenzene	C_6H_5Cl	112.6	132	
1.3-Dichloro-2-butene, cis and trans	$CH_3-CCl=CHCH_2Cl$	125	128-30	0.5
sym. Tetrachloroethane	$CHCl_2CHCl_2$	167.9	146.3	
1.4-Dichloro-2-butene cis and trans	$CH_2ClCH=CH-CH_2Cl$	125	152.5	2
1.4-Dichlorobutane	$CH_2ClCH_2CH_2-CH_2Cl$	127	161-63	
2.3.4-Trichloro-1-butene	$CH_2ClCHClCCl=CH_2$	159.4	60^{20} mm	0.2
1.1.2-Trichlorobutane	$CCl_2-CHClCH_2CH_3$	161.5		0.3
bis (2-Chloroethylether)	$(CH_2ClCH_2)_2O$	143	178	0.3
1.3.4-Trichloro-1-butene, cis and trans	$CH_2ClCHClCH=CHCl$	159.4		0.3
1.2.3-Trichlorobutane	$CH_3CHClCHClCH_2Cl$	161.5	165-67	
Pentachloroethane	$CHCl_2CCl_3$	203.3	162	1
1.2.4-Trichlorobutane	$CH_2ClCH_2CHClCH_2Cl$	161.5		0.3
1.2.4-Trichloro-2-butene	$CH_2ClCH=CCl-CH_2Cl$	159.4	67^{10}	1.1
				100 %

tification if all retention times of all peaks are in agreement with those of the standard (fig. 2 A). If the intensities of the peaks also agrees, a rough quantitation is possible (fig. 2 A,B). In other cases (fig. 2 E) only some of the retention times correspond with those of the standard (fig. 2 D). The result is then called indicative and quantitation is impossible at present. In still other cases peaks appear which are absent in the standard solution of the byproduct. The origins of these components are uncertain; they may be components of byproducts obtained during chlorination of other types of aliphatic hydrocarbons, but as the electron capture detector used is not specific to chlorinated hydrocarbons, they may not contain chlorine at all.

3 RESULTS

Geographical distribution. It will appear from fig. 1 that C-Cl has a wide distribution. In the Atlantic Ocean and the Barents Sea only surface water samples have been analysed. In some cases, i.e. Skagerrak and along the Norwegian coast, midwater and bottom water have also been taken. These samples show that C-Cl is not located to the surface water only and also that the peak pattern of the chromatograms changes somewhat with depth. The reason for this finding is still uncertain. Possibly, C-Cl may undergo changes in the eutrophic zone comparable to those experimentally induced by exposure to ultraviolet light, together with changes caused by the biological activity within this layer.

Relatively few biological samples have been analysed (about 80 samples from 18 different species), the material analysed includes pelagic and botton animals; stationary and migratory species, as well as zooplankton. It appears (fig. 1) that C-Cl is traced in the biological material collected in the Barents Sea, the Norwegian Sea and the North Sea. Although C-Cl is absent in some of the specimens tested, and also that unfiltered water samples have been analysed, the data (fig. 1) seems to demonstrate that these compounds have a wide distribution in the sea. Obviously, the C-Cl in the sea is of different origin, e.g. the presence of C-Cl in the water masses of the North Sea - Norwegian Sea and in that of the Irminger Current, strongly indicate that C-Cl in the sea originates from industries on both sides of the Atlantic Ocean.

Toxicity tests. It will appear from the diagrams in fig. 3 that the concentrations of C-Cl compatible with the "indefinite survival time" vary between about 2 and 20 ppm. The fish, cod and plaice, being the most susceptible, followed by Leander adspercus and Ophiura texturata. No heterogenity was observed in any of these populations. Due to the latent period between exposure and death in the common mussel, the complete toxicity curve cannot be drawn. The concentration of C-Cl giving the "indefinite survival time", however, appears to be within the magnitude of 20 ppm.

As regards C-Cl's effect on the photosynthetic activity, it appears (fig. 3) that a concentration of about 13 ppm (10 ul byproduct/l S.W.) causes an immediate 50 per cent reduction. It should, however, be noted that in some cases the lowest concentrations tested gave rise to an apparent activation of the photosynthetic activity of Dunaliella sp. Other experiments, using algae sampled in Oslo fjord, gave results confirming these statements.

The figures given above (fig. 3) have their significance when related to concentrations of C-Cl found in Nature. Such figures have been consistently omitted in the present paper, but one example will be given in order to make an assessment of the C-Cl risk possible. Thus the water sample from station 710 ("Johan Hjort", June 1970, see Introduction) shows the five main chromatographic peaks identical with the five main peaks on that of the standard. Evaluation of the concentration indicates that this particular water sample contained about 0.2 ppm C-Cl, which is just a magnitude of ten lower than the lowest concentration giving rise to an immediate effect (fig. 3). It should be stressed, however, that the amount found at station 710 is the highest observed so far.

Degradation and Accumulation. To one m^3 of sea water sampled at 71°NB, 20° EL and held at 9°C 1.4 ppm of C-Cl was added. The disappearance of the main components (2 - 6 in fig. 2 A) was followed during 9 days.

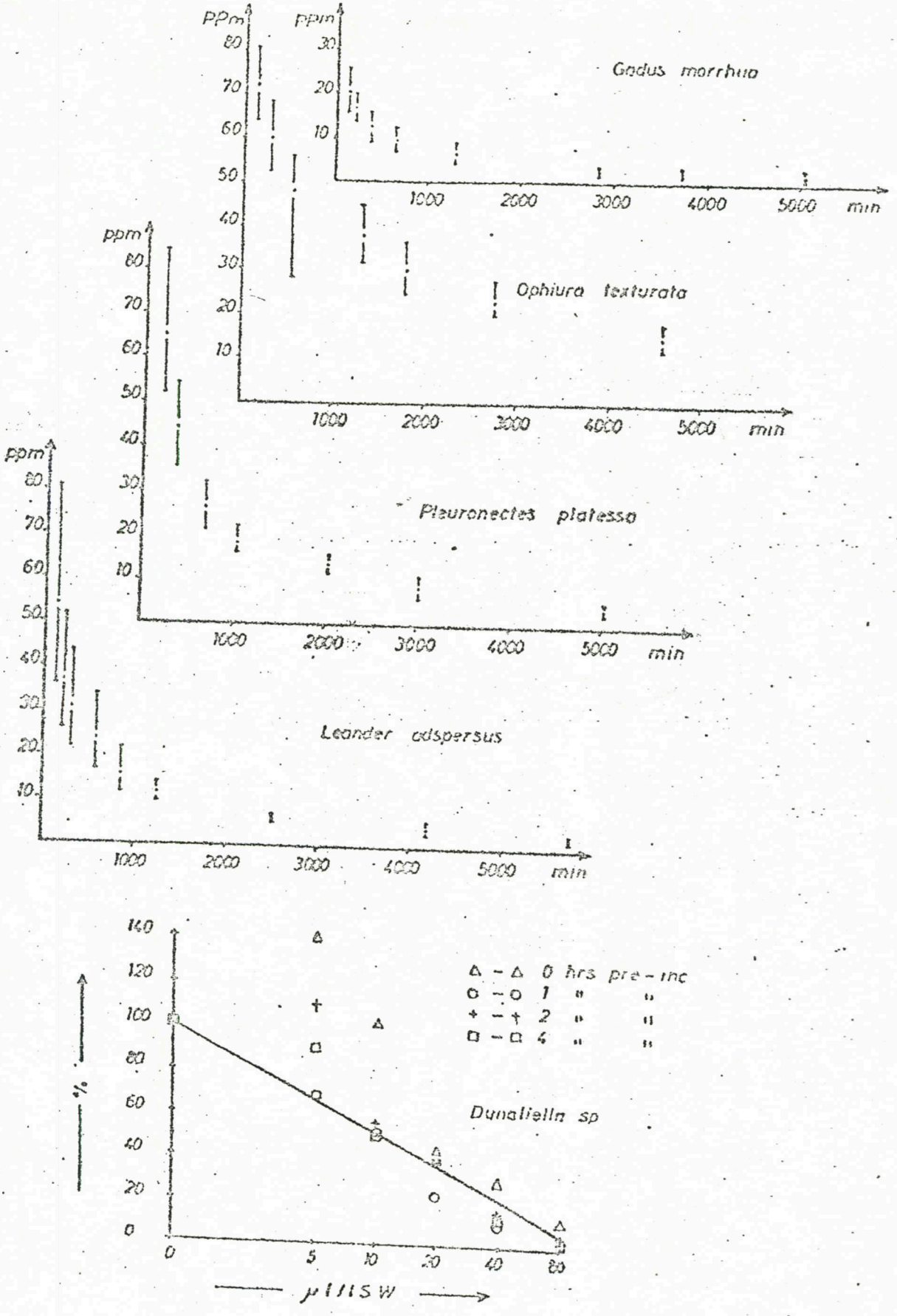

Fig. 3 Toxicity curves for C-Cl on four species of marine animals; and the effect on the photosynthetic activity of Dunaliella sp.

Table II The disappearance of C-Cl dissolved in water.

Incubation time	Amounts of compounds 2-6 (in per cent of theoretical)				
	2	3	4	5	6
0 days	90	97	82	96	95
3 "	19	85	74	94	86
5 "	8	92	54	82	75
7 "		72	55	91	78
9 "		64	42	67	68

On the second day a glass bottle was filled with one litre of water and 70 mg of Calanus finmarkicus was added. After two days at 4°C the plankton was separated in dead and live specimens and analyzed. The accumulation coefficient for component 2, 3, 4, 5 and 6 in relation to the concentration in the water was 23, 0, 102, 94 and 164 respectively for living Calanus and 0, 0, 0, 18 and 24 for dead specimens.

4 CONCLUDING REMARKS

The data given in the present paper evidently demonstrate the omnipresence of C-Cl in North Atlantic waters, and also, that C-Cl may exhibit a danger to marine organisms. It should be recalled, however, that the present paper is based on a very short period of research (July to Oct. 29th 1970). The knowledge as to the amount of byproducts from this particular industri, and also that dumping of these compounds into the North Sea occurs, made us feel that information on the problem is desired. On the other hand, this fact makes it clear that products made from chlorinated hydrocarbons are so widespread that it is possible that some sources of error have been overlooked in some cases. Therefore, samples with small peaks on the chromatograms corresponding to levels from 0,1 to 0,6 ng/g (ppb) has been regarded as negative.

During the degradation experiments it was noted that the C-Cl components disappeared at faster or slower rates, but the analytical method described does not detect these metabolites which might be as harmful as the C-Cl components themselves to living organisms. It has also found that in water with no biological activity, C-Cl remained unchanged up to 27 days at room temperature.

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