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EXPERIMENTAL DUMPING OF WASTE FERROSULFATE (COPPERAS)  
INTO THE SKAGERRAK

by

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INTRODUCTION

The production of  $TiO_2$  from ilmenite using  $H_2SO_4$  in dissolving the minerals, results in vast quantities of acidified  $FeSO_4$  waste. The waste is known as two somewhat different categories: The "Dünnsäure" which roughly consists of 10-20 %  $H_2SO_4$  and 15 %  $FeSO_4$  in water and the wet "Copperas" which mainly consists of ironsulphate in chrysaline form (75 %).

Disposal of "Dünnsäure" into the seas become a practice from several factories. For instance quantities of 200.000 tons  $FeSO_4$ /year are discharged this way from tankers into the New York bight and 100.000 tons  $FeSO_4$ /year into the North Sea 25 km NV of Helgoland. Harmful effects even in great dilutions have been shown experimentally using various marine organisms Kinne and Rosenthal 1967, Kinne and Schumann 1968, Halsband 1968, Kayser 1969) but little is known about the ecological effects in general (Redfield and Walford 1951, Hickel 1969). Weichard (1970) reported that "Dünnsäure" released into the propeller water of the ship was rapidly diluted, and caused only a short term effect on the oxygen-content and a reduction in pH of the water. Rachor (1970) investigated the disposal area of Helgoland, and demonstrated changes in organisms composition over a period of 4 years. He was unable, however, to draw any definite conclusion as to whether the changes were due to natural fluctuations or to starting effects from the waste disposals.

The effects of dumping "Copperas" into the sea is to our knowledge not investigated and there is reason to believe that this material will behave somewhat differently from the "Dünnsäure" in the marine environment, since it is in crystalline form and thus concentrated.

From the Norwegian  $TiO_2$  producer the waste is released through pipe lines into the lower part of the river Glomma which empties into the Oslofjord. Some effects in the river estuary has been reported on the fauna as well as on the flora and the bottom sediment.

In cooperation with the Norwegian producer of  $TiO_2$ , and The Norwegian Institute for Water Research, which made the studies of the river outlet, experimental dumpings were planned to collect information on the behaviour of disposed "Copperas" in the open Skagerrak waters. The purpose of the experiment was to study the general behaviour of the disposed material, in particular the discolouration, changes in turbidity, the effect on both primary production and oxygen content, as well as the scavenging effect of the ironhydroxide formed.

Two different dumping -sites were used for the experiments, one in the outer Oslofjord and one in the open Skagerrak at the eastern slope towards the Skagerrak deep. The watermasses at these localities are known to be a top layer of Baltic origin covering North Sea watermasses. The Baltic waters are usually identified by salinities less than 30 ‰.

Especially in the summer a pronounced stratification occurs between these layers. The movement of the surface waters depends mainly on wind conditions as has clearly been demonstrated by one of us (Ljøen 1971) fig. 1. Three situations of approximately one week intervals, demonstrates in the first sequence a piling up of the Baltic waters against the western coasts of Norway and Sweden. In the second situation different wind conditions off western Norway and in Skagerrak result in a piling up of the Baltic waters against the southern and southeastern Norwegian coast, and a lateral movement of the Baltic waters away from the coast.

The last situation demonstrates a transport of the Baltic water mainly southwards and a brake up of these waters into vortices. The sequence of the demonstrated situations result in a forth and back transport of the surface waters within the area, as well as a pumping effect of this water in and out of Skagerrak.

Prior to the experimental dumping some laboratory tests were carried out by the Titan Co., Fredrikstad, Norway, to investigate the solubility of the "Copperas" when released directly to sea-water. The results, which are given in table 1, demonstrates that pure "Copperas" as well as the iron-sulphate solution both were dissolved mainly in the upper 1 meter of a column. The above results indicated that "Copperas" when discharged either directly or as a solution would be distributed within the homogenous top layer of the sea. Some further experiments revealed that the iron-sulphate turned slowly into  $\text{Fe}(\text{OH})_3$ , a process which used oxygen and further reduced the pH of the waters.

Experiment 1. - Direct release of 80 tons "Copperas". Date: 27 - 28  
October 1970.

The "Copperas" had been stored in sacks for some weeks and consequently the crystals had clogged. With a current cross placed at 1 m, the contents were continuously dumped while the ship circulated around this drifter. During the operations (4 hrs) the drifter moved in a south-west direction over a distance of  $3\frac{1}{2}$  n. miles. At the start the weather was calm but a southeasterly wind developed during the dumping and increased in force to a gale before the end of the experiment.

Visual observations as well as chemical analyses of the contaminated waters showed that some of the material had been distributed within the upper water mass. Echo recording during the dumping, however, revealed that considerable amounts sunk right to the bottom, fig. 2. These findings were further confirmed by the transparency recordings. Although the dumping was made continuously the yellow brownish ferrihydroxide formed was localized as patches. Caused by the weather conditions a cessation in the sampling was found necessary after 6 hrs. By that time the patches had moved close to the shore, and the next day when the weather had calmed no sign of the waste was observed. This was probably caused by the gale which obviously had blown the dissolved iron waste ashore.

Experiment 2. - Eighty tons "Copperas" (= 33 t  $\text{FeSO}_4$ ) dissolved in hot water to 118 m<sup>3</sup>. Date: 11 - 12 May 1971.

The liquidized waste was pumped into the sea while the ship was circulating around a current cross placed in 1 m depth. Observations on S ‰ and t°C revealed a upper mixed layer of 5-7 m. The patch was just after dumping about 500 m across, giving a strong yellow brownish colour distinctly separating from the surrounding waters.

During the two previous days as well as during the whole experiment the wind was rather stable from south west, force 3-4 Bt. The patch was observed from the research vessel during 31 hrs. at the positions showed in the map Fig. 3 starting at the position B, 14 hrs. after the release the size of the patch was estimated to 2.500 by 500 m. The current cross in 1 m more or less followed the patch, whereas two current crosses placed in 10 and 15 m respectively showed a retarded movement of the subsurface waters, Fig. 3. The transparency measurements examples of which are shown in Fig. 4, ab, proved to be a suitable technique in identifying the vertical and horizontal distribution of the material showing good agreement with iron measurements done, Fig. 4c. During the situations A, B and C Fig. 3, samplings were made for iron measurements, giving the surface values shown in Fig. 3. Plotting the measured surface values against time, the maximum values recorded in each situation give an approximation of the centervalues of the patch Fig. 5, and a probable time scale for the disappearance of the discoloration. A slight decrease in the oxygen content of the contaminated water as compared with the outside pattern was observed in accordance with the findings of Weichard (1970) during and immediately after the release of 'Dünnsfure'. Chlorophyll and the primary production measured in simultaneous samples were used to calculate the turnover rates in the phytoplankton. The results after dillution indicated that the pollutant had primaraly an inhibitory effect which later seemed to act stimulating on the primary production.

## DISCUSSION

Toxicity of ironsulphate waste to marine animals, both on pelagic and bottom fauna are fairly well documented (Kinne and Rosenthal 1967, Kinne and Schumann, 1968). Like the findings by Ketchum et. al. (1958) our measurements of the rates of primary production at standarized condition indicated, however, that the contaminated sea water acted only negligably on the turnover rates in the phytoplankton, an initial decrease soon being counteracted by a slight increase.

Several ecological effects might, however, be expected when great quantities of ironsulphate are being introduced to the sea. The most pronounced are probably: 1) increased turbidity, 2) discolouration, 3) reduction in pH, 4) oxygenconsumption.

The former two would act on the light penetration. When the material is dissolved in the surface layers the available light energy would be reduced with a nearly proportional effect on the rate of integrated primary production (Berge 1969).

The considerable reduction in red light penetration observed here indicate that serious decrease in the integrated primary production this way has to be considered in a permanent dumping process of this material. Although not observed, changes in the mentioned parameters over longer periods must be considered harmful to the marine life.

The first experiment with crystalline "Copperas", showed that the material partly penetrated the pycnocline and sunk to the bottom. Deposited on the bottom the highly concentrated material would act both on the pH and the oxygen content of the water near the bottom and consequently on the organisms living there. In the actual region where important trawling for shrimps takes place, regular dumping of this kind would probably cause serious harm to these and other resources.

In the second experiment where dissolved "Copperas" was released the material dispersed in the water layer above the pycnocline and formed a strongly yellow-brownish coloured patch. The colour persisted and the patch increasing in size with time, was still distinctly observable after 2 days.

The flocculation of ferric-hydroxide progressed slowly. By vigorous stirring flocculation took place immediately, indicating that rough sea might speed up the process. The chemistry of the iron sulfate behaviour in sea water is not fully understood, but it is stated by Cooper (1948) that part of it will be complex bounded and remain in solution for a prolonged period.

The observed varied wind conditions and the rapid and great changes in the movement of baltic waters must be considered ordinary. It is thus not predictable where patches of contaminated water would be transported. Serial introductions of waste could this way be transported forth and back any place within the area as well as in and out of the Skagerrack

and along the south-western Norwegian banks. These areas are important nursery grounds for fish stocks, and harm to the fish recruitment cannot be excluded.

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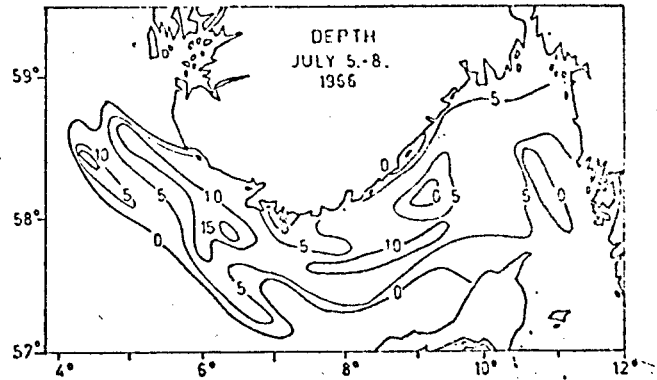
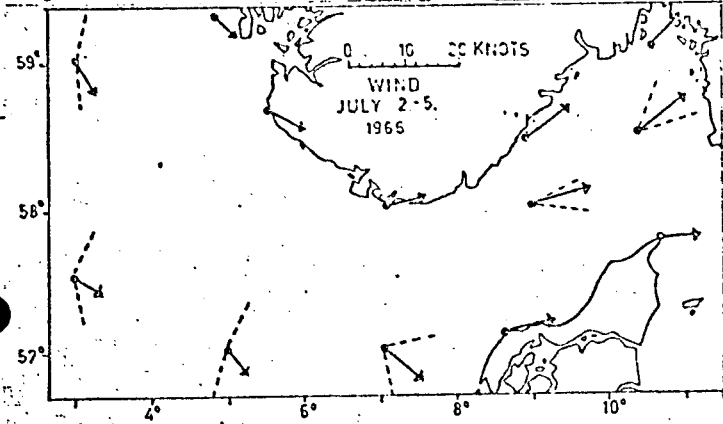
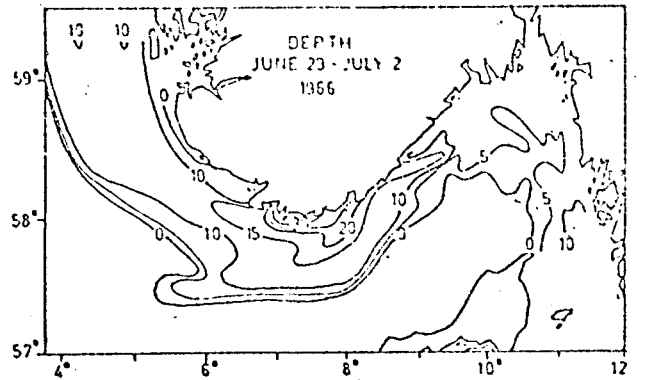
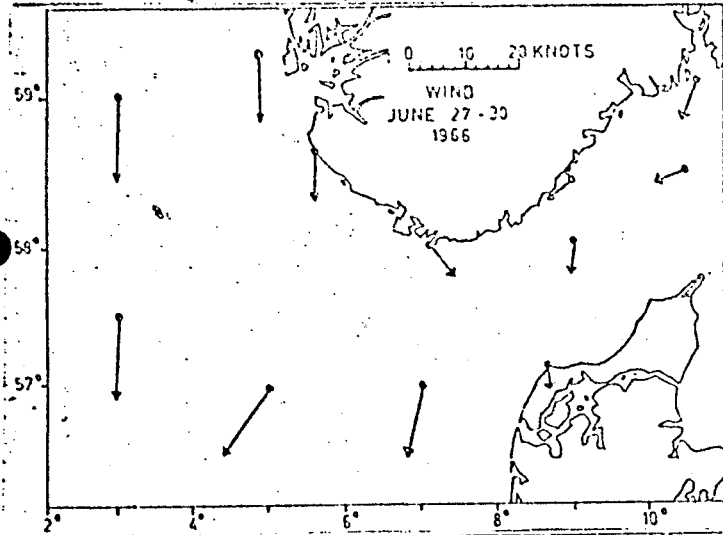
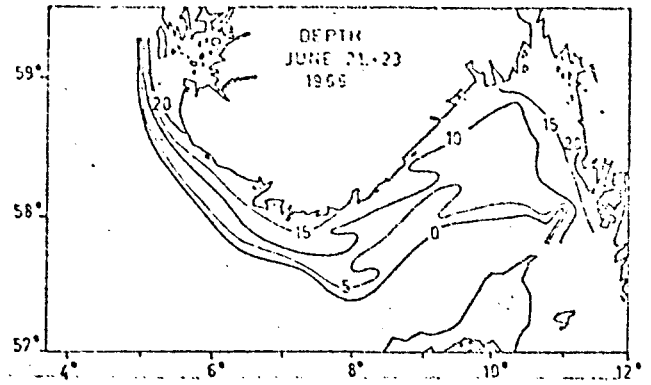
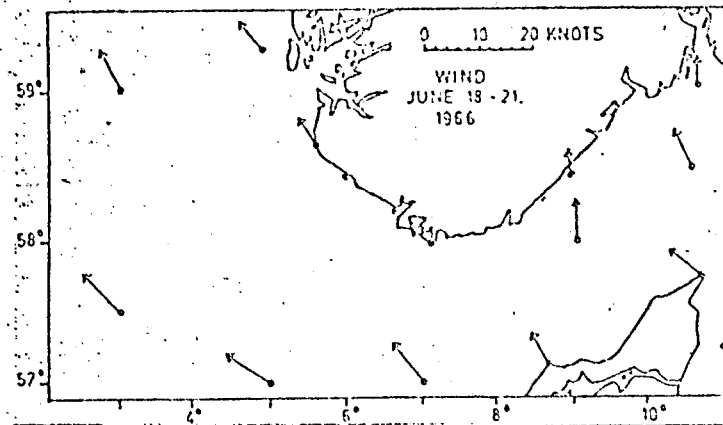
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Sample		27% sol. FeSO <sub>4</sub> , 40°C, sp.v. 1,34 Moist "Copperas" - 76% FeSO <sub>4</sub> ·7H <sub>2</sub> O							
Gramme FeSO <sub>4</sub>		3,7		37		37		370	
Time interval		1 min.	5 min.	1 min.	5 min.	1 min.	5 min.	1 min.	5 min.
Distance below surface	22	3,3	2,3	24,0	14,2	18,3	14,8	139	122
	48	2,1	2,0	16,6	15,0	16,1	13,6	139	122
	90	0,7	1,1	8,1	12,2	11,6	12,1	113	118
	127	0,02	0,44	0,5	7,9	4,9	9,6	84	111
Homogenous solution equals g/l FeSO <sub>4</sub>		1,17		11,7		11,7		117	

Table I. Vertical distribution of ironsulfate added in various concentrations to seawater at the top of a column, 1,4 m high and with a diameter of 4,6 centimeters.





Average wind conditions

Depths of 30 o/oo isosurface

Figure I

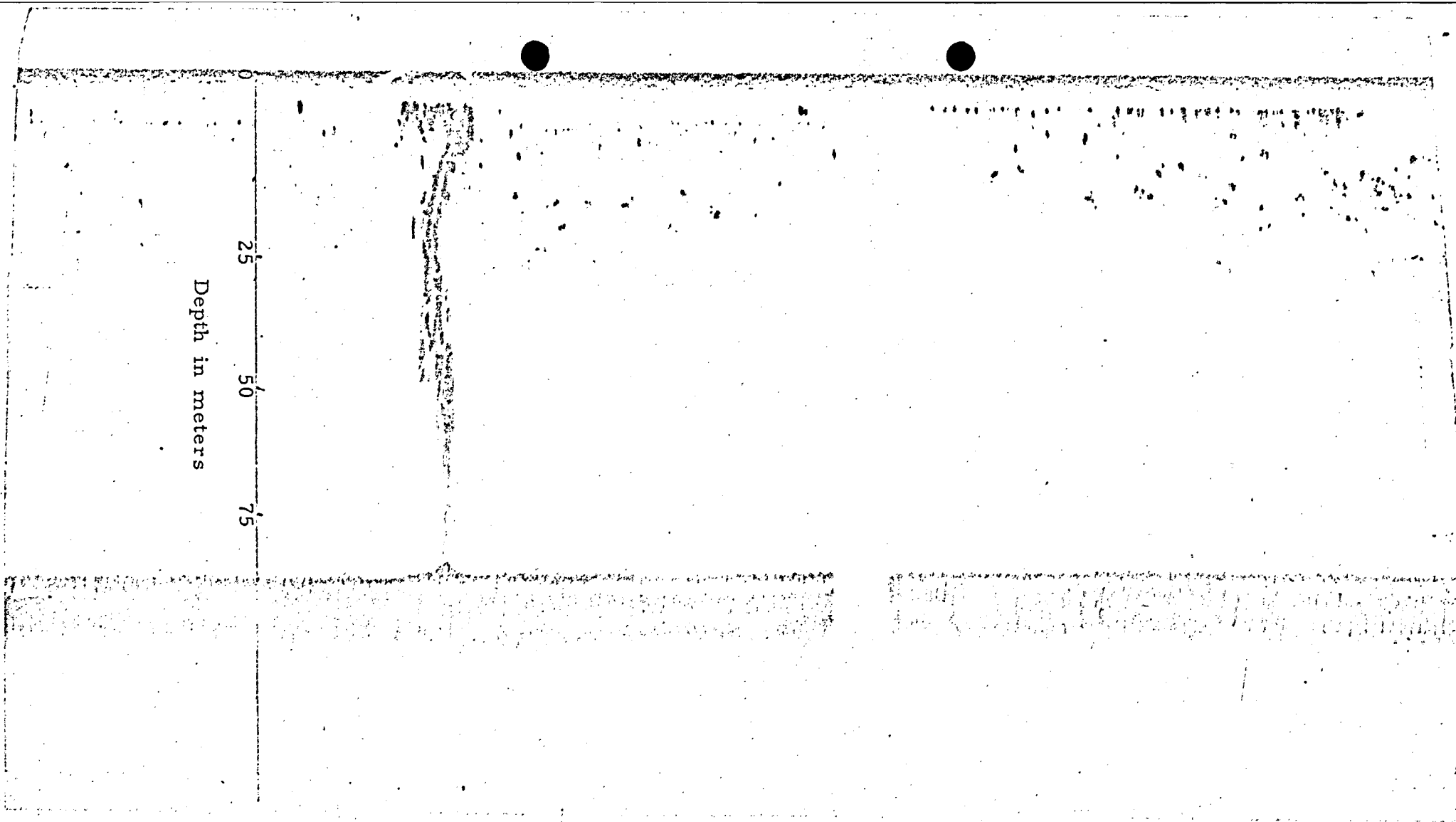


Fig 2. Echo recording showing the dumped "Copperas" penetrating to the bottom ( Simrad EH, scale 0 - 125 m, force 5 ).

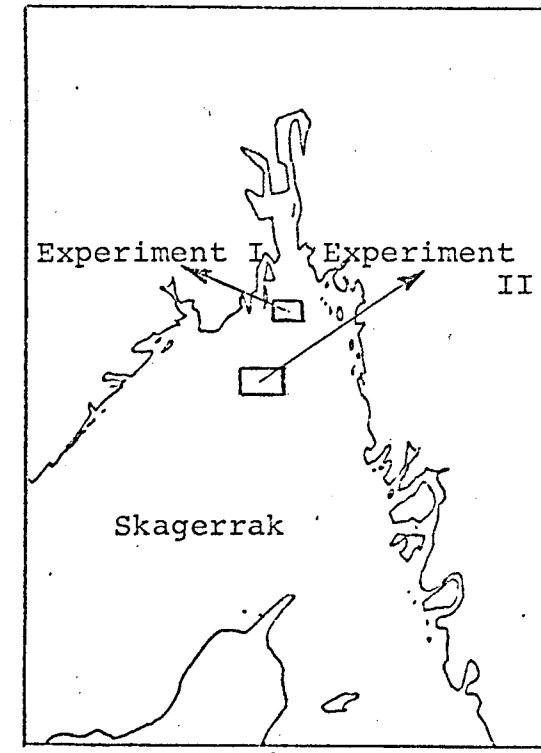
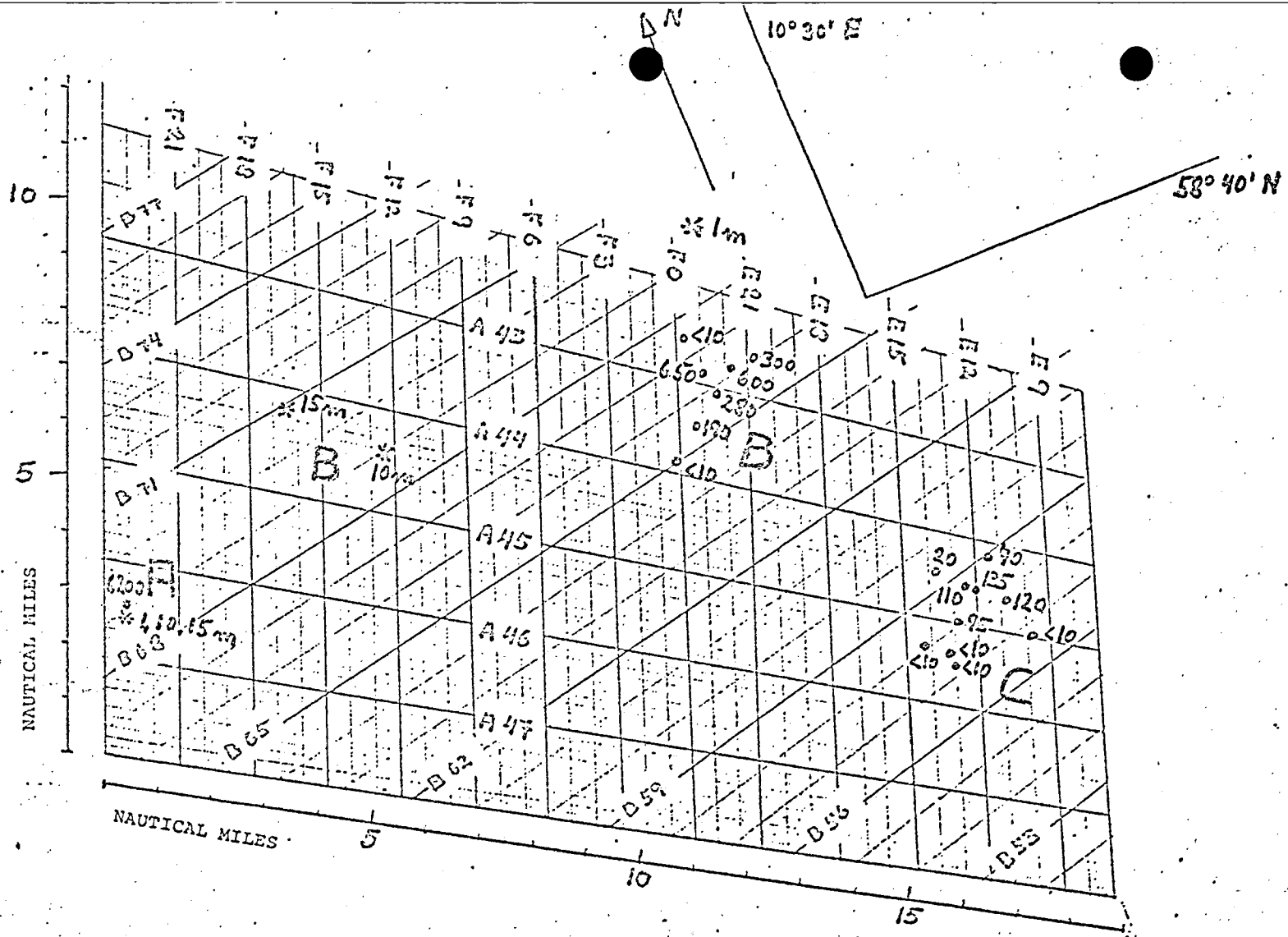
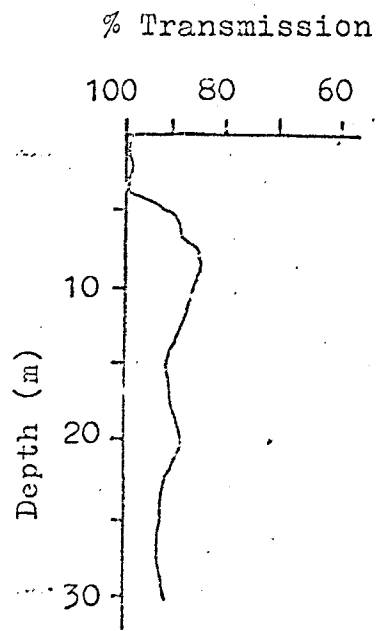


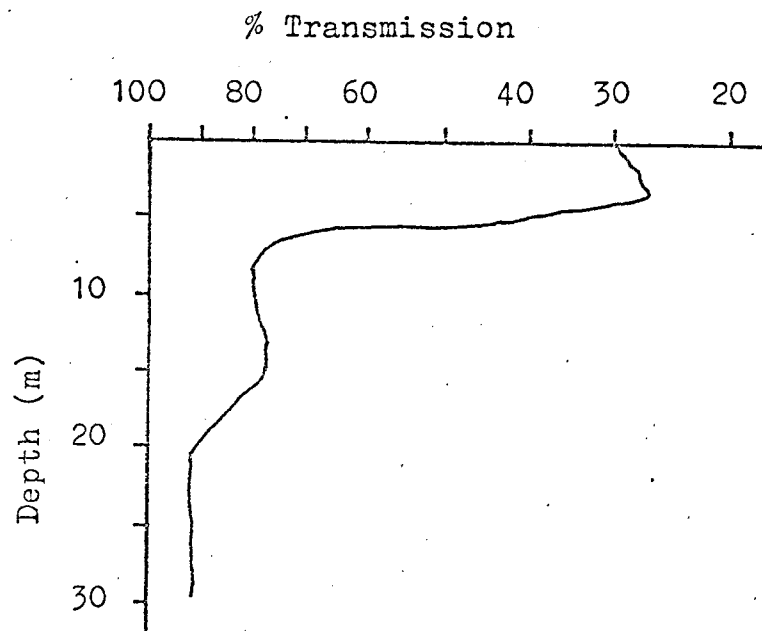
Fig. 3. Experiment II, the patch and drifter movements with the surface concentrations of iron in  $\mu\text{g/l}$  plotted on a Decca chart (Decca chain 10B/MP, Skagerrak).

Area map.



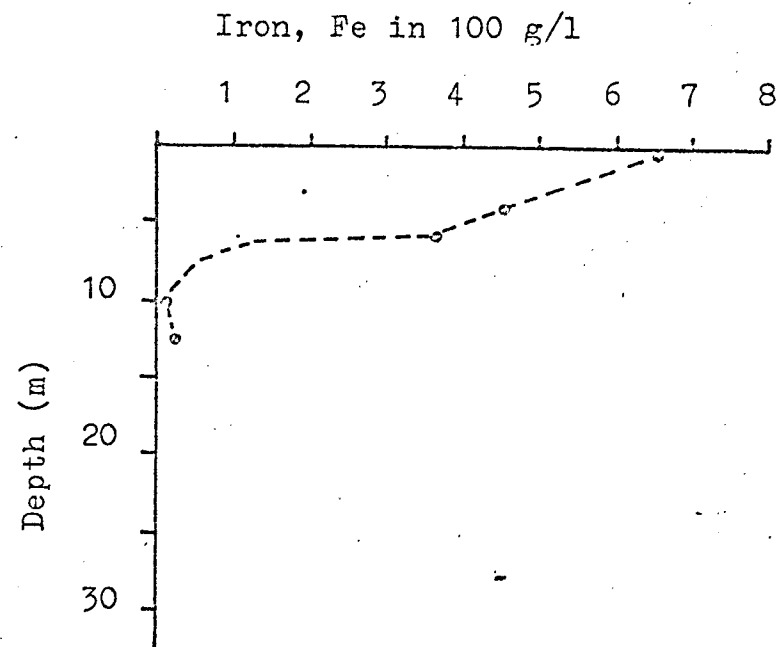
( a )

Station no. 159, 11.5.,  
6.15 p. m.  
Outside the "Patch".



( b )

Station no 160, 11.5.,  
6.30.p.m.  
Middle of the "Patch".



( c )

Fig. 4. (a) and (b) Vertical transparency measurements, % transmission of read light.  
(c) Vertical distribution of iron.

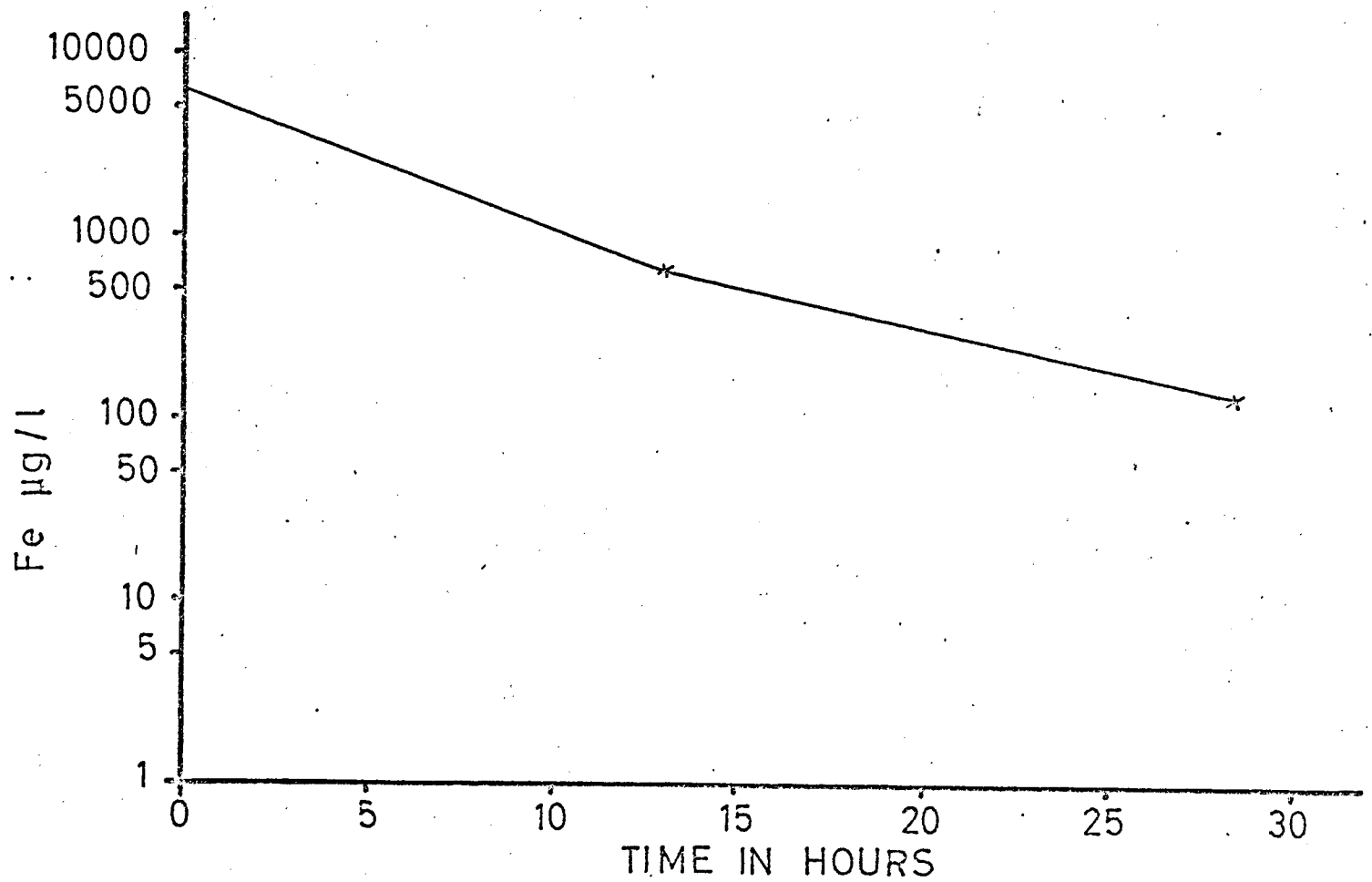


Fig. 5. Experiment 2, maximum surface values of iron in the middle of the patch plotted against time interval from the release of the iron sulphate.