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A dye experiment in the North Sea up to a very large scale

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Abstract

An instantaneous release of 334 kg rhodamine B was carried out in the Southern Bight of the North Sea in August 1979. The dye patch could be followed from a length scale of about 60 meters till scales of about 500 km during approximately 200 days. The patch was driven by residual currents along the Dutch coast through the German Bight to the Norwegian coast. The dispersion process described in terms of turbulent diffusion had a variable character. The behaviour of rhodamine in this experiment was surprising since the measurements indicate a spectacular increase of mass as long as it is assumed that the usual relation between fluorescence and mass is constant. The new fluorimeter, which was used for measurement of the seawater samples taken during the large scale surveys, had a detection limit of about 2 ng/l.

Introduction

Rhodamine B was developed as a dye, therefore it may be expected to attach easily to the seston in the seawater. The adsorption by the seston has been reported in many papers [1,2,3,4]. As the nature and the content of seston differ in time and place, it is no wonder that the reported losses are variable. Up till now it is impossible to predict these losses with sufficient accuracy. This is one of the reasons why rhodamine B is not an ideal tracer in spite of its frequent use and this dye is not suited for long continuous releases in turbid waters. An instantaneous release gives the possibility of compensating for the losses of mass or fluorescence yield by means of the mass balance. The complicated interaction between the dye and the seston may be one of the causes for the unusual results obtained: from about the fortieth day the mass seemed to increase linearly in time. We might not have found this amazing result if the diffusion process had not been exceptionally slow during the first 25 days, and if we had not had a new type of fluorimeter.

The synchronous modulation fluorimeter

This new type of fluorimeter was used for measurements of seawater samples when the concentrations were too small for the shipborne fluorimeters. The detection limit of a fluorescent tracer is often determined by the fluorescence of the seston and dissolved substances in the seawater. In order to decrease the detection limit, Rijkswaterstaat asked TNO* to improve the measuring method. The result was a new fluorimeter based on synchronous excitation spectrofluorimetry [5,6]. In such a spectrofluorimeter the excitation and analysis wavelengths are varied simultaneously while a constant wavelength difference is maintained. This difference is equalized to the wavelenght distance between the excitation and emission peaks of the tracer. Such a recorded emission spectrum gives a narrower fluorescence band and the background variations are smaller, so that the detection limit is lowered. Additionally in the TNO-fluorimeter the monochromators vibrate (30 Hz) and the fluorescence spectrum and its derivatives are determined simultaneously. The latter modifications make the instrument response much faster and narrow the fluorescence peak. The detection limit is about 2 ng l^{-1} rhodamine B in seawater containing less than 2% polluted river water.

The measurement of diffusion

The methods used during the first 25 days after the instantaneous release are rather common. Later we had to take water samples because of the low concentrations, which were measured by TNO. For a survey of the experiment see fig. 1.

Two release tanks (12 m^3 and 3 m^3) were placed on a release vessel in order to prevent contamination of the survey vessel. The survey vessel was a rented supply ship, "Normand Vester" equipped with a measuring pipe, winches for the Batfish-Variosens combination and containers wherein the instruments such as fluorimeters, datalogger, gyrocompass, radiopositioning etc. The seawater for the Turner-fluorimeters was pumped up from 2 and 5 meter below the surface.

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* Netherlands Organization for Applied Scientific Research

In order to prevent disturbance of the natural diffusion the horizontal surveys were not started before the horizontal dimensions of the patch were about 500 m. Before that, the ship took measurements of the vertical distribution with the Variosens (in situ fluorimeter) floating through the patch. The patch was continuously measured for about 200 hours except for an interruption between 100 and 126 hours. The number of surveys could be limited without loss of essential information because of the slowness of the diffusion at that time. The surveys after 600 hours were performed by the monitoring vessel "Holland" of Rijkswaterstaat. The lack of sensitive shipborne fluorimeters has led to a poor quality of the large scale surveys. Only survey 90 of the "Holland" seems to be complete, whereas survey 87 covered only half of the patch (see fig. 8).

Methods of obtaining the diffusion parameters

Aerial photography

The principles of the method were given by Roberts[7] in 1923. This method has been applied to dye patches since 1959[8]. Van Dam[9] describes the application of these principles to the analysis of aerial photographs of dye patches. In this connection some possible distributions of concentration are discussed now. A certain class of 2-dimensional distributions can be described by

$$C(A,t) = \frac{M\, b_1}{h_d\, \overline{A}(t)}\, e^{-b_2\left(\frac{A}{\overline{A}(t)}\right)^m} \qquad (1)$$

where

$$\overline{A}(t) \equiv \frac{\int_0^\infty A\, C(A,t)\, dA}{\int_0^\infty C(A,t)\, dA} \qquad (2)$$

Further we define

$$G(t) \equiv \frac{C(0,t)\, h_d}{M} = \frac{b_1}{\overline{A}(t)} \qquad (3)$$

$$\overline{A}(t) \propto t^b$$

$C(A,t)$: concentration distribution as function of the enclosed area A at the time t,
A : area enclosed by the isoline with concentration C,
M : released mass,
h_d : penetration depth,
$G(t)$: normalized maximum concentration
and b, b_1, b_2, m are constants.

In practice A is very often replaced by πr^2 (r = radii of 'equivalent circles' as introduced by Joseph and Sendner[10]) and the names of the distributions usually refer to the expressions in terms of r.
E.g. $b_1=b_2=m=1$: "Gaussian distribution"
$b_1=3$ $b_2=\sqrt{6}$ $m=\frac{1}{2}$: "exponential distribution".

Let C_v be the concentration on the contour enclosing the visible area A on an aerial photograph . At the beginning the visible area will grow until the continuing dilution will make the patch disappear. Therefore, at some time t_{max}, A_v will be maximal and

$$\left[\frac{d\,A_v}{dt}\right]_{t=t_{max}} = 0 \tag{4}$$

One may deduce from (1) and (4)

$$\frac{b_1\,M}{C_v\,h_d} = e^{\frac{1}{m}}\,\overline{A}(t_{max}) \tag{5}$$

$$\overline{A}(t_{max}) = A_{v\,max}\left[m\,b_2\right]^{\frac{1}{m}} \tag{6}$$

$$A_v(t) = \overline{A}(t)\,b_2^{-\frac{1}{m}}\left\{\ln\left[\frac{(e\,m\,b_2)^{\frac{1}{m}}\,A_{v\,max}}{\overline{A}(t)}\right]\right\}^{\frac{1}{m}} \tag{7}$$

$\overline{A}(t)$ in (7) may be solved graphically. In order to find out which distribution would fit the data best, we measured the visual areas a second time looking through a neutral density filter. Then $\overline{A}(t)$ was solved again but necessarily for a shorter time interval (fig. 2, 3). If the correct distribution had been chosen, then the second curve $\overline{A}(t)$ would coincide with the first $\overline{A}(t)$. With this criterion the Gaussian distribution fitted better than the exponential distribution (fig. 3a, 3b).

Fluorimetric ship surveys

For the tentative results we used the following relations

$$G(t) = \frac{C(0,t)}{\int_0^\infty C(A,t)\,dA} \qquad \text{top concentration at "open sea"} \qquad (8)$$

$$G(t) = \frac{C(0,t)}{2\int_0^\infty C(A,t)\,dA} \qquad \text{top concentration near the coast} \qquad (8a)$$

$$\sigma^2 \overset{def}{=} \frac{\overline{A}(t)}{\pi} = \frac{b_1}{\pi G(t)} \qquad (9)$$

$$K_g(t) \overset{def}{=} \frac{1}{4}\frac{d\sigma^2}{dt} \qquad (10)$$

$$h_d(t) = \frac{M}{\int_0^\infty C(A,t)\,dA} \qquad (11)$$

The definition of σ^2 agrees with Okubo's[11] σ_{rc}^2. K_g is a generalized diffusion coefficient[12].

Results

Horizontal diffusion

The tentative results are presented in fig. 4. The diffusion parameters of the last survey no. 91 were deduced from an extrapolation of $\int_0^\infty C(A,t)\,dA$, figure 9, because the quality of that survey was too bad for a determination of this integral. The deviation of the points from the line for $t < 0,3$ h may be explained by the finite extent of the patch at $t=0$.

The initial area was about 2000 m^2. If the starting distribution has the same character as the distributions later on , a time shift of about 0,1 h is sufficient to get the curve of an ideal release. The discrepancy between the last seven aerial photographs and the first ship surveys is not understood yet. Probably the hypothesis of the constancy of the lowest visible concentration is not entirely correct. Compared with other experiments in the North Sea the diffusion was extremely slow between 120 and 600 hours. The diffusion coefficient K_g was about 1,4 $m^2 s^{-1}$ and constant for scales of diffusion between about 600 m and 12000m (fig. 6). The results after 1000 hours when the patch had been driven away from the release point over a distance of about 100 km, agree very well with an extrapolation of the RHENO-experiment[14] (fig. 5 and fig. 6).

Vertical diffusion

The first observations in the vertical which were made after about one hour, gave an almost homogeneous distribution over 25 m. This means that the vertical diffusion coefficient must have been as large as 0,1 $m^2 s^{-1}$.

Residual currents

The positions of the maximum concentrations are given in figure 7. The displacements per day during the first 600 hours were about 1 - 1,5 km. The yearly averages measured by the light vessels "Noord Hinder" and "Texel" are about 4 km a day (Eulerian!). After 600 hours the displacements per day were about 3 to 5 km. The position of the maximum concentration of the last survey is ambiguous, so that the estimation of the residual current from survey 90 till survey 91 may range from 2 km to 8 km a day.

Mass balance

Setting up a mass balance is a very useful check on the quality of the surveys of the patch. Formula (11) may be used for this check. If it is supposed that the penetration depth h_d equals the sea depth, then the apparent mass increased considerably after 600 hours (fig. 10a). When the mass is supposed to be constant and the usual relation between fluorescence and concentration is used, the penetration depth decreases from about 30 m in the beginning to about 1 m at the end (fig. 10b). The mass balance of a selection of the surveys during the first 600 hours is very plausible. The small deficits of mass may be explained by adsorption losses and the small surplus of mass during that period may be attributed to experimental errors. The water samples after 600 hours were taken from about two meters below the sea surface. This means that the concentrations of successive samples of surveys 89 and 90 could have differed much from each other because of the vertical ship movements. These differences have not been observed. Rhodamine losses of about 50% are not unusual in turbid coastal areas, thus in that case the penetration depth would have been once more a factor 2 smaller. A mass surplus after 460 hours was also observed during the RHENO-experiment, although much less pronounced, whereas the penetration depth continuously increased. Therefore, it seems improbable that the spectacular behaviour of Rhodamine B is due to a decreasing penetration depth. Therefore the question arises why the fluorescence increased.

As known[13] the fluorescence yield in very diluted solutions is proportional to the quantum efficiency and the effective cross section for the absorption of a photon. The quantum efficiency is almost 1, therefore a great increase is impossible. On purely physical grounds it is difficult to imagine how the effective cross section may change. Moreover an increase of the product of quantum efficiency and the effective cross section of rhodamine B in distilled water has never been reported. A biochemical explanation seems most promising, because the increase of the apparent mass or the effective cross section started after some adaptation time, which was about 20 days for the RHENO-experiment and about 30 days for this experiment. But if biochemical processes appear to be responsible, then the question arises how the horizontal distributions will be affected and which seas will be suited for this kind of large scale experiments.

Acknowledgements

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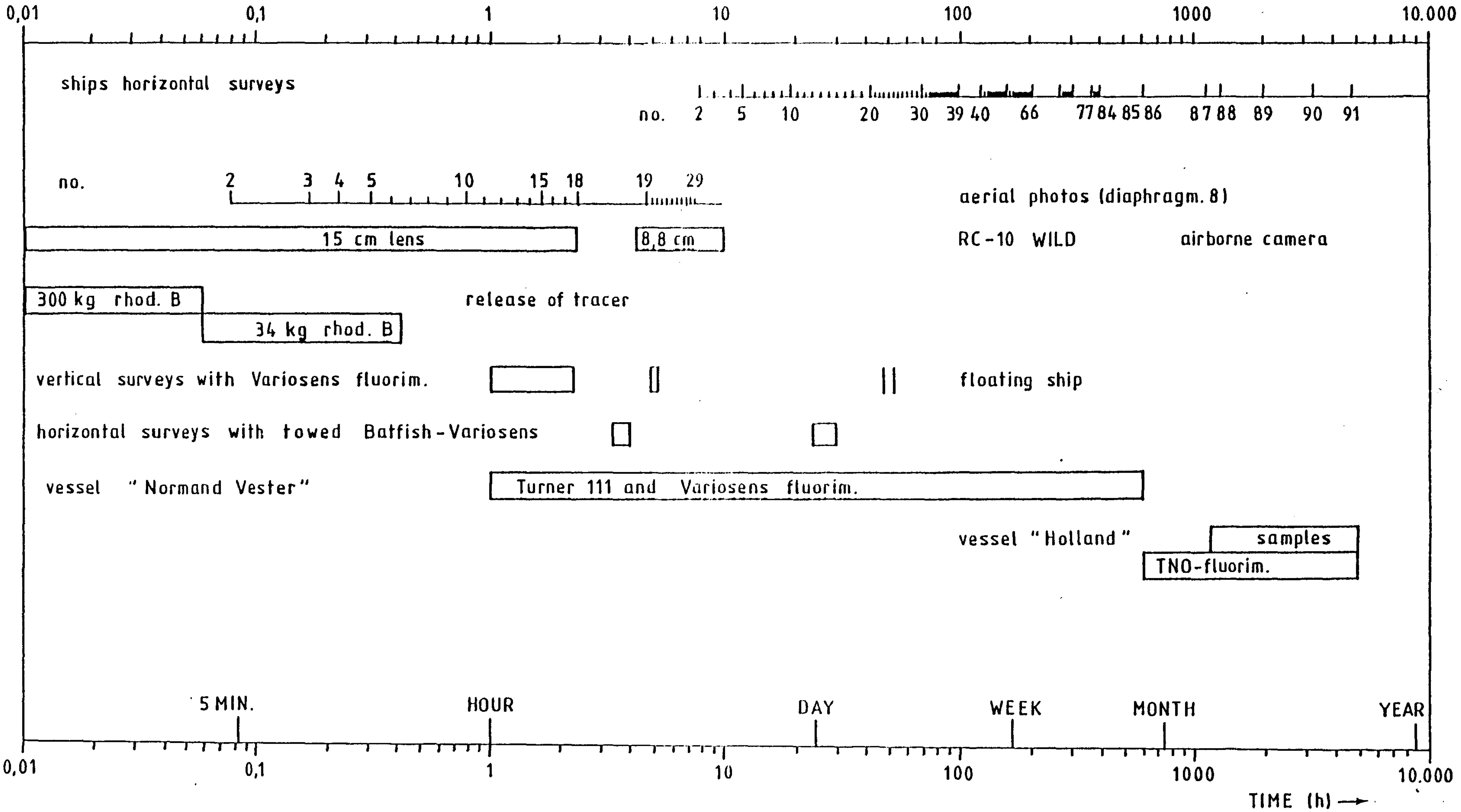


Fig.1 survey of the dye experiment.

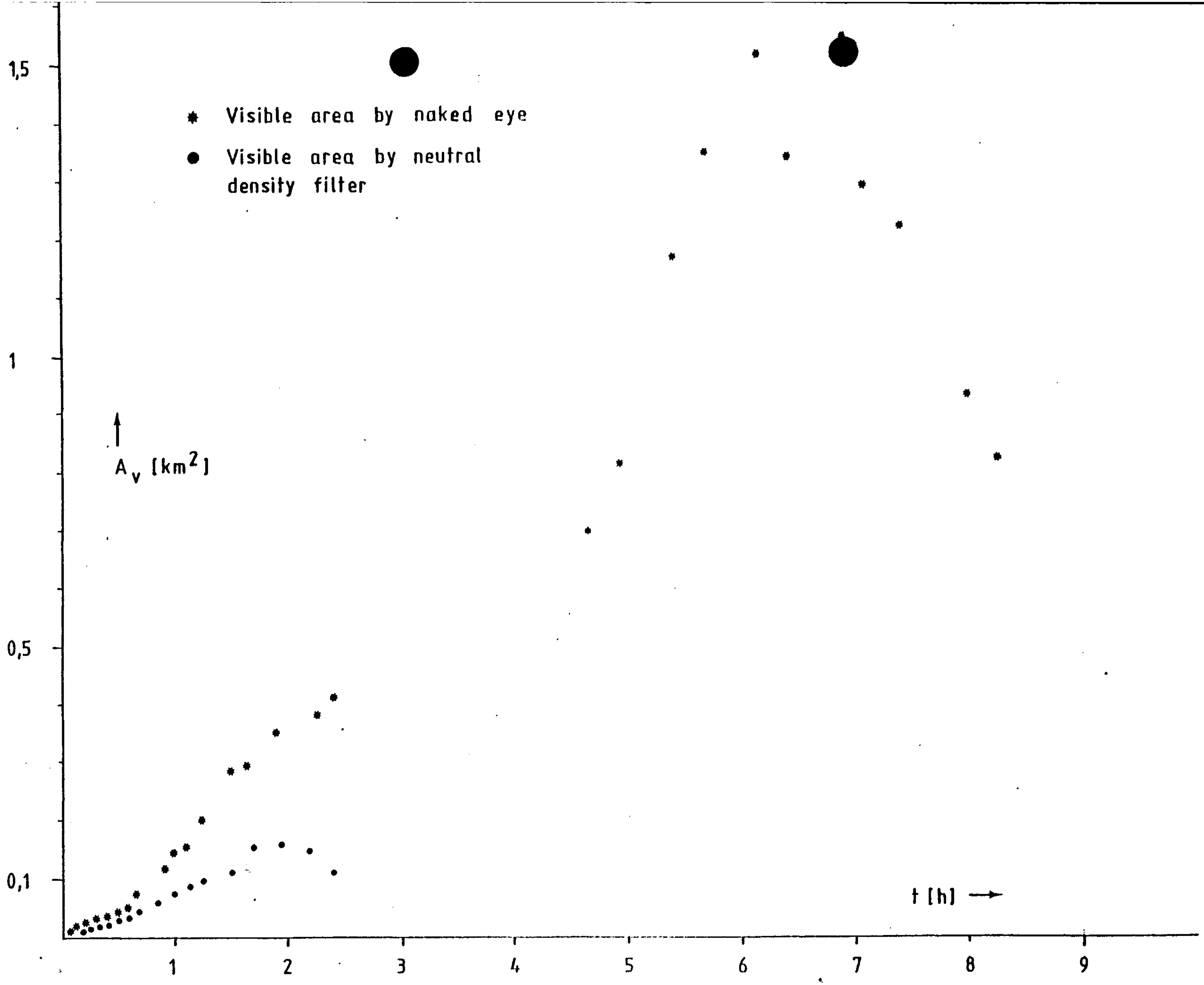


Fig. 2 The visible area of the dye on the photos versus the time after the end of the 300 kg release.

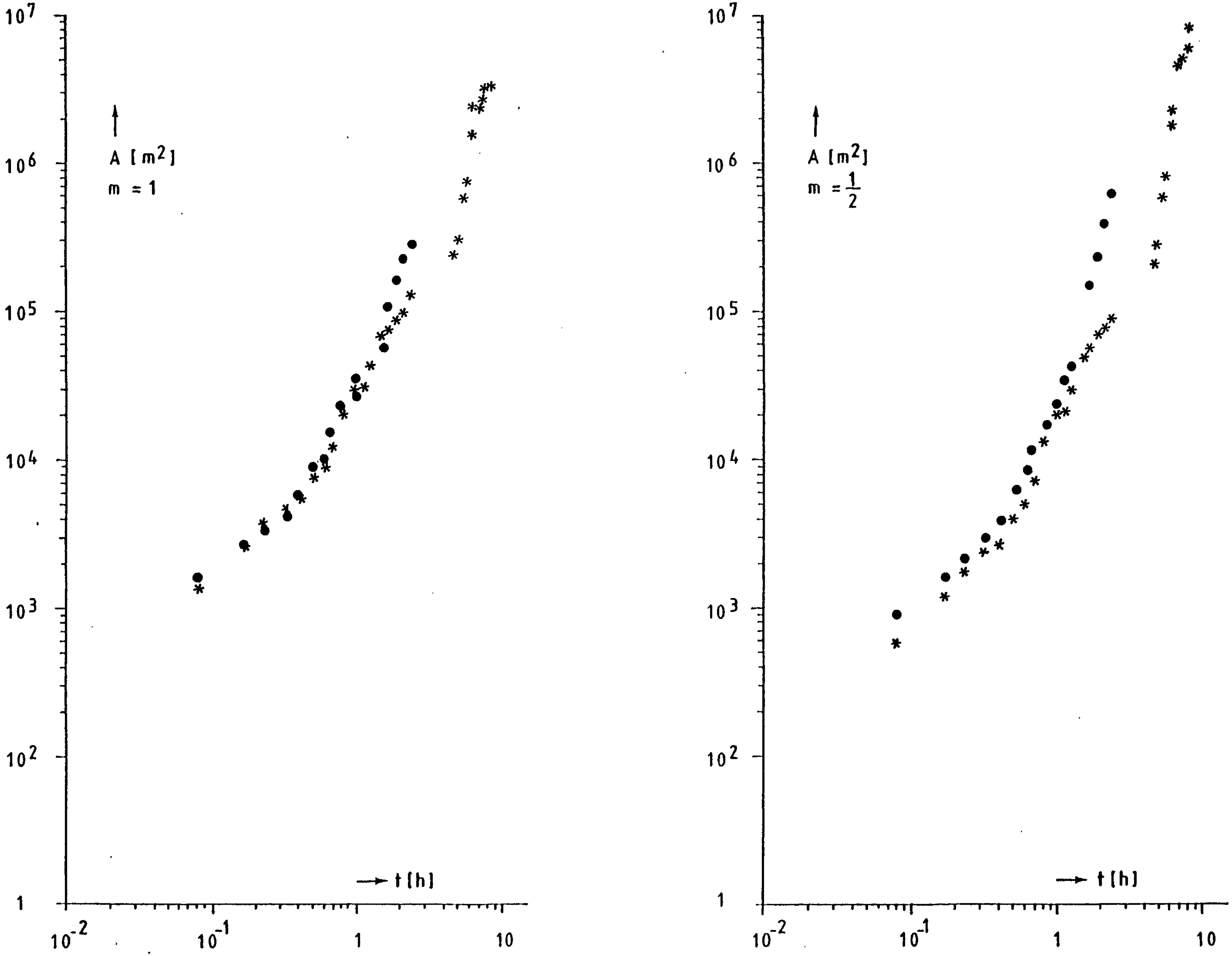


Fig. 3 The expectation value of A graphically solved for m = 1 and m = $\frac{1}{2}$ respectively versus the time after release.

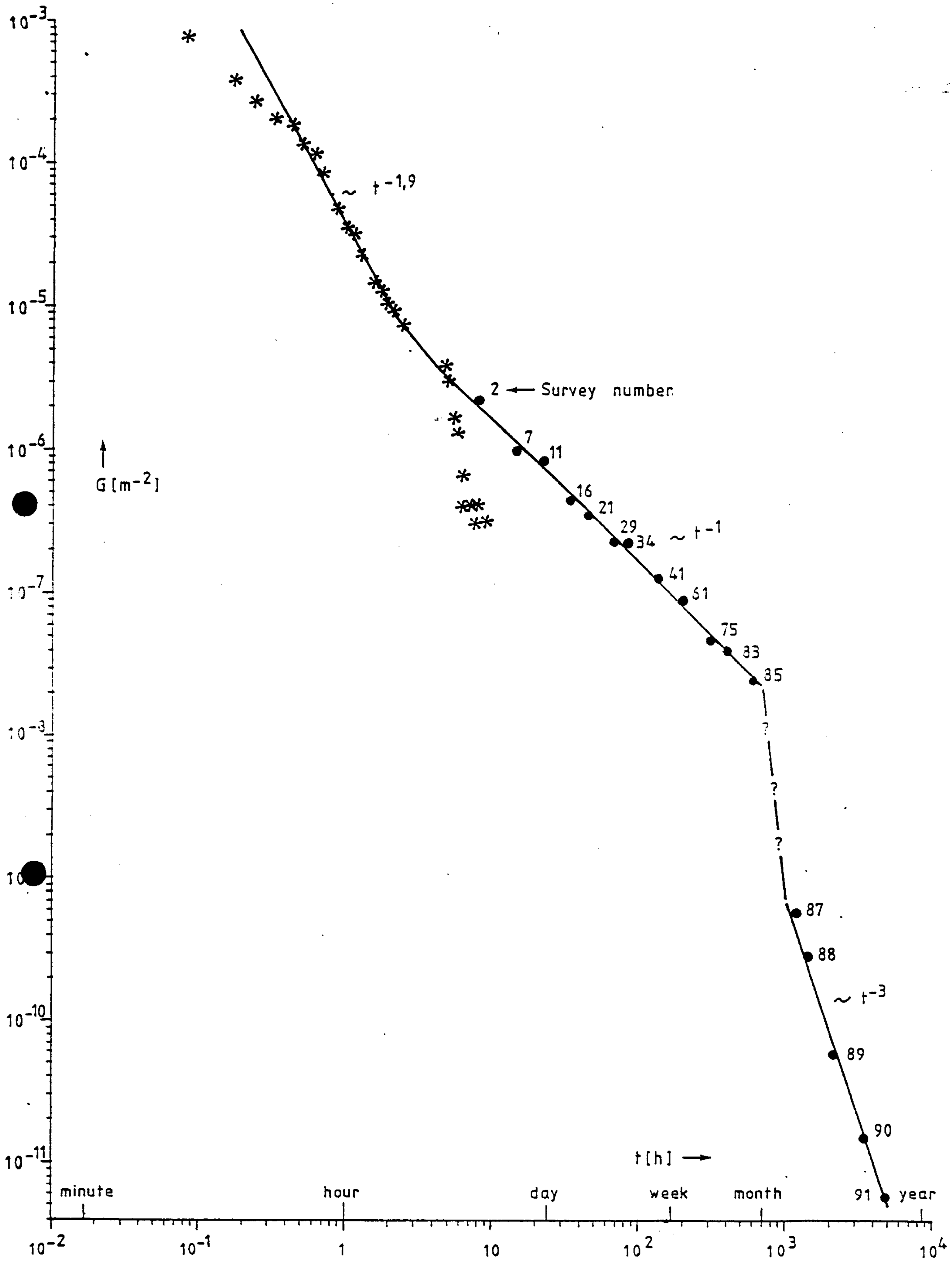


Fig. 4 The normalized maximum concentration during the 1979 experiment versus time after release. Note, that survey 85 was the last in the neighbourhood of the release point.

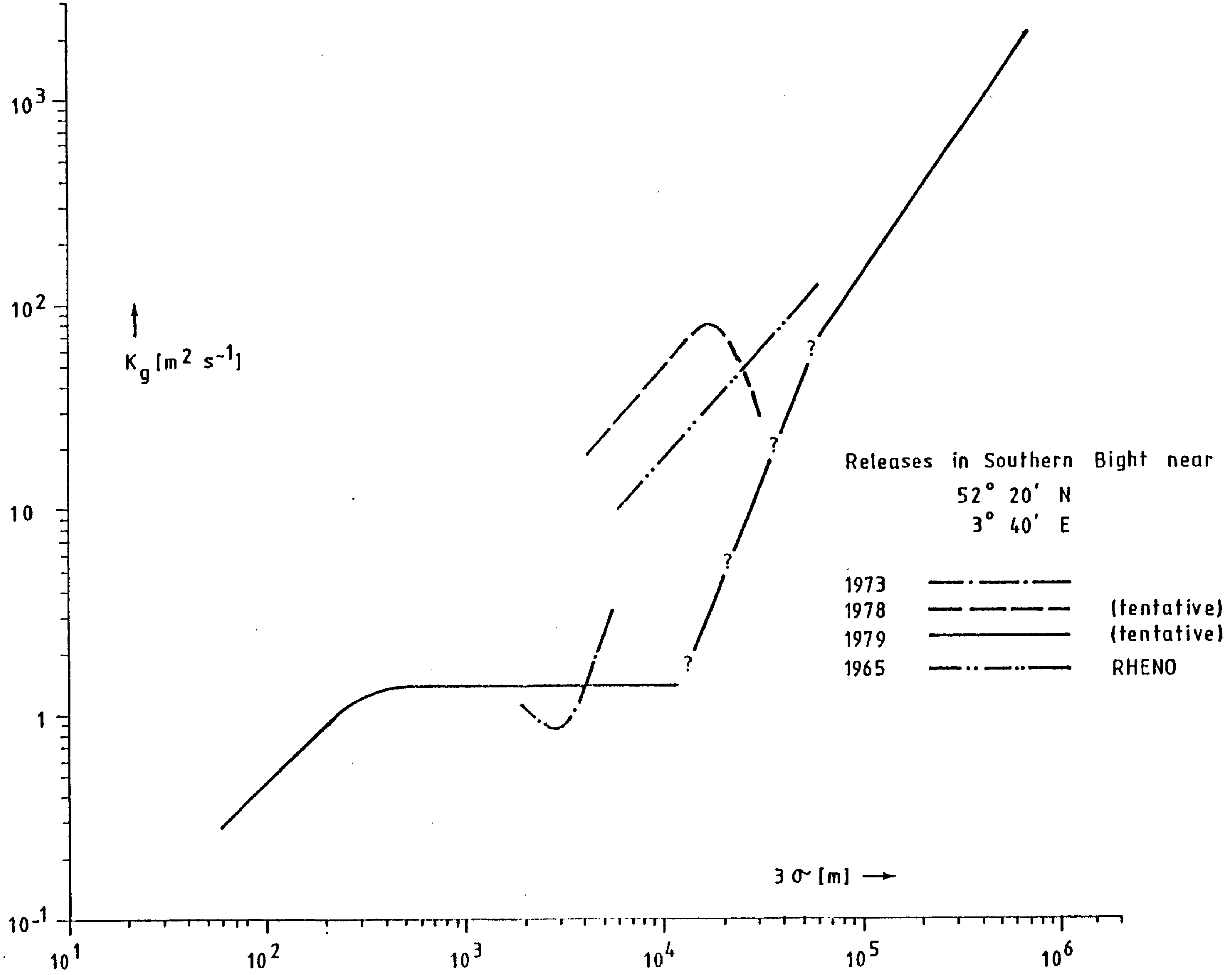


Fig. 6 The horizontal diffusion coefficient K_g of the experiments in the same region versus the scale of the patch 3σ

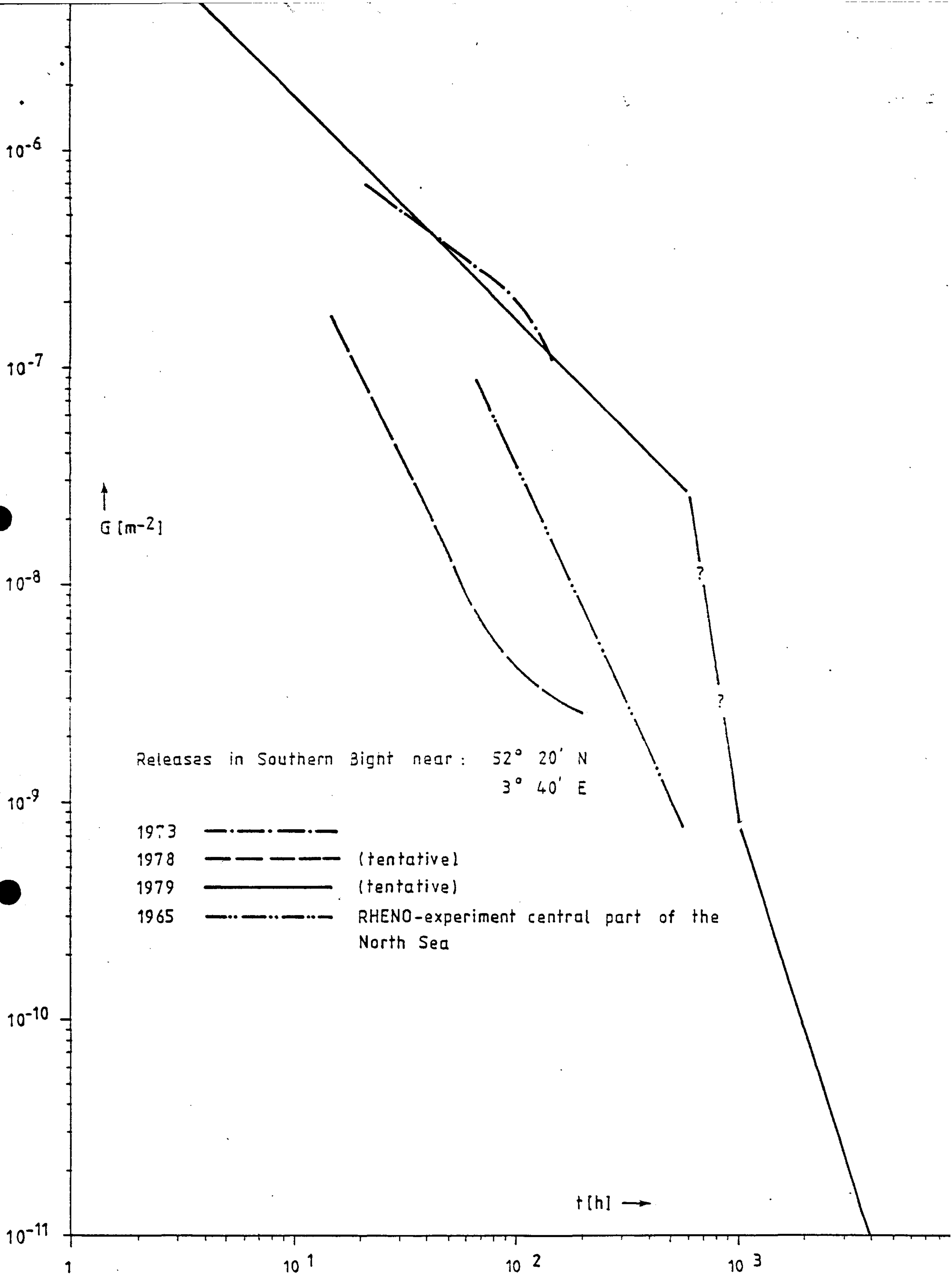
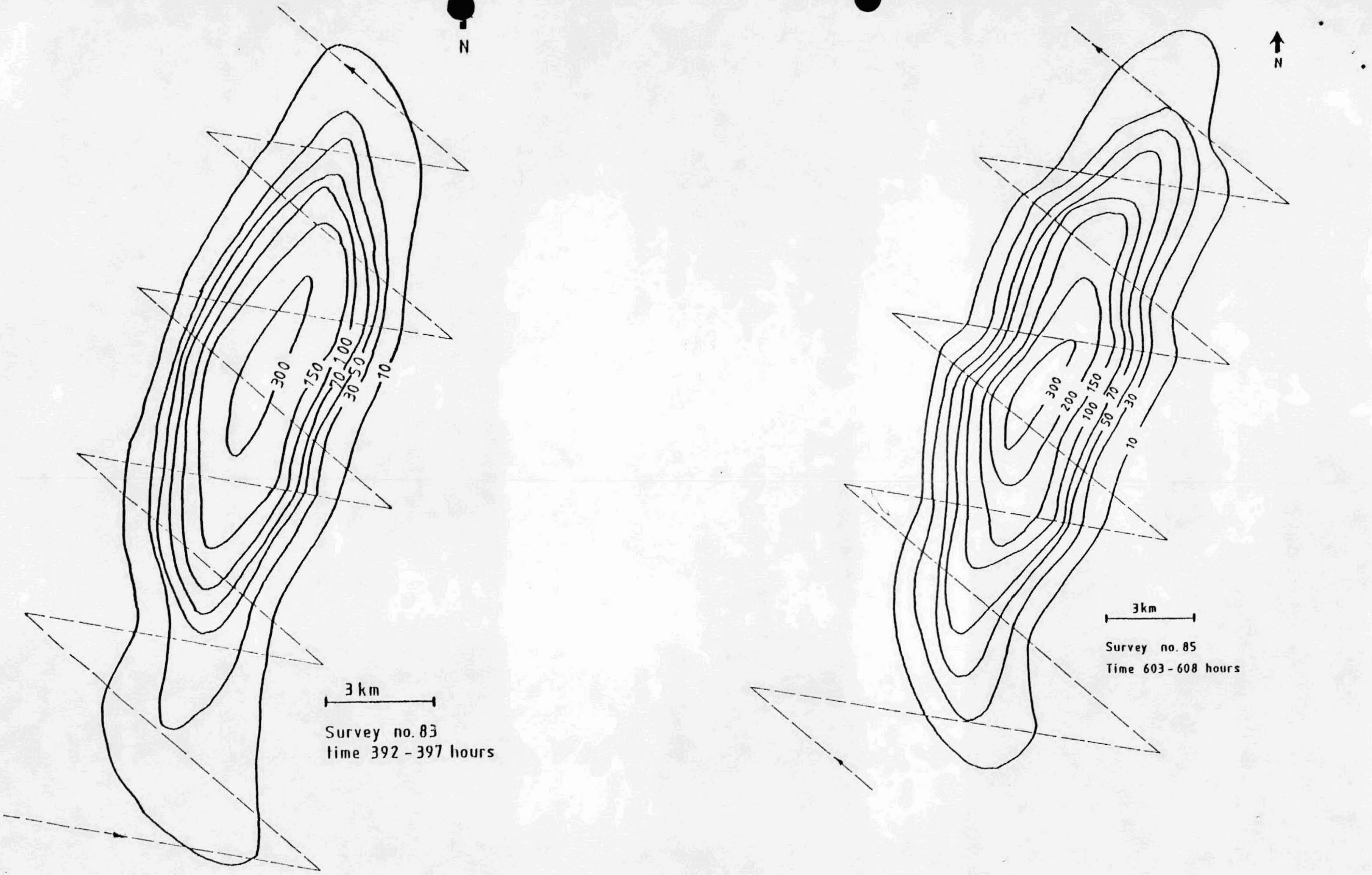


Fig. 5 The normalized maximum concentrations of experiments in the same region as function of the time after release.

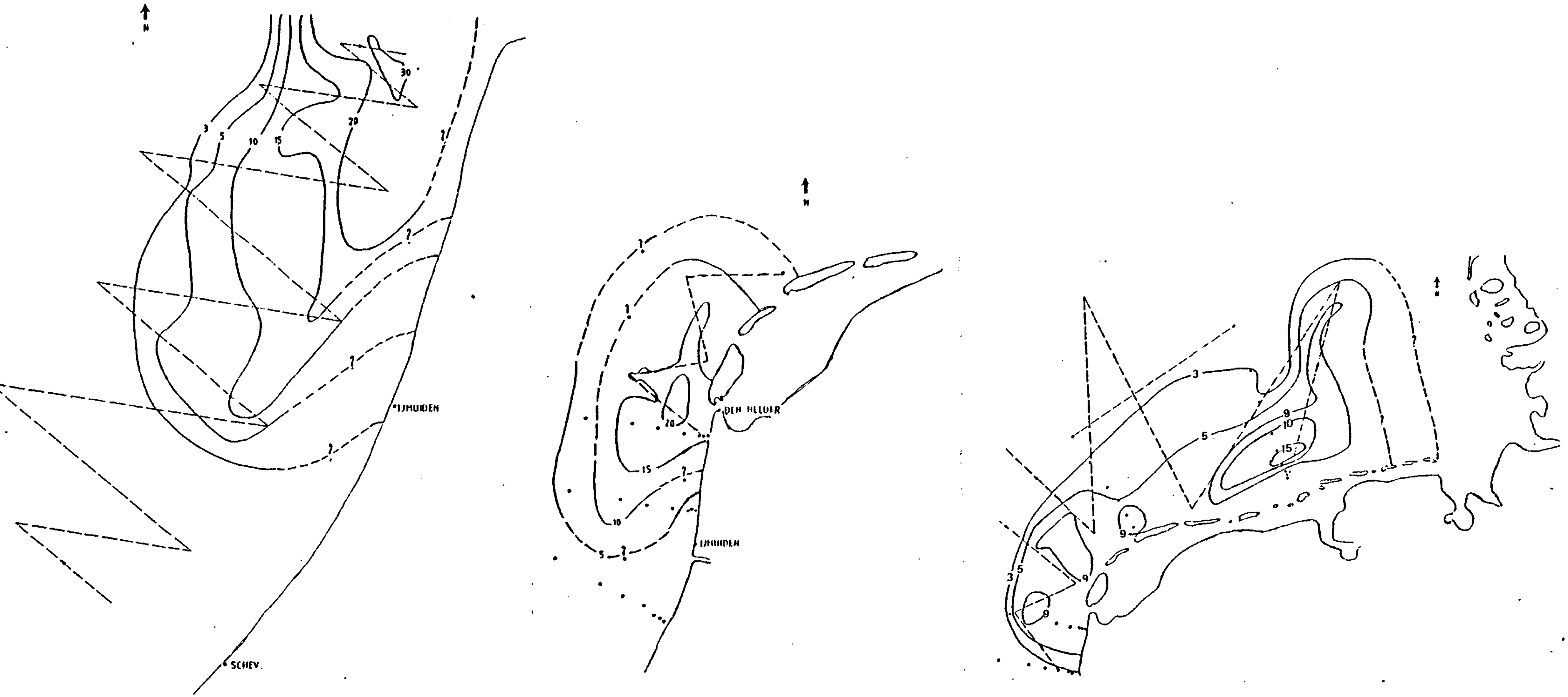
Fig. 7 The positions of the maximum concentrations during some surveys.



Survey no. 83
time 392 - 397 hours

Survey no. 85
Time 603 - 608 hours

Fig. 8a Two examples of the small scale surveys.
Concentrations (ng/l) were measured with shipborn fluorimeters.



10 km

--- Sampling interval: 5 min.

Survey no. 87

Time 1114 - 1141 hours

20 km

--- Sampling interval: 3 min.

Survey no. 88

Time 1307 - 1333 hours

- Stations "Holland"

30 km

--- Sampling interval: 10 min.

Survey no. 89

Time 1960 - 2023 hours

- Stations "Holland"

Fig. 8b The large scale surveys no. 87, 88 and 89.
Concentrations (ng/l) were measured with the TNO-fluorimeter.

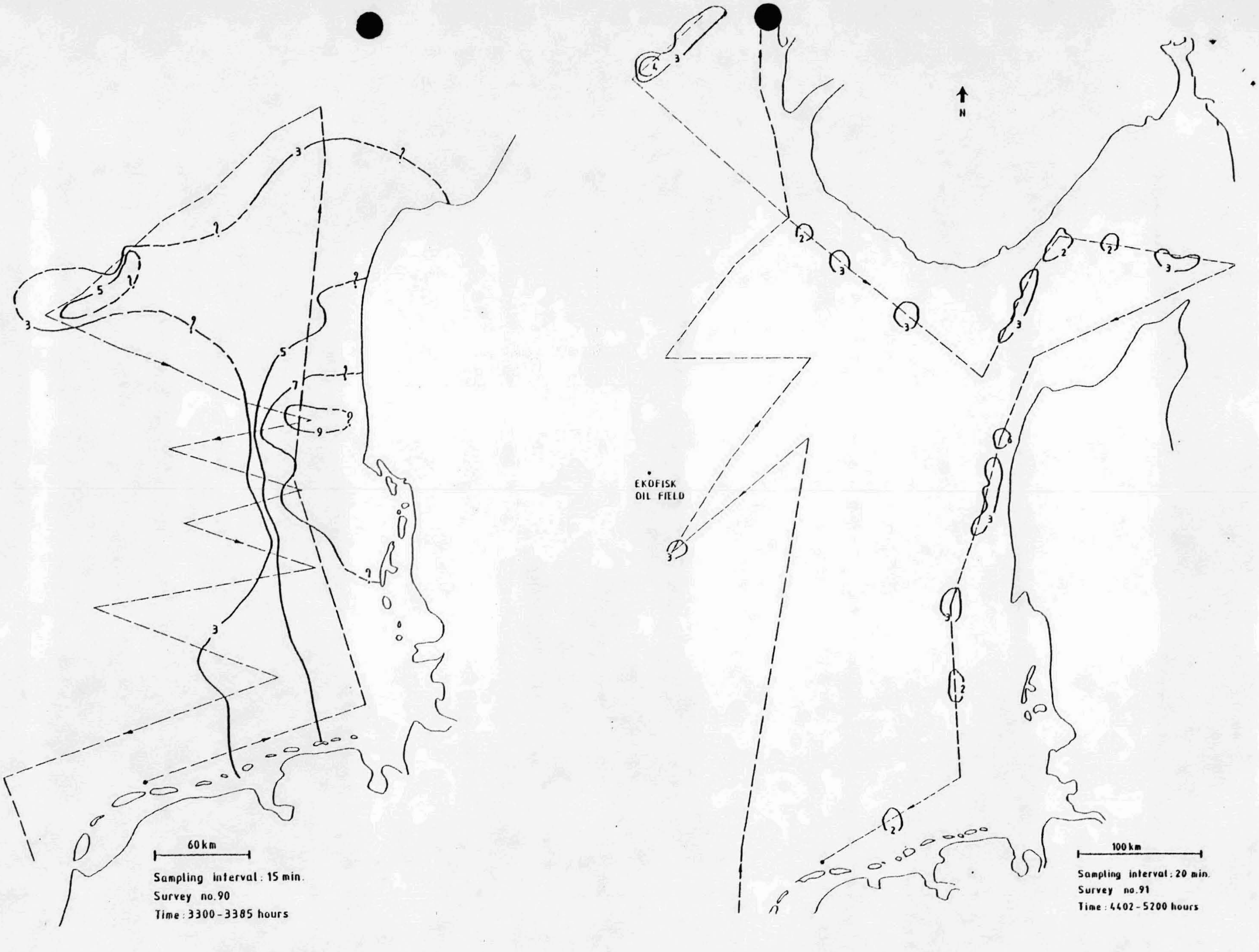


Fig. 8c The large scale surveys no. 90 and 91
Concentrations (ng/l) were measured with the TNO-fluorimeter

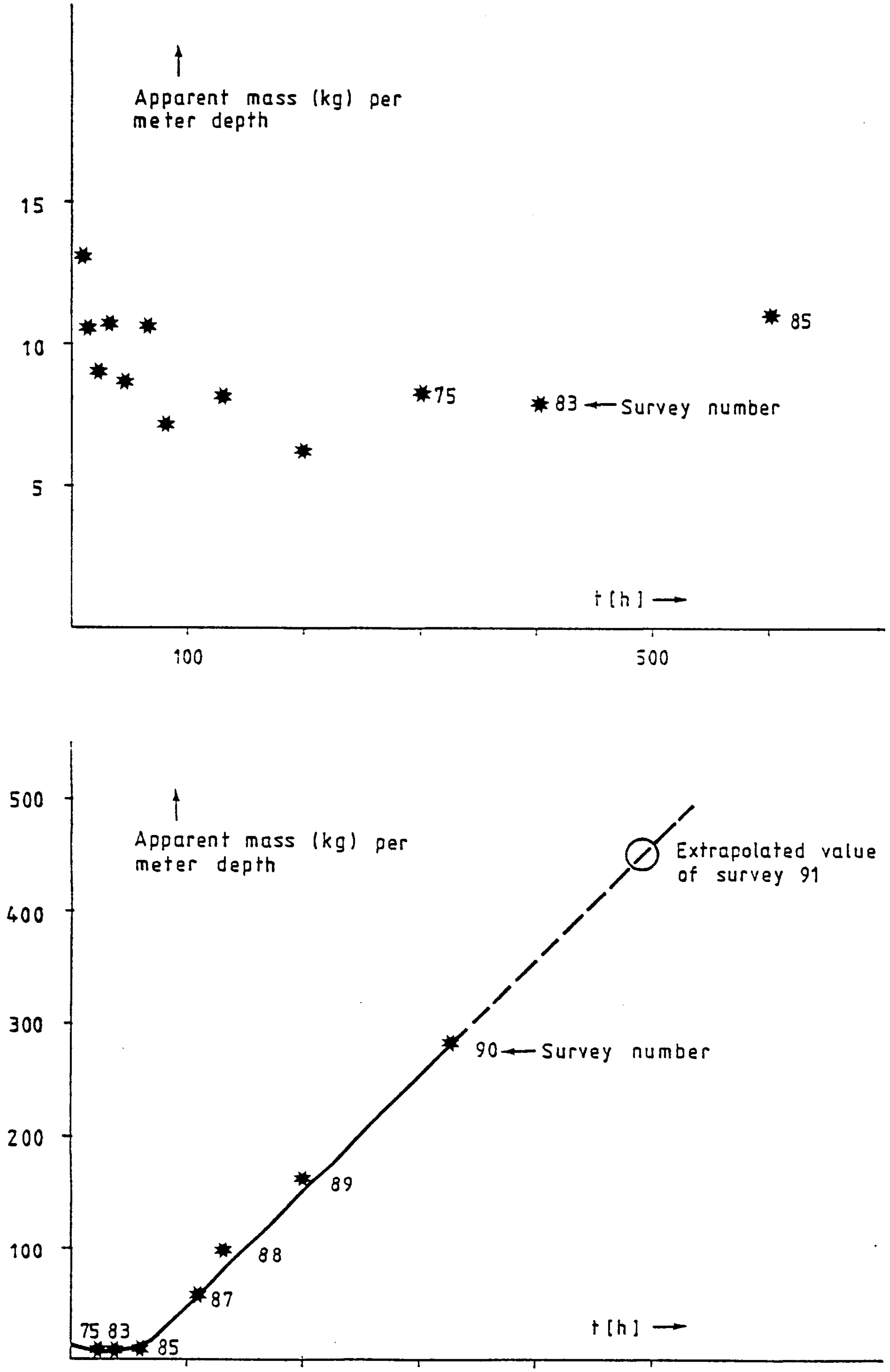


Fig. 9 Apparent mass per meter $\int_0^\infty C(A)\,dA$ as a function of time, if C is calculated on the basis of usual relation between fluorescence and mass.

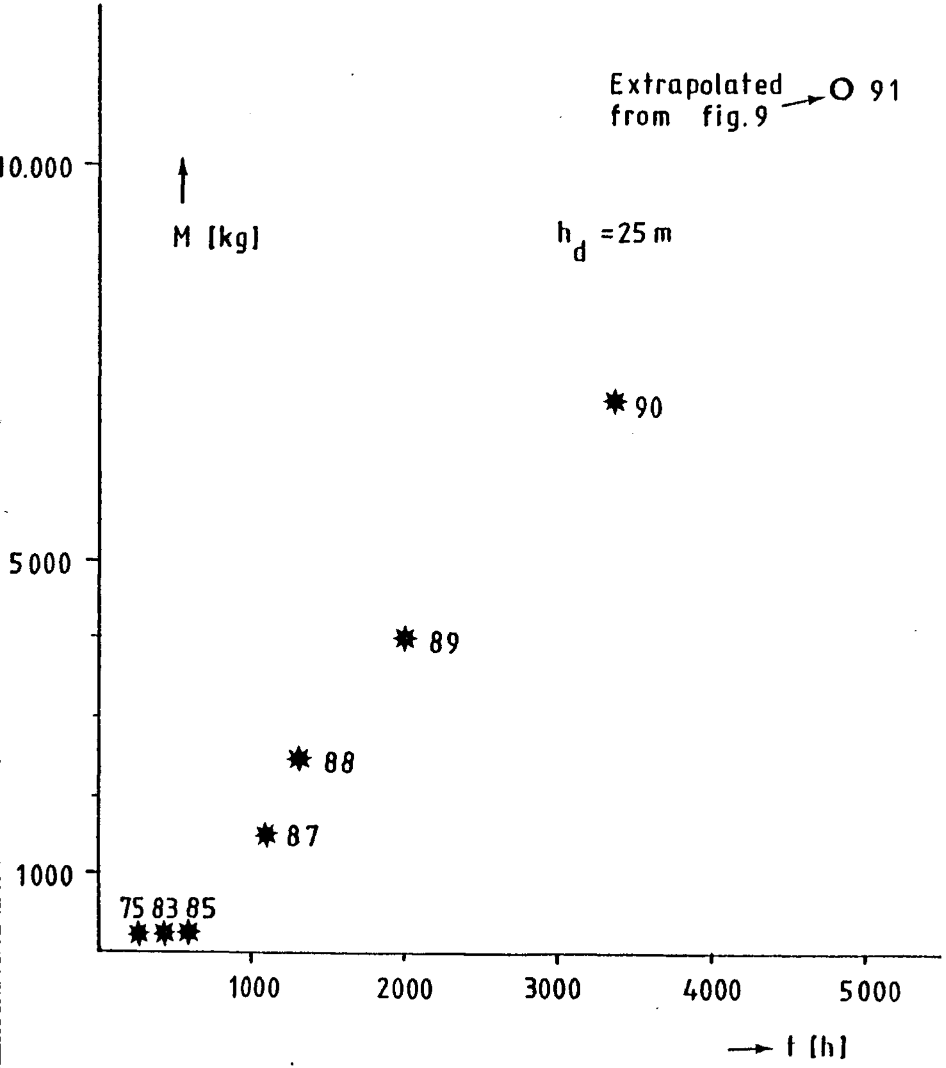


Fig. 10a The apparent mass versus time if penetration depth is constant.

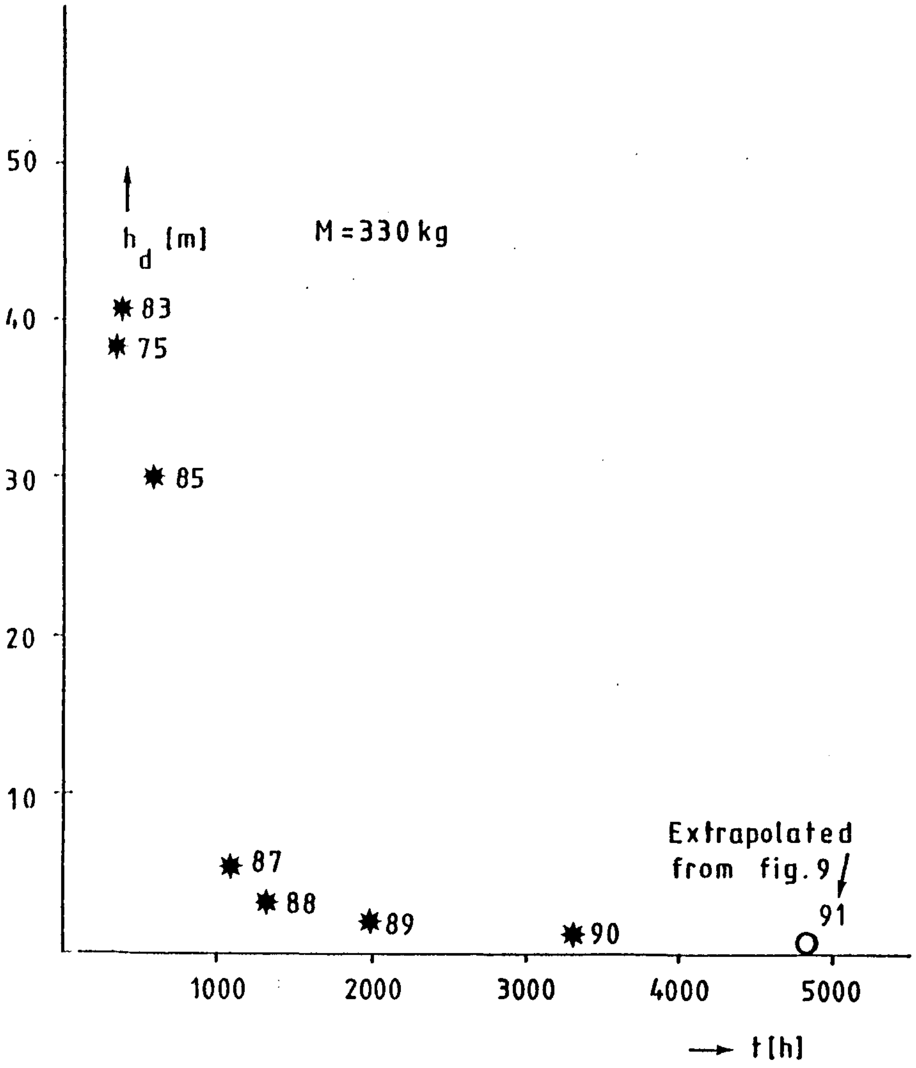


Fig. 10b The penetration depth versus time if the mass is constant.