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TIME-RELATED CHANGES OF ORGANIC AND INORGANIC NITROGEN AND OTHER INTER-RELATIONSHIPS IN THE SOUTHERN NORTH SEA OFF THE DUTCH COAST; A STATISTICAL ANALYSIS.

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Time-related changes of organic and inorganic nitrogen and other inter-relationships in the southern North Sea off the Dutch coast; a statistical analysis.

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ABSTRACT

Monthly measurements of nutrients and salinity have been performed at sixteen selected locations in the Dutch coastal area over the period 1980 - 1983. From these nutrient data organic nitrogen contents were calculated as the difference between total nitrogen (both dissolved as particulate) and the sum of nitrate, nitrite and ammonia concentrations.
By means of a multiple linear regression model applied to combined sub-datasets of two neighbouring locations the authors were able to elucidate the influence of five variables (nitrate, nitrite, ammonia, salinity and river Rhine discharge) on the occurrence of organic nitrogen (ORGN). T - ratios and fractions for each variable to total variance of ORGN were calculated, resulting in a spatial distribution of significant and non-significant contributions to ORGN.
Partial regression plots were produced in order to identify outlying data points, whereas most of them could be omitted on account of very high values of ORGN in the winterperiod. The relative influences of these five variables on the spatial occurrence of ORGN, indicated by their contributions to total variance of ORGN reflects closely the average distribution of river Rhine water in the Dutch coastal area.

INTRODUCTION

This paper gives a preliminary description of the nutrient variations in space and time in the Dutch marine waters and concerns mostly with the changes of and relations between organic and inorganic nitrogen in that part of the coastal area that is directly influenced by the river Rhine outflow (see fig. 1).

Large quantities of nutrients (nitrate, ammonia, phosphate) from domestic and industrial sources are carried to the coastal waters by the freshwater run-off from the Rhine and some minor sources. This nutrient enrichment of the Dutch marine environment has effected an increasing eutrophication in this area during the last decades (1,2), concomitantly with higher production of organic material.

Due to the south-north directed residual-current along the Dutch coast the out- flowing Rhine water is transported in northerly direction, producing a flowing pattern with low salinities parallel to the coast. This plume of river water contains a relatively high amount of suspended matter and can therefore be observed from space by remote sensing techniques distinctly separated from surrounding water masses(3,4).
Simple dilution by mixing of river water and sea water results in a conservative behaviour of nutrients in the coastal zone, e.g. a linear decrease with increasing salinity. However several other processes can also have a strong impact on the nutrient concentrations, such as primary production, mineralisation, adsorbatory and sedimentary processes. Due to these influences deflections from conservative mixing can be found with higher or lower nutrient values than expected from mixing only.

As a result two important gradients occur in the Dutch coastal zone. Going offsshore from the Dutch coast salinity increases gradually and nutrient concen- trations decreases and going to the north from Hoek van Holland to Texel com- parable changes in these parameters are detectable. As a matter of fact a lot of fluctuations and anomalies in the overall distribution of nutrients will often occur due to stream variations, windintensity, phytoplankton blooms and changes in the river outflow.

In this complex picture of nutrient movements we have tried to elucidate the relation of the organic nitrogen content to some crucial variables as salinity, inorganic nitrogen species (nitrate, nitrite and ammonia) and the monthly averaged discharge of the river Rhine. By applying an interactively used multiple regression model it was possible to identify extraordinary data points and to correct for it.
The aim of this paper was to reveal the possible usefulness of such a regression model to interprete nutrient data sets in estuarine waters.

METHODS AND ANALYSES

Analytical methods:

Water samples (surface) were collected every month from ships of Rijkswaterstaat at selected locations along the Dutch coast. The position of the sampling sites are shown in figure 1, arranged in four lines off Callantsoog, Egmond, Noordwijk and Terheyden respectively. After transportation to the laboratory the samples were filtrated through 0.45 u Oxoid filters and kept deep frozen until analysis.

All analyses, except for ammonia, were carried out with Technicon Auto-analyzerr II equipment. Total-nitrogen analyses were performed in the unfiltered water according to the method of Koroleff (5). Nitrogen compounds were oxidized to nitrate by boiling with an alkaline persulfate solution. Nitrate ions were reduced then in a Cd - Cu reductor column and subsequently analyzed as nitrite ions according to the method of Bendschneider and Robinson (6), whereby nitrite reacts to a diazo compound with sulfanilamide and then couples with a diamine to form a reddish-purple Azo dye.

Ammonia analysis was performed according to the manual method as described by Koroleff (7), with citrate buffer as a complexing agent to avoid precipitaties of calcium- and magnesiumhydroxides at the alkaline pH of the reaction mixture as described by Solorzano (8).

Description of variables:

TOTN = total nitrogen.
NTRA = nitrate.
NTRI = nitrite.
AMMO = ammonia.
SALI = salinity.
RAF = river Rhine discharge / monthly averages(9).
ORGN = TOTN - NTRA - NTRI - AMMO = organic nitrogen.

Statistical analysis:

A multiple linear regression model is used to examine the relation between ORGN and the following nominated carriers: NTRA, SALI, AMMO, NTRI and RAF at different locations (see fig. 1). The following combined datasets were compiled:

C310, C1020, C2030	C310 = C3 + C10; C3 = 3 km off the coast at Callantsoog.
E310, E1020, E2030	
N310, N1020, N2030	
T310, T1020, T2030	
CE3, CE10, CE20, CE30	CE3 = C3 + E3
EN3, EN10, EN20, EN30	
TN3, TN10, TN20, TN30	

On each of these combined datasets multiple regression of ORGN on the other carriers was carried out. Plots of residuals against fitted values did not show any significant trend and the residual Gaussian quantile - quantile plots were reasonable straight.

In order to identify extraordinary data points partial regression plots for the carriers NTRA, SALI and AMMO were produced (10). As an example a partial reg- gression plot for NTRA and dataset EN20 is given in fig. 2. On the Y-axis the residuals from the least-squares regression of ORGN on the other carriers except NTRA is plotted(r1) and on X-axis the residuals from the regression of NTRA on the other carriers(r2).
This plot has a least squares slope equal to the regression coefficient of NTRA in the full model and least squares residuals equal to the final residuals of the full multiple regression model.
If the outlying data points in the partial regression plots seem to be unrealistic after inspec- tion of the observed values, they were omitted from the datasets. An other multiple regression was then carried out with the reduced dataset. In our example in fig. 2 five points have been omitted as indicated.
One of these points (with the lowest r1 value) has negative value for ORGN and the other four points have a value for TOTN which is too high for the winter period (January, February and March), and is probably caused by false measurements.

RESULTS

Gradients:

In figure 3 some examples of the occurrence of nutrient gradients in the Dutch coastal area are drawn. Mean values of TOTN, NTRA and AMMO for the summer period (June - October) of the years 1980 - 1983 have been used. The decreasing con- centrations of the nutrients at longer distance from the coast are in agreement with the salinity distribution of figure 4. The lowest salinity values off Terheyden indicate percentages of Rhine water greater than 30 %. The continious mixing with the inflowing freshwater diminishes the concentration of the nutrients also in northerly direction (fig 3B), hence much lower values are found off Callantsoog.
The strong influence of the discharge of the river Rhine is shown in fig 4A a and 4B. The high discharge of freshwater in August 1980 produced lower salinitities at longer distances from the coast and would also have a large impact on the nutrient values in the northern part of the coastal area.

The relationship between nutrient concentration and salinity is shown for nitrate and ammonia in fig 5, estimated with data of the winterperiod of 1981/1982. Nitrate behaves conservatively due to normal mixing, while ammonia shows a non-conservative behaviour with lower values than according to mere mixing processes.

Seasonal changes:

The seasonal changes in organic nitrogen and nitrate, given as the monthly mean values at 20 km off the Dutch coast, are depicted in fig. 6. Low values for organic nitrogen could be calculated in the wintermonths and elevated valuess in the summer period, corresponding with the growing season. For nitrate an reversed picture has been obtained. It is thereforeclear that an inversely linear relationship for nitrate and organic nitrogen has been visualized: consumption of nitrate by the phytoplankton to produce organic nitrogen.
In figure 7A one can observe a large deviance for this relationship due to the influence of many other variables, which all have a more or less strong impact on the formation of organic nitrogen.

Hence, a multiple regression model applied to the total data set of the examined time period might reveal more information about local impacts of each variable on the production of organic nitrogen.

Trend analysis:

To apply multiple regression analysis on the total dataset obtained from the monitoring program of 1980 till 1982, it was necessary to deduce if a significant change in the nutrient load of the coastal area did occur during this time interval Only without the occurrence of such a change it was allowed to integrate all sub-datasets of the different years of investigation to one combined dataset for each two localities. To perform such a trend analysis the relation of total nitrogen and nitrate to salinity was estimated. The concentrations of these nutrients at a fixed salinity for each year establishes then the yearly fluctuations of the nutrient influx and could reveal a possible trend. Only data collected in the winterperiod (Dec, Jan and Feb) have been used to avoid impacts of primary production and mineralisation processes(11).
The results of this exercise are shown in fig. 7B. The variation of nitrate lies within the range of the standard error, hence no significant trend has been demonstrated.

Multiple linear regression:

The configuration of the regression model is as follows:

$$ORGN = A + Bx(NTRA) + Cx(SALI) + Dx(AMMO) + Ex(NTRI) + Fx(RAF)$$

The coefficients B to F represent the regression coefficients in the full regression model. T - ratios (= estimate of the regression coefficient in the full model divided by its standard error) have been calculated to reveal significant terms in this model. For t - ratios smaller than 2, the variable should not be accepted as significant term. Tables 1 - 2 give the t - ratios and the fractions of the total variance of ORGN accounted for by NTRA, SALI and AMMO. These fractions are reproduced in figures 8a, 9a and 10a, whereas the spatial configurations of the t - values for the five variables are given in figures 8 - 12.

From the configurations of the t - values and the fractions of total variance of ORGN for NTRA, SALI and AMMO the following general remarks can be made:

1. Nitrate(NTRA) has in the whole coastal area (except for C310 and CE3) significant contributions to the total variance of ORGN (organic nitrogen) with the highest fractions at 3 and 20 km off the coast andminimum values at about 10 km (fig. 8, 8a, values within rectangles).
2. At longer distance from the coast the significant fraction to total variance for the salinity (SALI) increases, while at 10 km hardly any significant contribution is observable (fig. 9, 9a, values within rectangles).
3. At scattered locations ammonia (AMMO) appears to have a minor fraction to total variance of ORGN with the highest values near Callantsoog (fig. 10, 10a). However, at 10 km off the coast no significant contribution could be detected(values within rectangles).
4. Nitrite (NTRI) has only significant contributions to the total variance of ORGN near the river Rhine outflow(fig. 11,values within rectangles).
5. Only at about 10 km off the coast the discharge of the Rhine has a significant contribution to ORGN (fig. 12,values within rectangles). With all the other datasets of the combined locations no significant contribution has been found.

All the above mentioned features can be related unequivocally to the plume of river Rhine water outflowing into the Dutch coastal zone: Rhine water contains high amounts of suspended matter and therefore turbidity is highest at those locations in the coastal area where the percentage of river Rhine water is maximal, consequently at about 10 km off the coast.
Light intensisity might be here occasionally the limiting factor for primary production (12) and will therefore be more important for the production of organic nitrogen than the elevated nutrient concentrations present in excess. It is also evident that the discharge of the Rhine will have some impact just at these lo- cations because of its positive correlation to the turbidity of the coastal zone. At longer distance from the coast light intensity increases highly and so nitrate and salinity (closely related to nutrient concentrations, see above) become more important for the formation of organic nitrogen.
Simularly, nitrate and ammonia exhibit significant contributions to ORGN with a strong impact on its formation at the shallow waters inshore, where light intensity is not limiting.
Nitrite is an intermediate compound in mineralisation processes and will have more influence on the formation of organic nitrogen at locations where mineralisation is favoured above primary production, thus near the outflow of river water into the coastal area, because of the high concentrations of suspended matter present and stimulated bacterial activity (12).

Conclusions:

- At about 10 km off the Dutch coast minor contributions to the total variance of ORGN have been estimated for nitrate, ammonia and salinity, while river Rhine discharge exhibited the only significant contribution just at this very distance from the coast.

- The spatial configuration of the relative importance of the five variables in terms of accounting for the total variance of =organic nitrogen, measured over a time period of three years, reflects closely the average distribution of the plume of river Rhine water outflowing in the North Sea along the Dutch coast.

- From our results it can be inferred that the application of an interactively used multiple regression model may be very valuable to reveal the influence of nutrient enrichment of coastal and estuarine zones on the production of organic material.

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TABLE 1. Calculated t values and fractions of total variance of ORGN from the multiple regression model.

variate	C310 t ratio	C310 fraction of total variance	C1020 t ratio	C1020 fraction of total variance	C2030 t ratio	C2030 fraction of total variance	E310 t ratio	E310 fraction of total variance	E1020 t ratio	E1020 fraction of total variance	E2030 t ratio	E2030 fraction of total variance
NTRA	0.30	-	4.37	0.19	2.13	0.06	4.33	0.22	3.76	0.15	4.62	0.17
SALI	2.50	0.08	3.63	0.12	3.70	0.18	2.57	0.07	3.40	0.13	6.79	0.36
AMMO	3.38	0.16	0.38	-	1.49	0.03	0.94	0.01	1.22	0.02	2.07	0.03
NTRI	0.28		0.31		0.22		0.65		0.78		0.43	
RAF	0.79		2.63		1.61		0.83		0.57		0.39	
	N310		**N1020**		**N2030**		**T310**		**T1020**		**T2030**	
NTRA	4.15	0.21	5.37	0.22	4.94	0.17	2.73	0.08	2.92	0.10	4.01	0.15
SALI	4.03	0.20	4.09	0.13	4.45	0.14	5.06	0.29	4.03	0.20	6.41	0.40
AMMO	1.87	0.04	3.47	0.09	2.28	0.04	2.13	0.05	2.00	0.05	2.45	0.06
NTRI	0.80		4.58		5.62		2.39		0.77		0.02	
RAF	1.15		0.79		0.36		0.76		1.49		0.40	

TABLE 2. Calculated t values and fractions of total variance of ORGN from the multiple regression model.

variate	CE3 t ratio	CE3 fraction of total variance	CE10 t ratio	CE10 fraction of total variance	CE20 t ratio	CE20 fraction of total variance	CE30 t ratio	CE30 fraction of total variance
NTRA	1.01	0.01	4.21	0.17	4.41	0.20	3.03	0.09
SALI	3.51	0.16	1.85	0.03	4.72	0.22	5.96	0.35
AMMO	3.93	0.20	0.30	-	2.57	0.07	0.53	-
NTRI	0.02		0.51		0.15		0.73	
RAF	0.48		1.98		1.07		0.04	

variate	EN3 t ratio	EN3 fraction of total variance	EN10 t ratio	EN10 fraction of total variance	EN20 t ratio	EN20 fraction of total variance	EN30 t ratio	EN30 fraction of total variance
NTRA	4.08	0.20	3.05	0.10	7.12	0.21	3.06	0.11
SALI	3.07	0.16	1.41	0.02	7.04	0.20	5.22	0.31
AMMO	2.11	0.05	0.03	-	5.61	0.13	0.46	-
NTRI	0.89		1.97		7.01		0.30	
RAF	1.44		1.88		0.92		0.42	

variate	TN3 t ratio	TN3 fraction of total variance	TN10 t ratio	TN10 fraction of total variance	TN20 t ratio	TN20 fraction of total variance	TN30 t ratio	TN30 fraction of total variance
NTRA	3.55	0.13	3.11	0.10	5.77	0.20	3.45	0.14
SALI	5.40	0.31	3.78	0.15	6.09	0.23	5.00	0.29
AMMO	1.40	0.02	1.64	0.03	2.89	0.05	1.59	0.03
NTRI	1.98		2.32		5.41		0.21	
RAF	1.12		3.03		0.30		0.31	

FIG. 1: THE DUTCH COASTAL AREA WITH THE SAMPLING SITES.

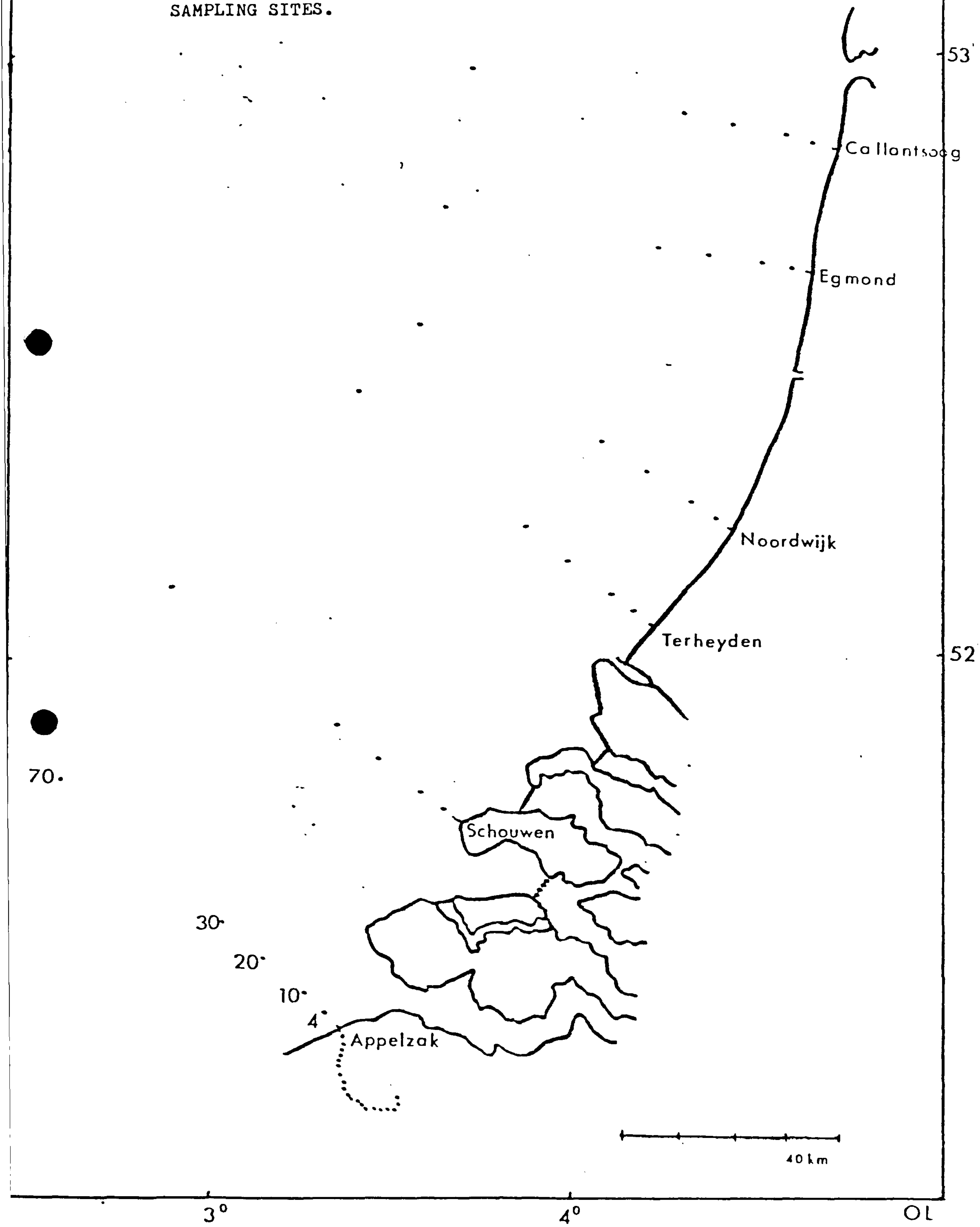
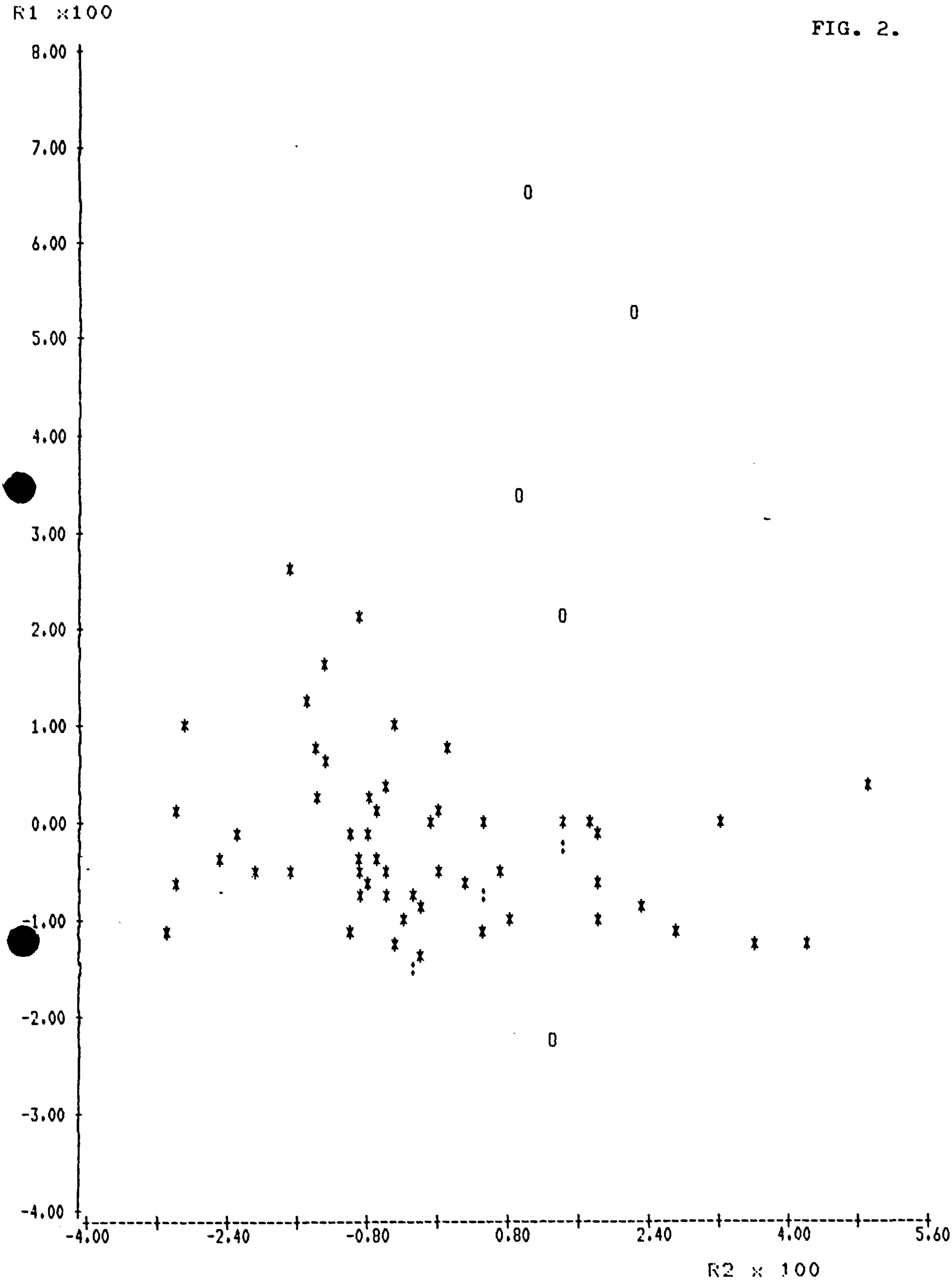


FIG. 2.



PARTIAL REGRESSION PLOT FOR NTRA

******: NOT OMITTED
000000: OMITTED
:::::::: DATA OVERLAP

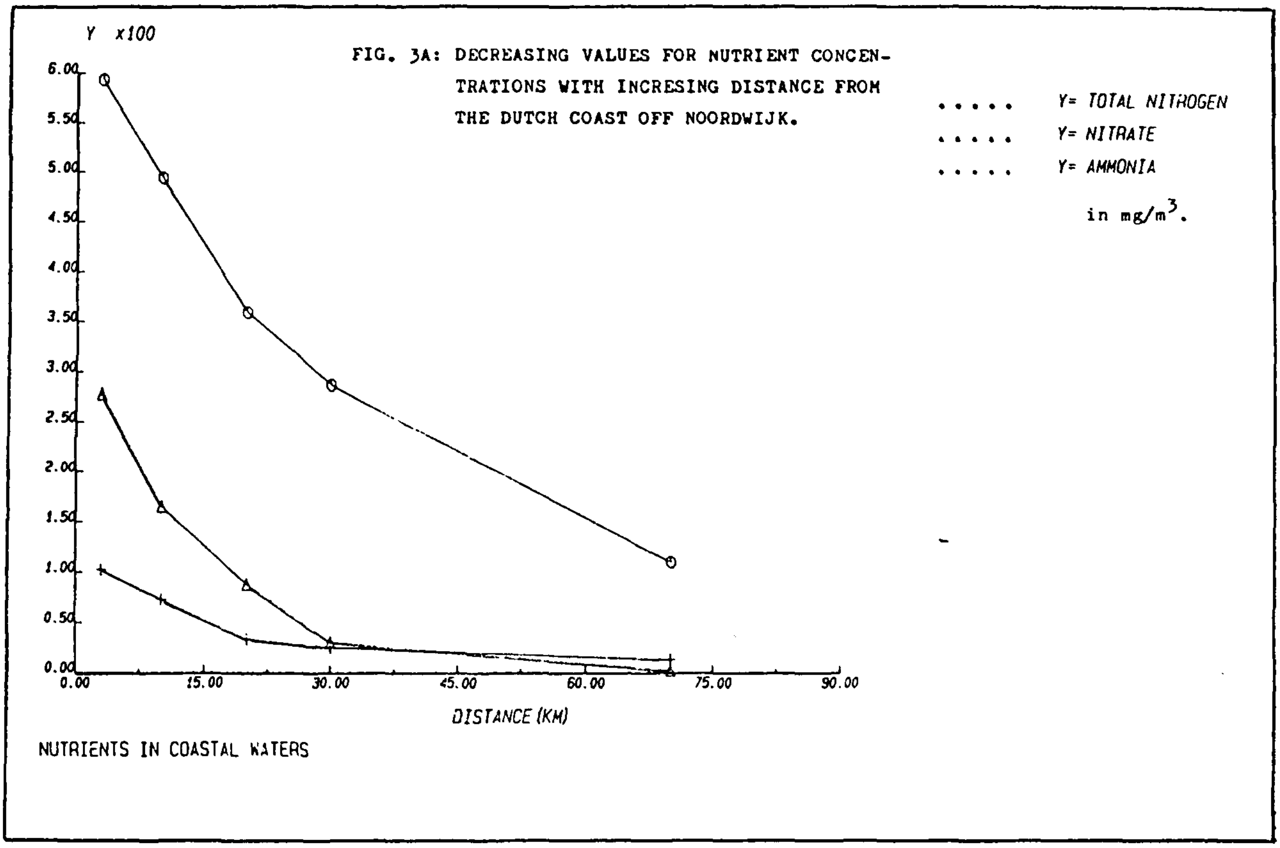


FIG. 3A: DECREASING VALUES FOR NUTRIENT CONCENTRATIONS WITH INCRESING DISTANCE FROM THE DUTCH COAST OFF NOORDWIJK.

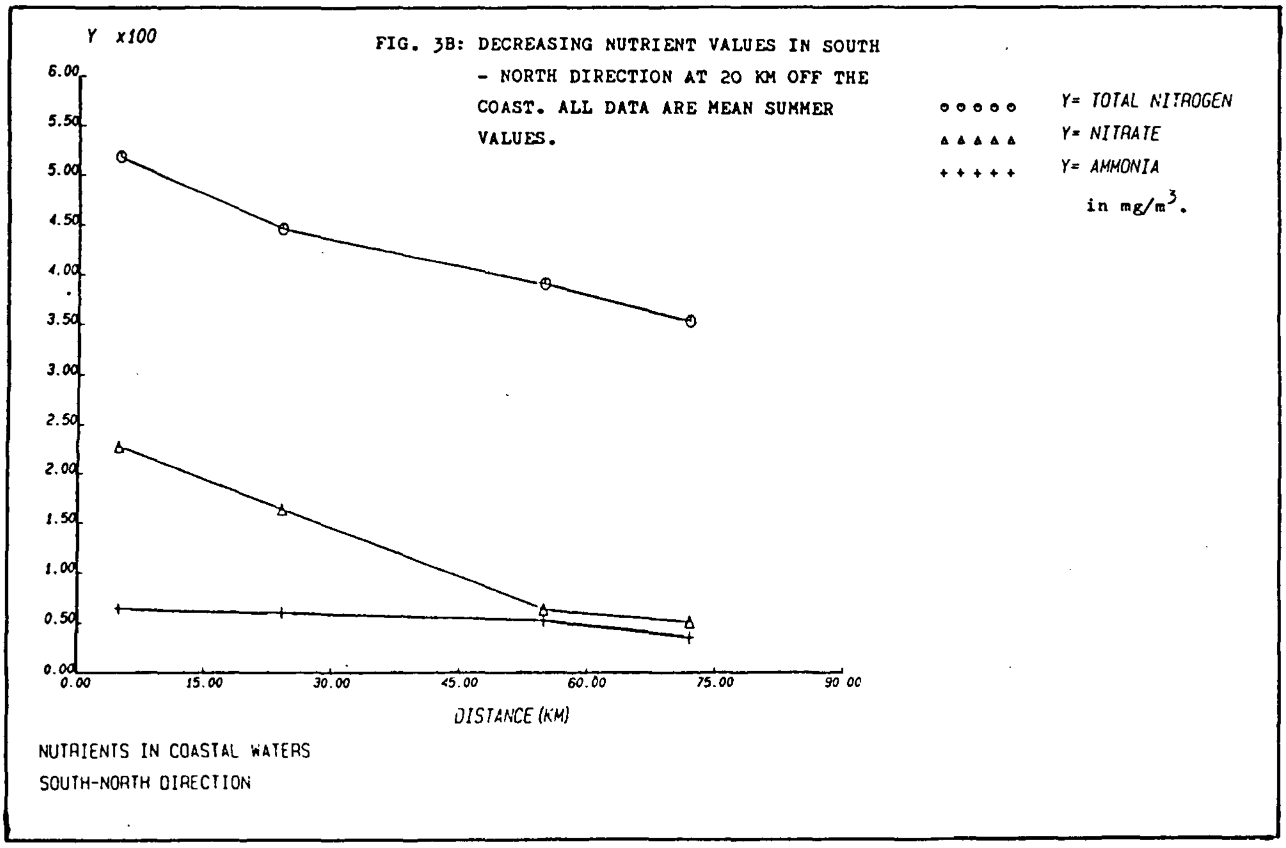


FIG. 3B: DECREASING NUTRIENT VALUES IN SOUTH - NORTH DIRECTION AT 20 KM OFF THE COAST. ALL DATA ARE MEAN SUMMER VALUES.

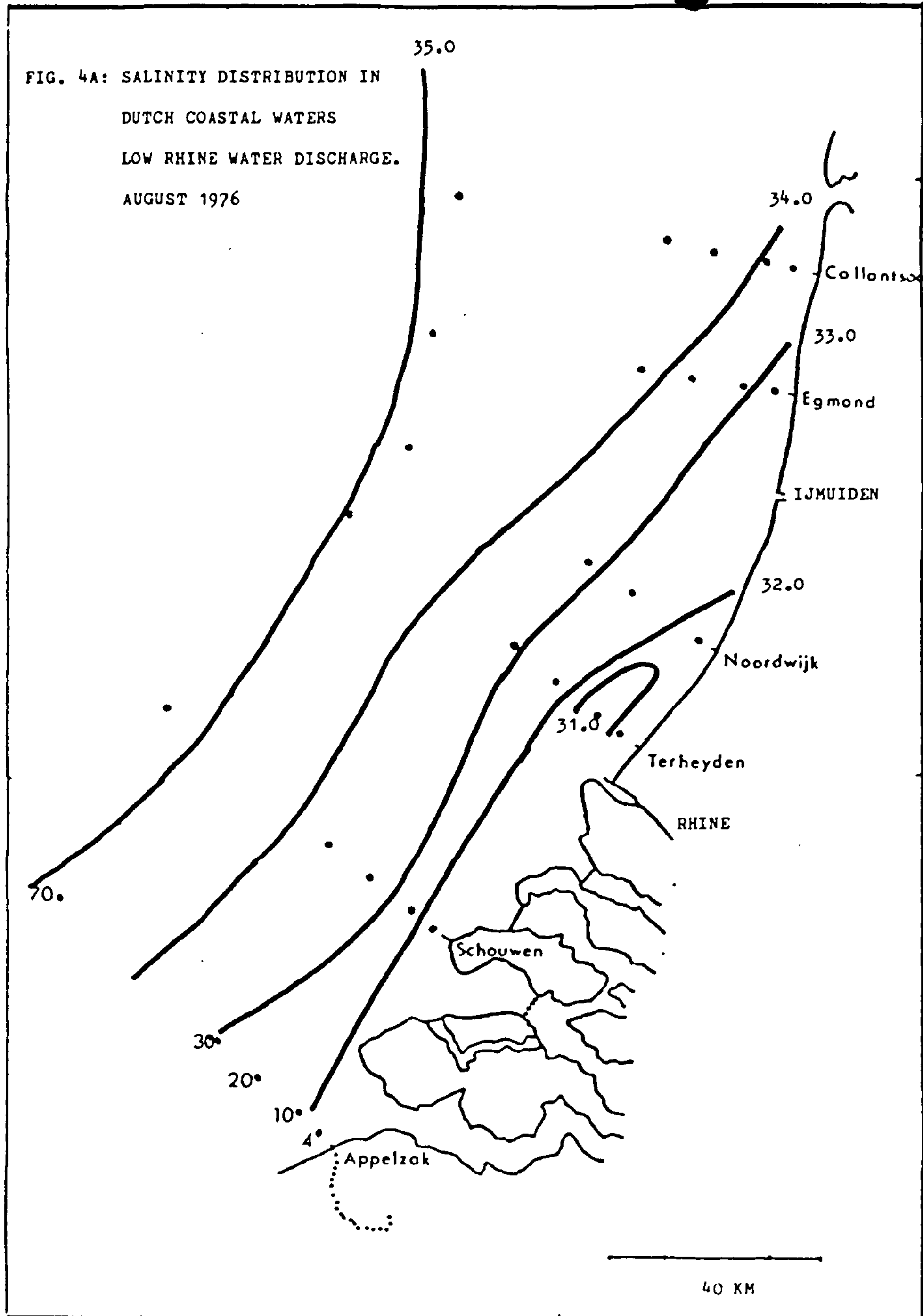


FIG. 4A: SALINITY DISTRIBUTION IN DUTCH COASTAL WATERS LOW RHINE WATER DISCHARGE. AUGUST 1976

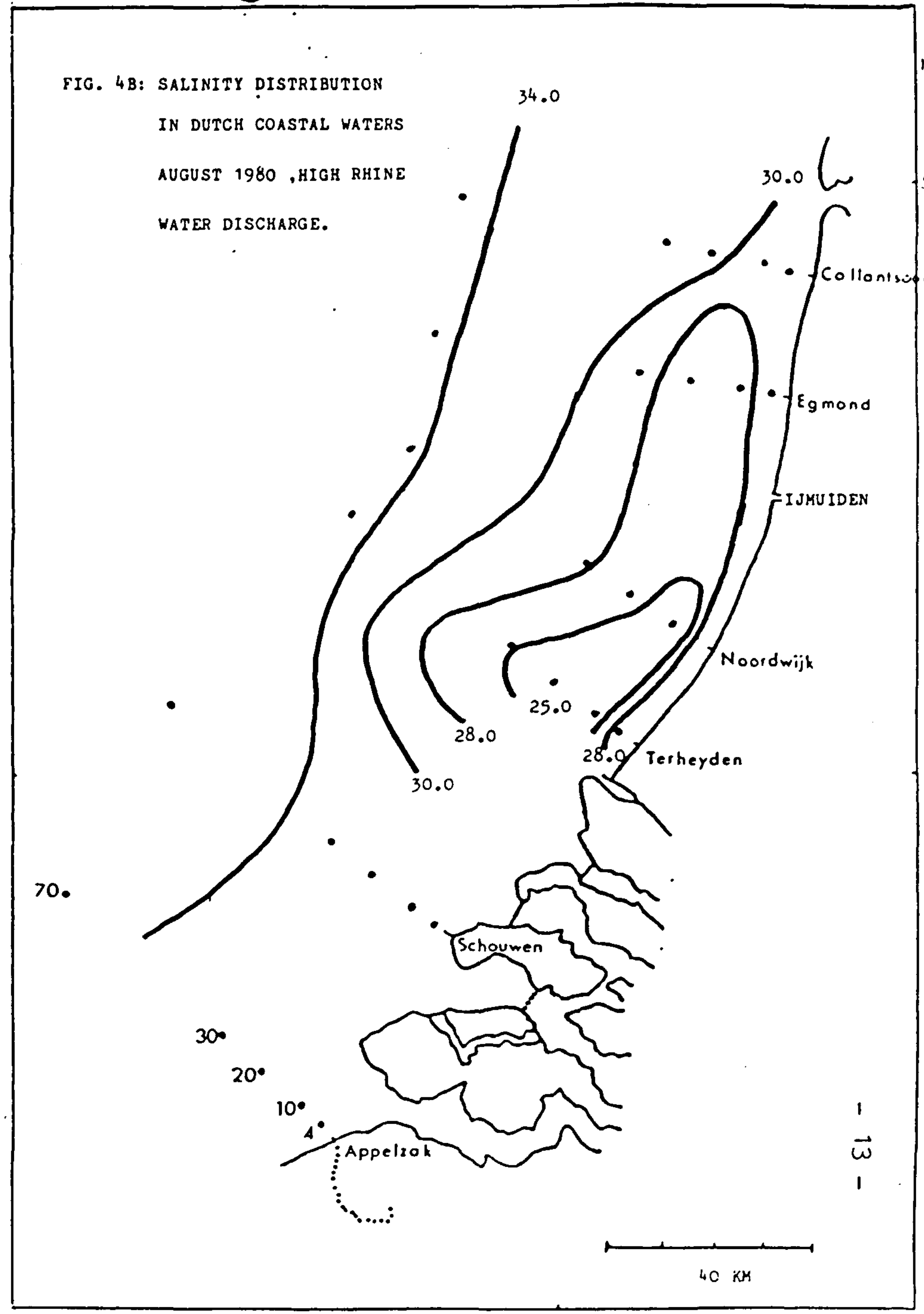
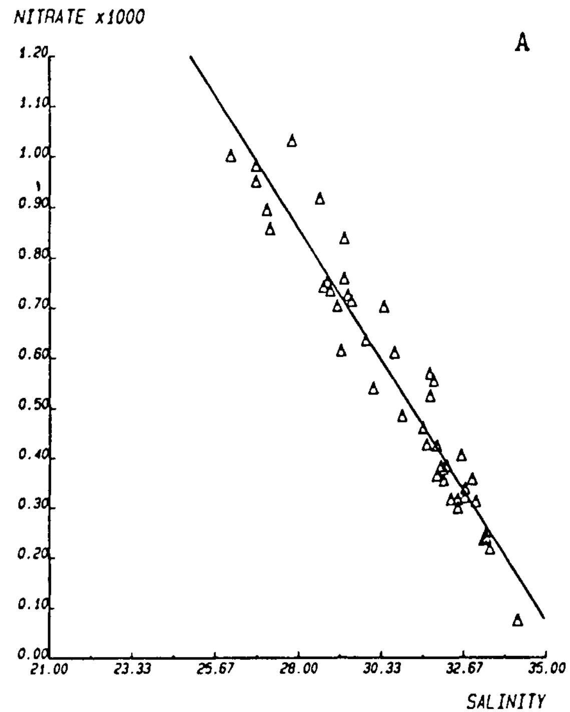
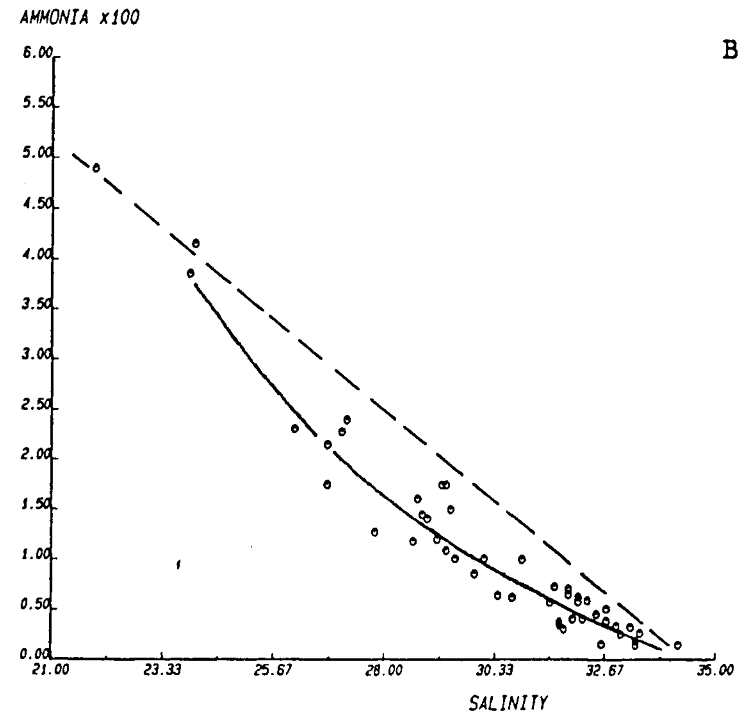


FIG. 4B: SALINITY DISTRIBUTION IN DUTCH COASTAL WATERS AUGUST 1980 ,HIGH RHINE WATER DISCHARGE.

FIG. 5: CONSERVATIVE AND NON-CONSERVATIVE BEHAVIOUR OF NITRATE (A) AND AMMONIA (B) RESPECTIVELY, DURING THE WINTERPERIOD OF 1982. DATA USED WERE MEASURED AT ALL SAMPLING SITES.



RELATIONSHIP NUTRIENTS AND SALINITY
CONSERVATIVE BEHAVIOUR OF NITRATE



RELATIONSHIP NUTRIENTS AND SALINITY
NON-CONSERVATIVE BEHAVIOUR OF AMMONIA

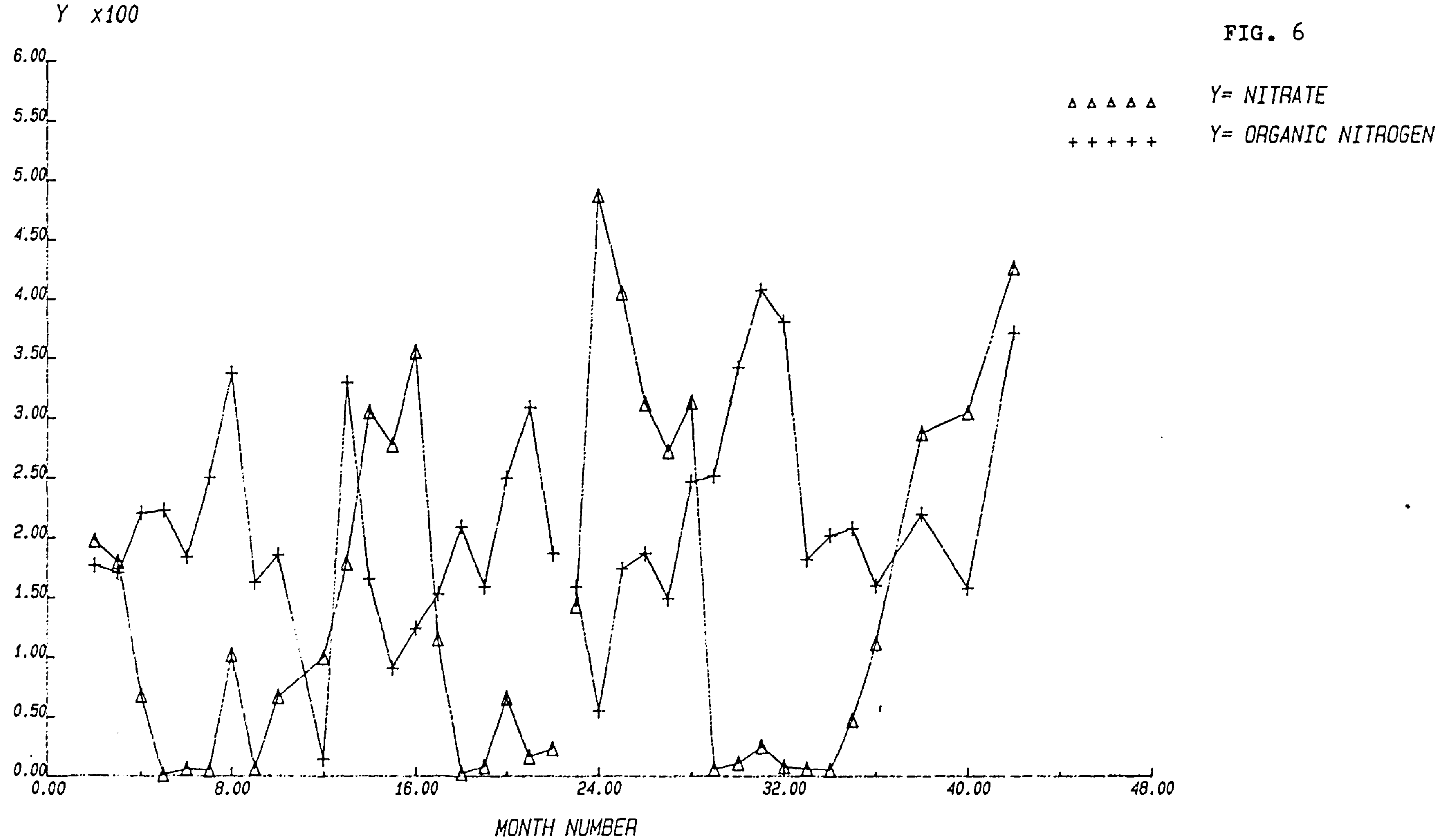
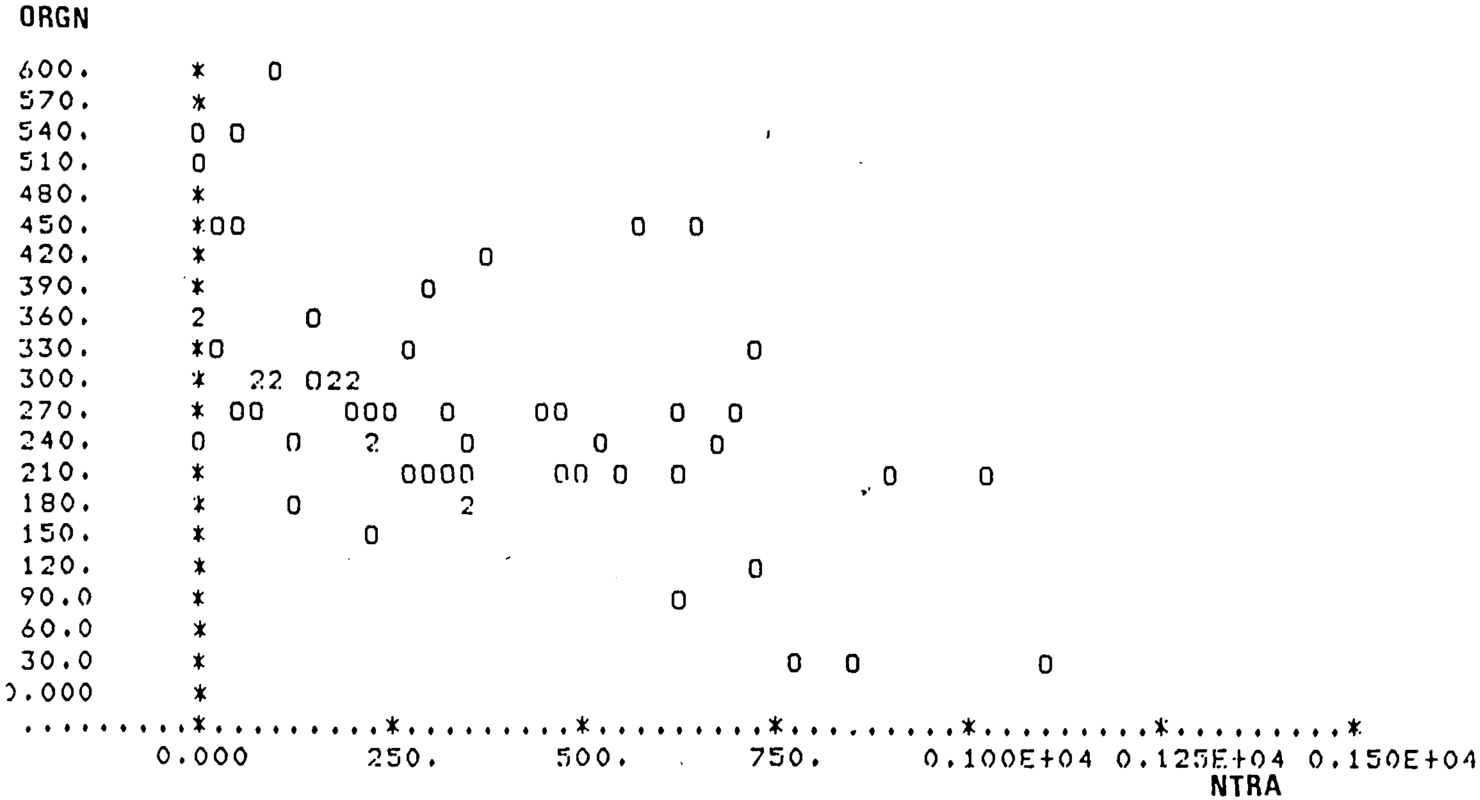


FIG. 6

SEASONAL VARIATIONS OF NUTRIENTS

ORGANIC NITROGEN AND NITRATE AT 30 KM OFF THE COAST

FIG. 7A Plot of ORGN versus NTRA for data set EN10.



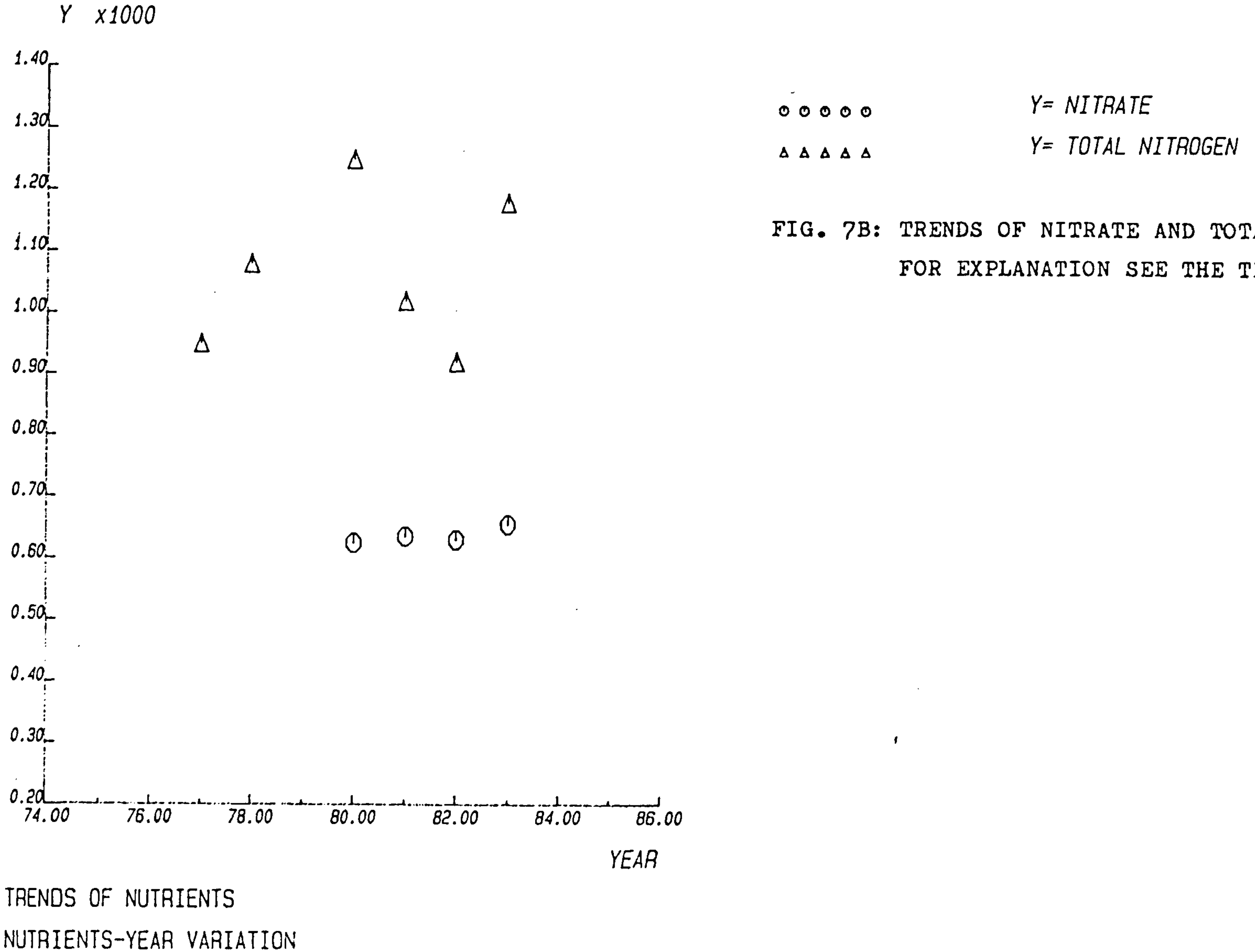


FIG. 7B: TRENDS OF NITRATE AND TOTAL NITROGEN. FOR EXPLANATION SEE THE TEXT.

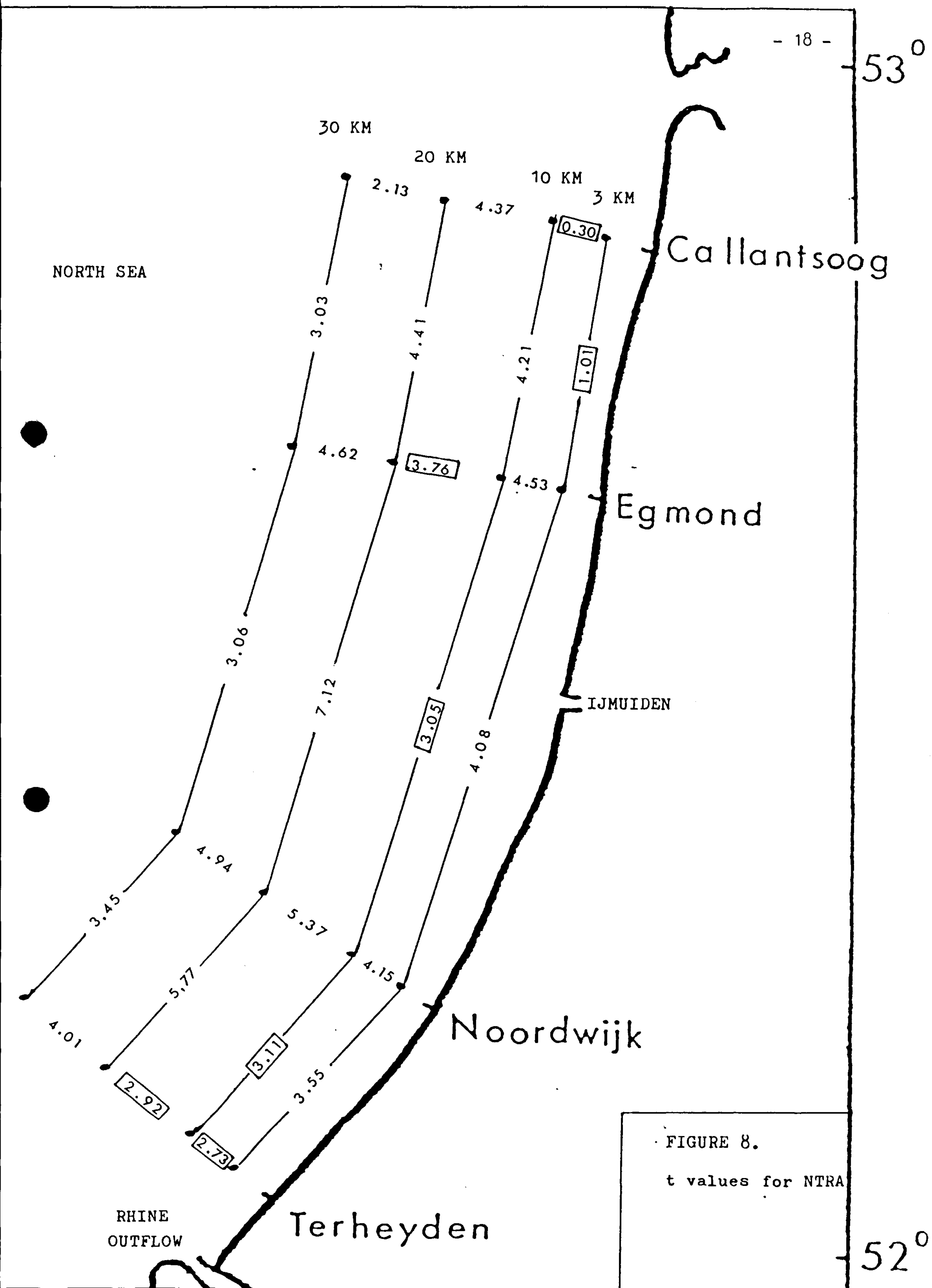


FIGURE 8.

t values for NTRA

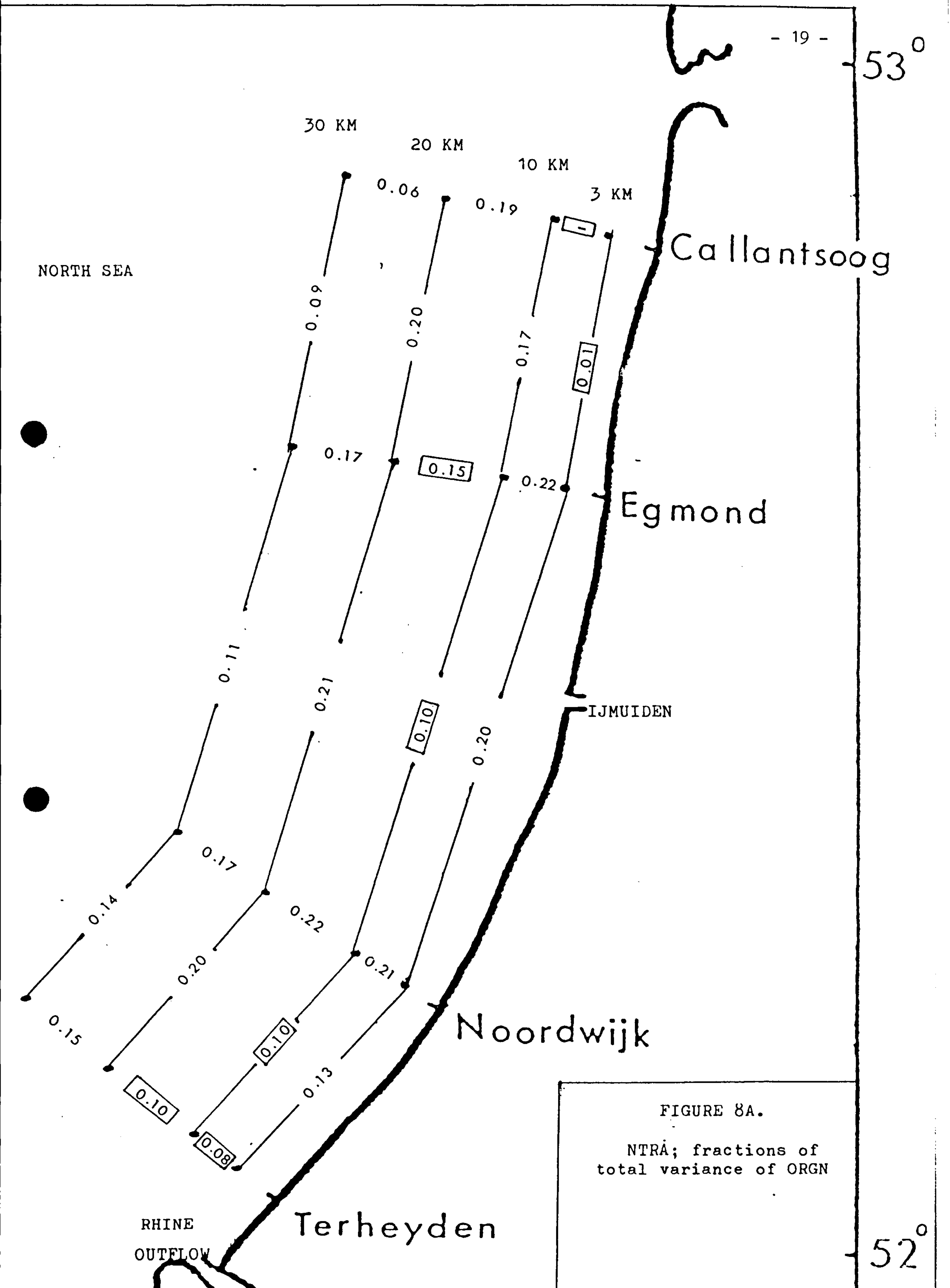


FIGURE 8A.

NTRA; fractions of total variance of ORGN

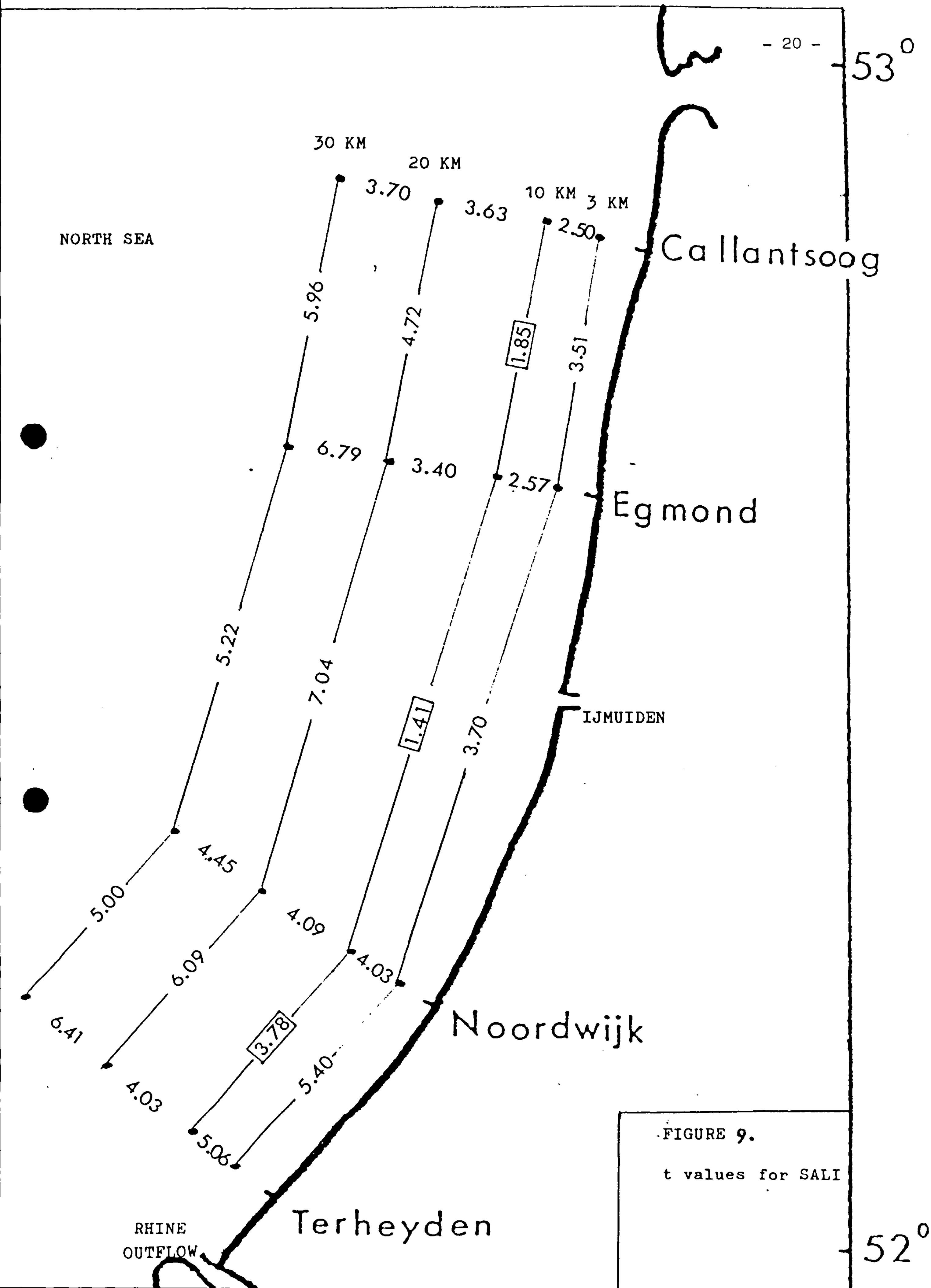


FIGURE 9.

t values for SALI

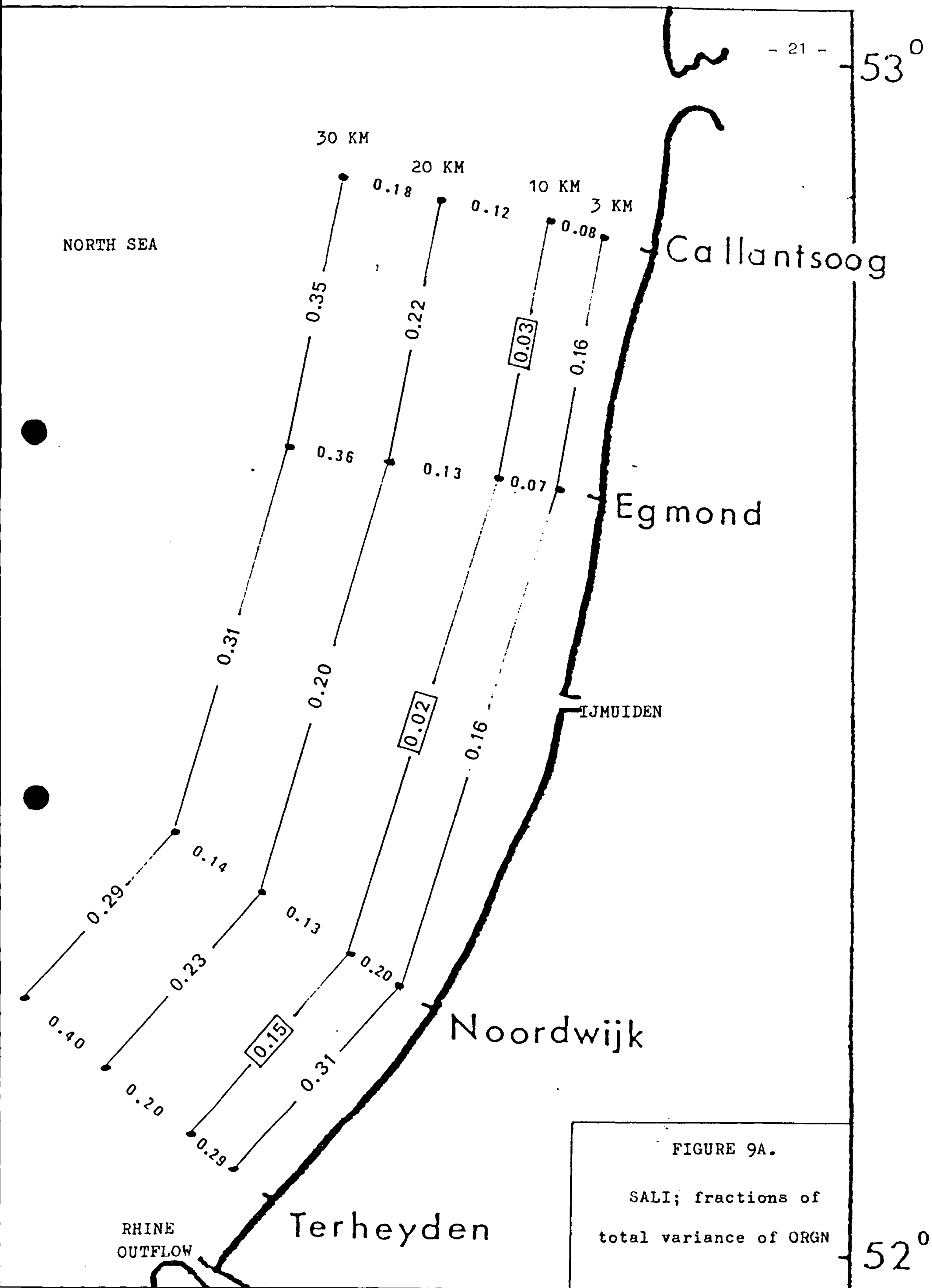


FIGURE 9A.

SALI; fractions of total variance of ORGN

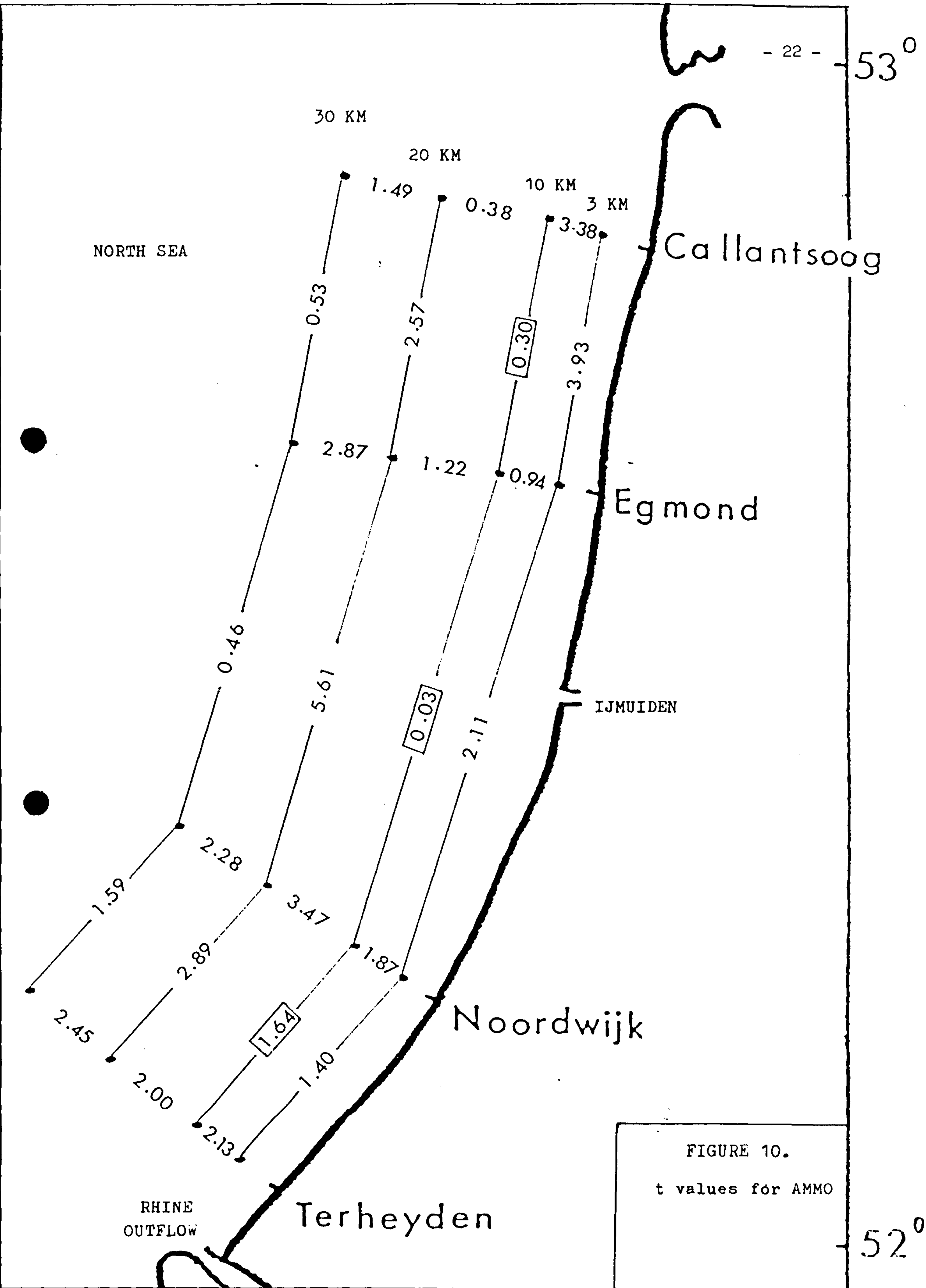


FIGURE 10.

t values for AMMO

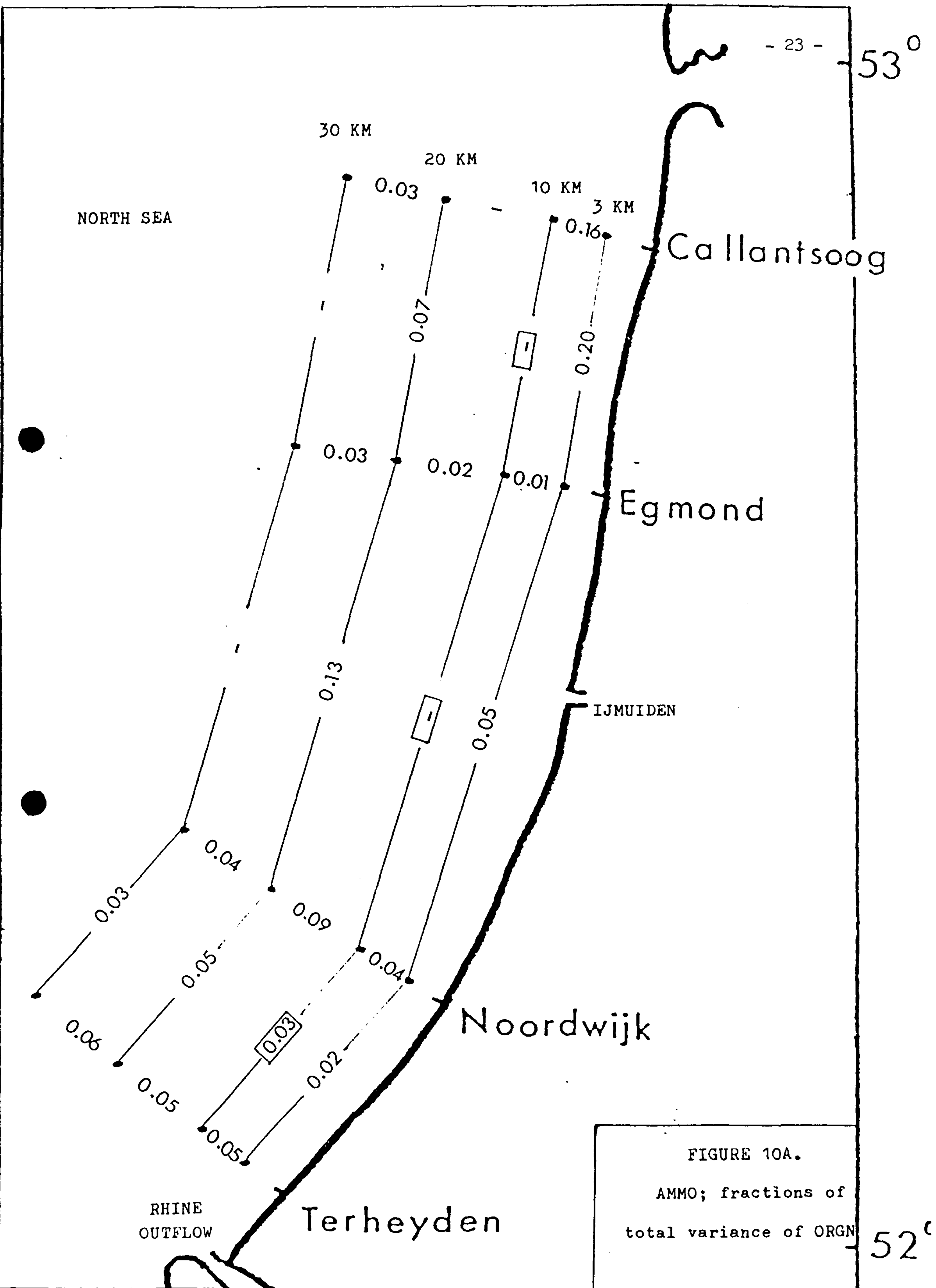


FIGURE 10A.

AMMO; fractions of total variance of ORGN

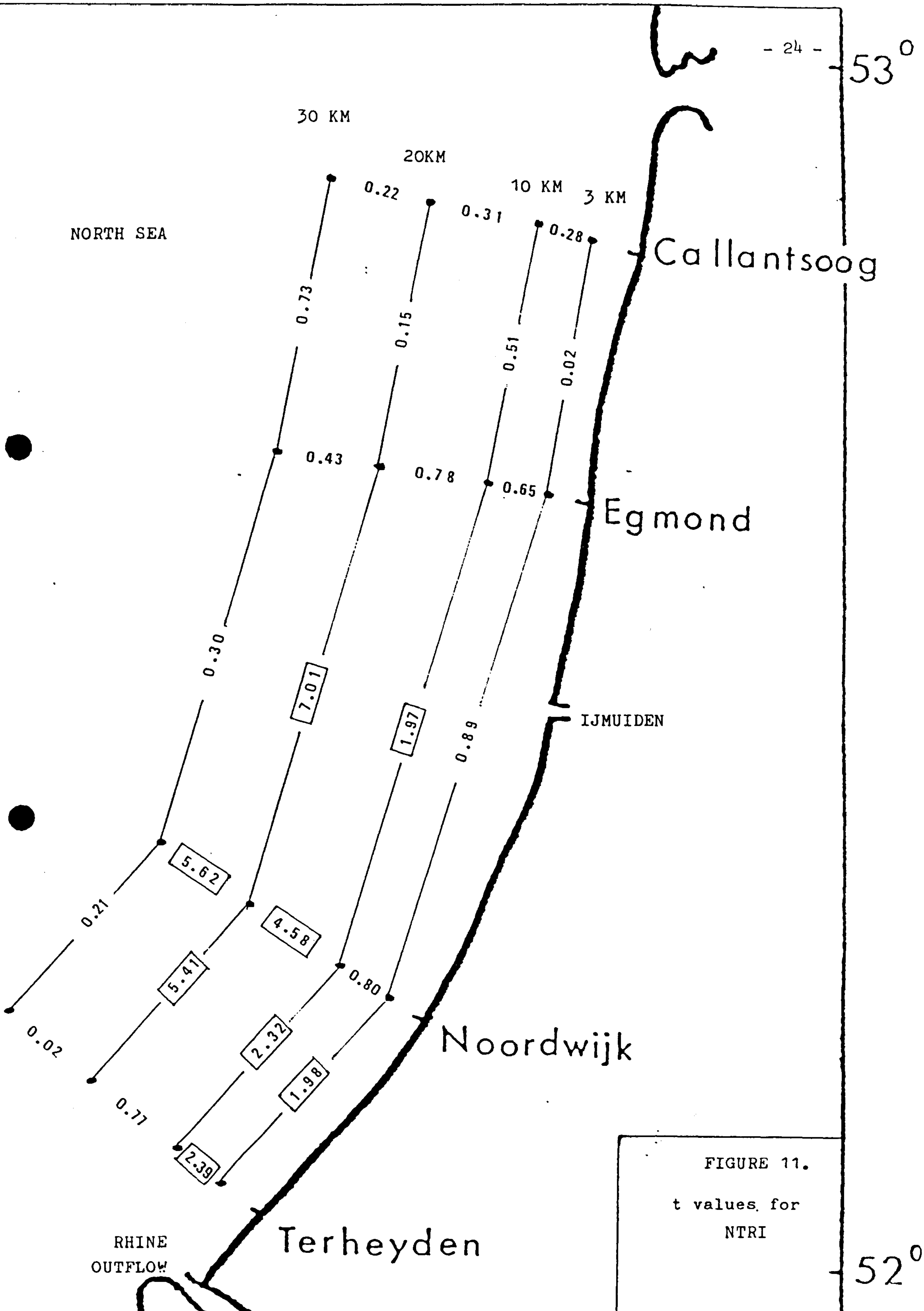


FIGURE 11.

t values for NTRI

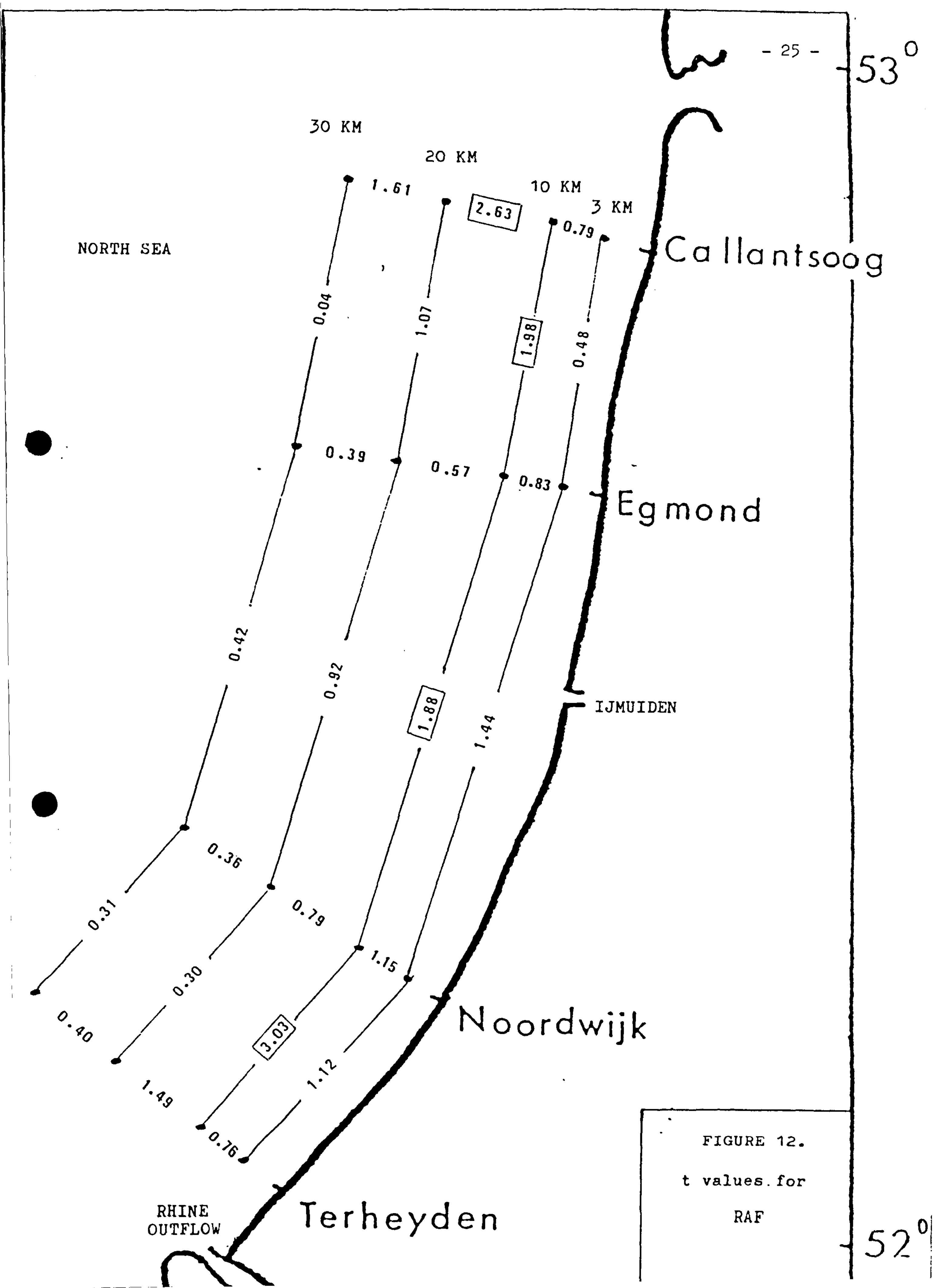


FIGURE 12.

t values for

RAF