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## Introduction

As part of a continuing study of the possible ecological effects of oil pollution in eastern Canadian marine waters, we have investigated the occurrence of some saturated hydrocarbons in seawater. Since the concentrations of individual hydrocarbons are extremely low (ng/l), considerable effort had to be extended initially to develop suitable sampling and analytical methods. Environments investigated include Bedford Basin (a coastal inlet at the head of Halifax Harbour), the St. Lawrence River, the Gulf of St. Lawrence, the Scotia Shelf and the Sargasso Sea (Fig. 1).

## Methods and Materials

Triplicate 12 liter samples of seawater were collected at 2 m with a glass bottle sampler described by Gordon and Keizer (1974) and at 50 m with a glass-teflon sampler which was lowered closed and opened at depth. Samplers were rinsed thoroughly with doubly distilled pentane before use. Water samples were extracted immediately (i.e. within 4 hrs) with pentane (100 ml/3 l of seawater); a bottle rinse was included with the sample. On longer cruises the extracts were stored in the freezer until they were processed in the laboratory. Test recoveries of spiked samples and exhaustive extraction of natural samples gave recoveries of greater than 80% for saturated hydrocarbons with boiling points equal to or greater than n-pentadecane (15). Water was carefully removed from the extracts in small separatory funnels and then a small amount of anhydrous sodium sulfate was added. The pentane was decanted into a Kuderna-Danish concentrator and the extract was concentrated to 10.0 ml. Most extracts were then analyzed by fluorescence (Gordon and Keizer, 1974) then concentrated to 0.5 ml. The extracts were placed on a prerinsed column of

alumina (activated at 400C for 16 hr, deactivated 5% with water) on silica gel (activated at 250 C for 16 hr, deactivated 5% with water) in a 60 x 3 mm glass column and the saturated fraction was eluted with 3.5 ml of pentane. The eluate was concentrated under a stream of pure nitrogen to 100 µl. Twenty microliter aliquots were placed in aluminum capsules and evaporated almost to dryness following which the capsules were sealed by a cold weld.

The capsules were injected using an MS-41 sampling accessory into a PerkinElmer 3920 dual flame ionization gas chromatograph fitted with a 12' x 8" o.d. stainless steel column loaded with 60/80 mesh Chromosorb W(AW) coated with 3% Apiezon L. The pristane-n-heptadecane (C17) pair were adequately separated for quantitation but the phytane-octadecane (C18) pair were not. Compounds were identified by comparison of retention times with those of pure n-alkane standards obtained from Applied Science. Calculations were based on peak areas. n-Alkanes from n-tetradecane (C14) to n-heptacosane (C27) were quantified along with pristane and any other major peaks.

Fluorescence contour plots were generated with an off-line plotting routine (General Purpose Contouring Program, Calcomp. Corp.), using a PDP8 (Digital Equipment Corp.) computer to drive a Calcomp 563 plotter (Hargrave and Phillips, 1974).

## Results

### A. Bedford Basin

Concentrations of total n-alkanes in seawater from Bedford Basin varied from 25 to 590 ng/l during 9 sampling dates from January 13, 1975 to May 22, 1975 (Figure 2). On each date the concentrations observed in each of the three replicates varied considerably at both depths. On two thirds of the sampling dates the ranges of the replicates from 2 and 50 m overlapped. Qualitatively, the pattern of n-alkane peaks of samples from both depths on all dates are very similar. n-Heptadecane (C17) or n-octadecane (C18)were most abundant, n-eicosane (C20) or n-heneicosane (C21) the least, with concentrations increasing towards the end of the chromatogram (Figure 3). There were variations in the peak heights for compounds other than the n-alkanes. The concentration of pristane was occasionally high and the appearance of a strong peak with a retention index of 2020 or 2060 was noted in a number of samples. There was no correlation between high concentrations of pristane and the appearance of the 2020 or 2060 peak.

On 7 of the 9 sampling dates in Bedford Basin, the seawater extracts were also analyzed by fluorescence (Figure 4).

Concentrations (expressed as crude oil equivalents) varied from 1.5 to 9.1 µg/liter at 2 m and from 1.2 to 4.0 µg/liter at 50 m. The range of the three replicates is also indicated in Figure 4. On 6 of the 7 sampling dates the concentrations at 2 m were significantly greater than those at 50 m. The fluorescence contour plots did not vary with depth or with time (Figure 5). It is interesting to note that there is a positive and significant correlation, between the total n-alkane concentrations and the "oil" concentrations determined by fluorescence. For 2 m samples $n = 21$, $r = .511$ and $P < .01$ and for 50 m samples $n = 19$, $r = .403$, $P < .1$.

B. Scotia Shelf

Samples were collected at 2 and 50 m at Station 1 (see Figure 1). The concentration of total n-alkanes averaged 90 ng/l (78-99) at 2 m and 127 ng/l (80-154) at 50 m (Figure 6). The pattern of n-alkanes was similar to the Bedford Basin samples. High concentrations of pristane were observed in 2 of 3 samples from both depths. In all of the 50 m samples and one 2 m sample a strong peak with a retention index of 2022 was observed.

The results of the fluorescence analysis at this station were quite variable (Figure 7). The contour plots were also quite unusual exhibiting several maxima and minima (Figure 8). These contours do not resemble the samples from Bedford Basin or any petroleum products analyzed in this laboratory.

C. Gulf of St. Lawrence

Samples were taken at three stations in the Gulf, locations 30, 41 and 53 in Figure 1. Total n-alkane concentrations ranged from 24 to 209 ng/l in the 2 m samples, and from 76 to 1005 in the 50 m samples (Figure 6). The concentrations at Station 53 were significantly lower at both depths than at the other stations. At all three stations the concentrations were significantly higher at 50 m than at 2 m. A strong peak with a retention index of 2050 was observed in the 50 m samples.

Fluorescence analysis of these samples showed less variability. Concentrations ranged from 0.7 to 1.1 µg/l with no significant differences between stations, however, at Station 30 the concentrations at 50m were greater than that at 2 m (Figure 7). The contour plots were quite similar to those from Bedford Basin. There was no correlation between total n-alkane concentrations and oil concentrations estimated by fluorescence.

D. St. Lawrence River

Samples were collected from two locations, 41 and 46 (Figure 1). There was a difference in total n-alkane

concentrations at 2 m at the two stations, Station 41 was higher, but not at 50 m (Figure 6). Concentrations were greater at 50 m, 137 to 372 ng/l, than at 2m, 34 to 96 ng/l.

Concentrations of oil estimated by fluorescence ranged from 0.4 to 1.1 µg/l. Again there was a difference in concentrations at 2 m at the two stations but Station 46 had the higher concentration. There was no difference at 50 m. At Station 46, concentrations at 2 m were greater than those at 50m. Contour plots were similar to those from Bedford Basin and there was no correlation between chromatographic and fluorescence results.

E. Sargasso Sea

Samples collected in the Sargasso Sea were only analyzed for n-alkanes. Three of four samples from 2 meters had concentrations less than the blank, approximately 20 ng/l. The fourth sample had a concentration of total n-alkanes of 118 ng/l. Five samples from 50 meters had concentrations ranging from 54 to 145 ng/l.

## Discussion

Despite considerable overlap in concentration (Table 1), and the basic similarity of chromatograms and fluorescence contour plots some regional differences are apparent. The concentration of n-alkanes in the Sargasso Sea are the lowest encountered in any of the sampling areas. This could be indicative of the low biological productivity of the area. Surprisingly, concentrations from 50 m in the Gulf and the St. Lawrence River were similar and sometimes greater than those determined in Bedford Basin which is in the midst of a highly industrialized and heavily populated metropolitan area. The lack of correlation between the chromatographic and fluorescence data for the Gulf do indicate that the source of the hydrocarbons extracted from the Gulf is different than that from Bedford Basin.

It was noted that for the samples from Bedford Basin, there was a positive correlation between total concentrations of n-alkanes and "oil" determined by fluorescence while for the Gulf of St. Lawrence there was no correlation. From this fact and the appearance of the fluorescence contours, it seems reasonable to conclude that hydrocarbons detected in the Gulf of St. Lawrence were of biogenic origin. The use of the fluorescence method to determine "oil" for these samples will therefore give misleading results. In Bedford Basin the situation is quite different and from the positive correlation of chromatographic and fluorescence results and appearance of the contour plots it appears that there is a strong contribution from petroleum derived

hydrocarbons to the total hydrocarbon content of Bedford Basin waters.

The variation of total n-alkane concentrations in the Gulf and in Bedford Basin with depth is also of interest. In Bedford Basin concentrations at 2 m are consistently greater than at 50m. This is to be expected of a water column where the input of hydrocarbons is from the surface, i.e. oily discharges from ships, sewage and storm sewer outfalls. In the Gulf the opposite is true, 50 m samples consistently had higher concentrations than 2 m samples.

The pattern of n-alkane peaks in all chromatograms was very similar. In Bedford Basin and on the Scotia Shelf high concentrations of pristane were occasionally observed (i.e. the n-C17 to pristane ratio was less than one). Peaks with retention indices of 2020, 2060 and 2460 were observed in some samples from Bedford Basin, the Scotia Shelf and the Gulf. There is no correlation of the presence of these peaks with high pristane or high total n-alkane concentrations. The peak at 2020 could well be the C21 hexaene identified by Blumer *et al* (1970). This compound 3,6,9,12,15,18-heneicosa-hexaenewas found in algae and zooplankton. The appearance of these compounds in the extracts suggests the presence of an organism in which these compounds predominate. It was suggested by Blumer *et al* (1970) that identifying and tracing such compounds can be of value in studying the dynamics of food chains.

Concentrations of n-alkanes in marine waters have been reported by a number of workers. Two methods have been used to estimate total saturated hydrocarbons: 1) concentrations of individual n-alkanes are summed or 2) the saturate fraction from the liquid chromatographic column is weighed. Both methods are subject to a great deal of inaccuracy. We have employed the former approach and therefore concentrations reported here may only be compared with those obtained in a similar manner. Concentrations obtained by weighing will include hydrocarbons other than n-alkanes (all those compounds which do not pass through the GLC column or are not recolved on the column) and therefore will tend to be higher.

The results obtained here are comparable to those reported by Mackie *et al* (1974) for Scottish waters. They analyzed a slightly wider boiling range of hydrocarbons, (nC18 to nC33) and concentrations of 210 to 3,100 ng/liter were determined but a similar distribution of hydrocarbons was observed. Parker *et al* (1972) analyzed seawater from the Gulf of Mexico for hydrocarbons reporting concentrations of 78 to 1,100 ng/liter. Again the distribution of hydrocarbons observed, i.e. the shape of the chromatograms, are similar. Iliffe and Calder (1974) and Barbier *et al* (1973) have published similar looking chromatograms

for other parts of the world's oceans but the concentrations reported are determined by weighing and are not directly comparable.

The "oil" concentrations determined by fluorescence are generally lower in the Gulf of St. Lawrence than in Bedford Basin. The highest concentration observed in the Gulf was 2.0 µg/l, as compared with 9.3 µg/l in Bedford Basin. The contour plots were also different. Plots from Bedford Basin bear some resemblance to plots for oil standards but a number of the contour plots from the Gulf of St. Lawrence exhibited a wide variety of maxima and minima. This would indicate substantial diversity in the chemistry of the waters of the Gulf and the monotony of the chemistry of the waters of Bedford Basin.

In a previous paper (Gordon *et al*, 1974), we observed that the standard deviation for samples (2 l) collected in the Northwest Atlantic and analyzed by fluorescence was rather large, in most cases approximately equal to the mean. It was felt that this indicated patchiness, in the distribution of hydrocarbons in seawater. The samples analyzed in this work were larger in volume (12 liter) and as expected the range of replicates for these samples is much less (Figs. 4,7).

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Table 1 - Range of concentration of total n-alkanes and estimated concentration of oil in the 5 sampling areas.

| Region | Total n-alkane concentration ng/l 2m | 50m | Estimated oil concentration µg/l 2m | 50m |
|---|---|---|---|---|
| Bedford Basin | 65-590 | 25-395 | 1.6-9.3 | 1.4-4.3 |
| Scotia Shelf | 78-99 | 80-154 | 0.2-0.8 | 0.2-2.0 |
| Gulf of St. Lawrence | 24-209 | 76-1005 | 0.6-1.1 | 0.5-1.5 |
| St. Lawrence River | 34-96 | 137-372 | 0.5-1.1 | 0.4-0.9 |
| Sargasso Sea | ND[1]-118 | 54-145 | - | - |

[1]Not Detected

Figure Legends

Figure 1 - Sampling locations for the Scotia Shelf (01), the Gulf of St. Lawrence (06,30,53) and the St. Lawrence River (41,46). The Sargasso Sea samples were collected at 26°N 62°40'W.

Figure 2 - Concentrations of total n-alkanes (C14 to C27) in Bedford Basin at 2m (0) and 50m (Δ) with the range of the three replicates indicated.

Figure 3 - A typical chromatogram of hydrocarbons extracted from seawater. This chromatogram exhibits a high concentration of pristane as well as a very large peak with a retention index of 2020.

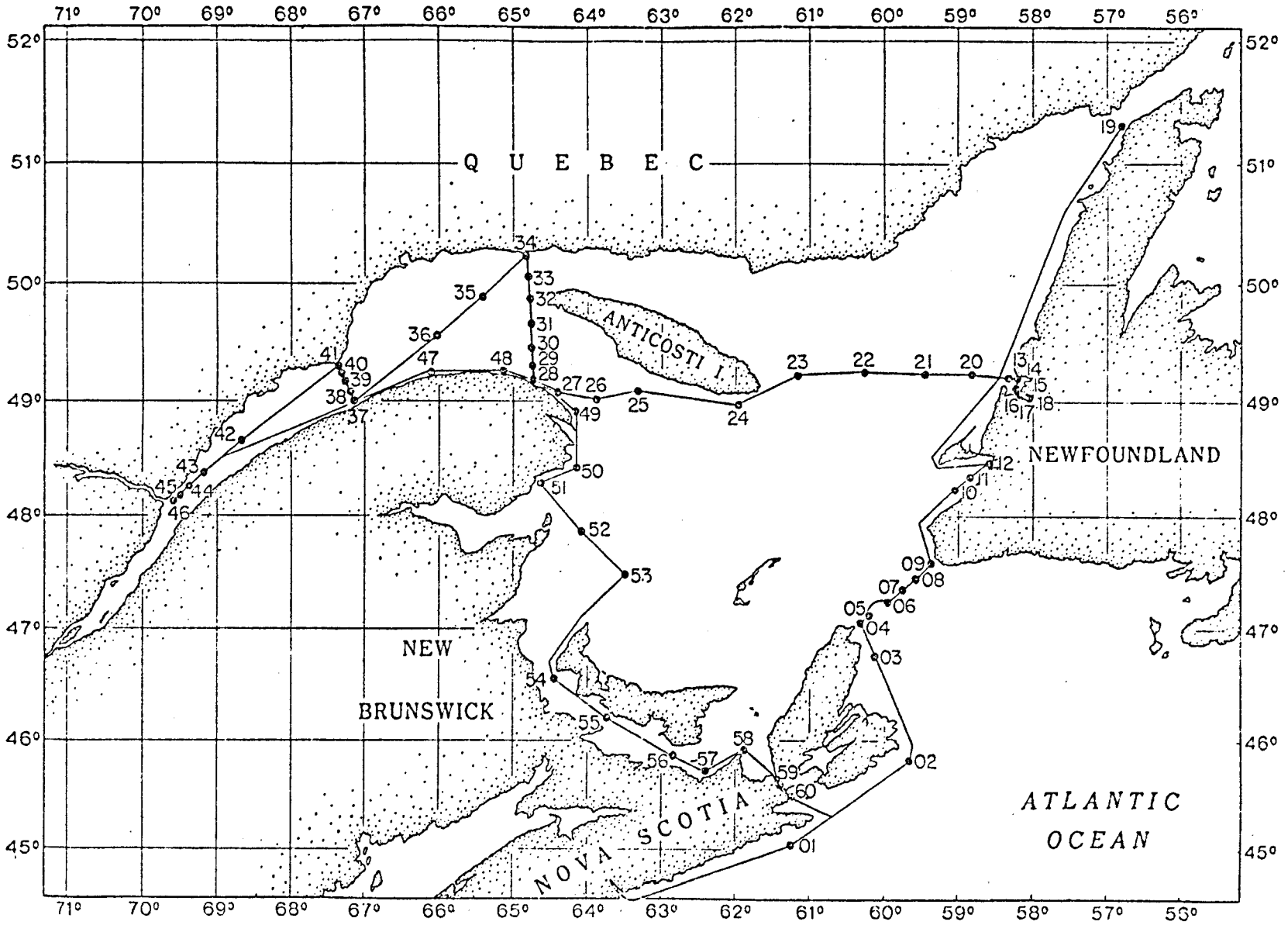
Figure 4 - Estimates of oil concentrations determined by fluorescence in Bedford Basin at 2m (0) and 50m (Δ) with the range of the three replicates indicated.

Figure 5 - Typical fluorescence contour plots for extracts from 2m (A) and 50m (B) in Bedford Basin.

Figure 6 - Concentrations of total n-alkanes (C14 to C27) from locations in Figure 1 at 2m (0) and 50m (Δ) with the range of the three replicates indicated.

Figure 7 - Estimates of oil concentrations determined by fluorescence for locations in figure 1 at 2m (0) and 50m (Δ) with the range of the three replicates indicated.

Figure 8 - Fluorescence contour plots for extracts from 2m (A) and 50m (B) from station 01 (Figure 1).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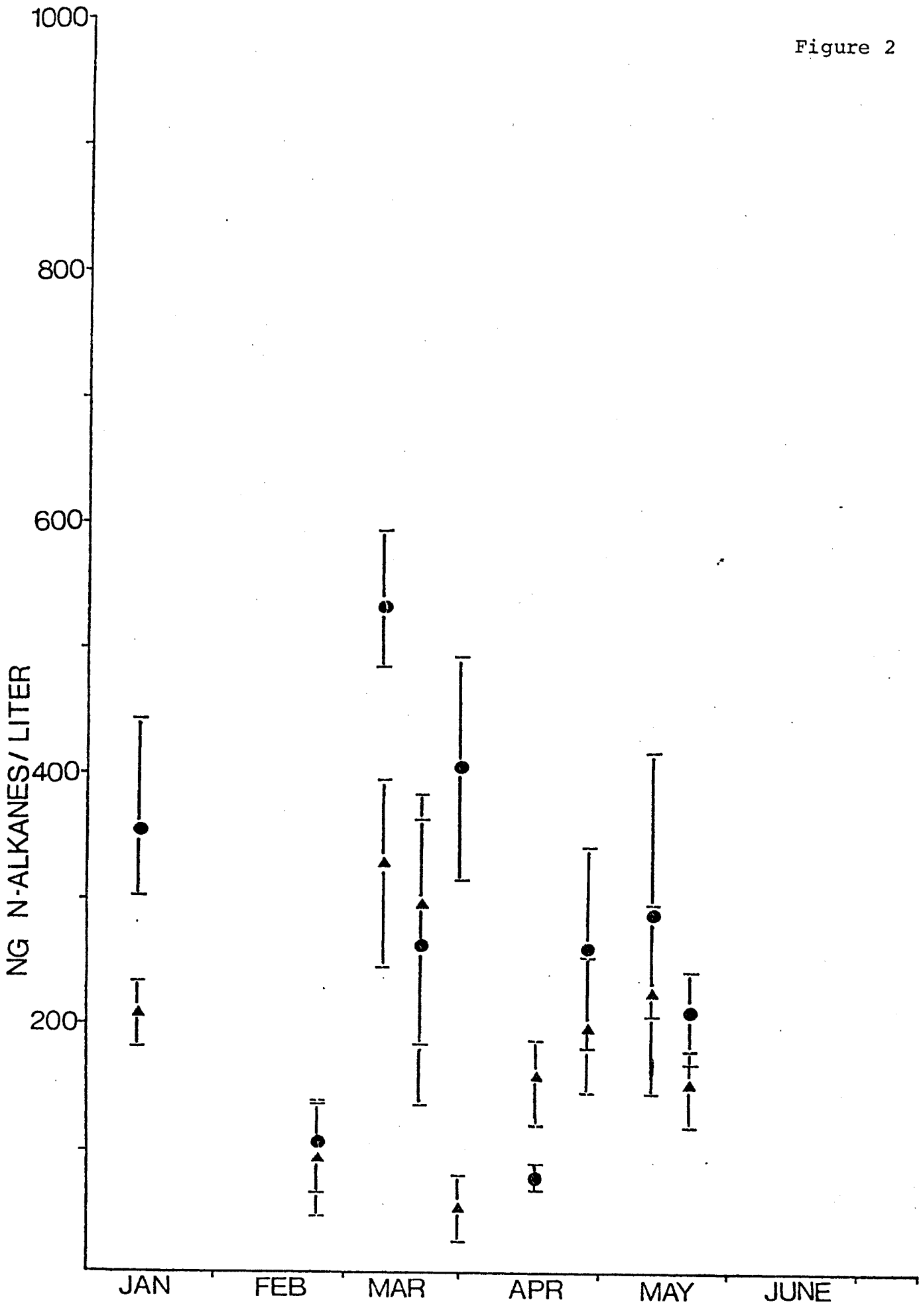
52°
51°
50°
49°
48°
47°
46°
45°
Q U E B E C
ANTICOSTI I.
NEWFOUNDLAND
NEW
BRUNSWICK
NOVA SCOTIA
ATLANTIC
OCEAN
01 02 03 04 05 06 07 08 09 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

Figure 1

Figure 2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400
200
NG N-ALKANES/ LITER
JAN
FEB
MAR
APR
MAY
JUNE

Figure 3

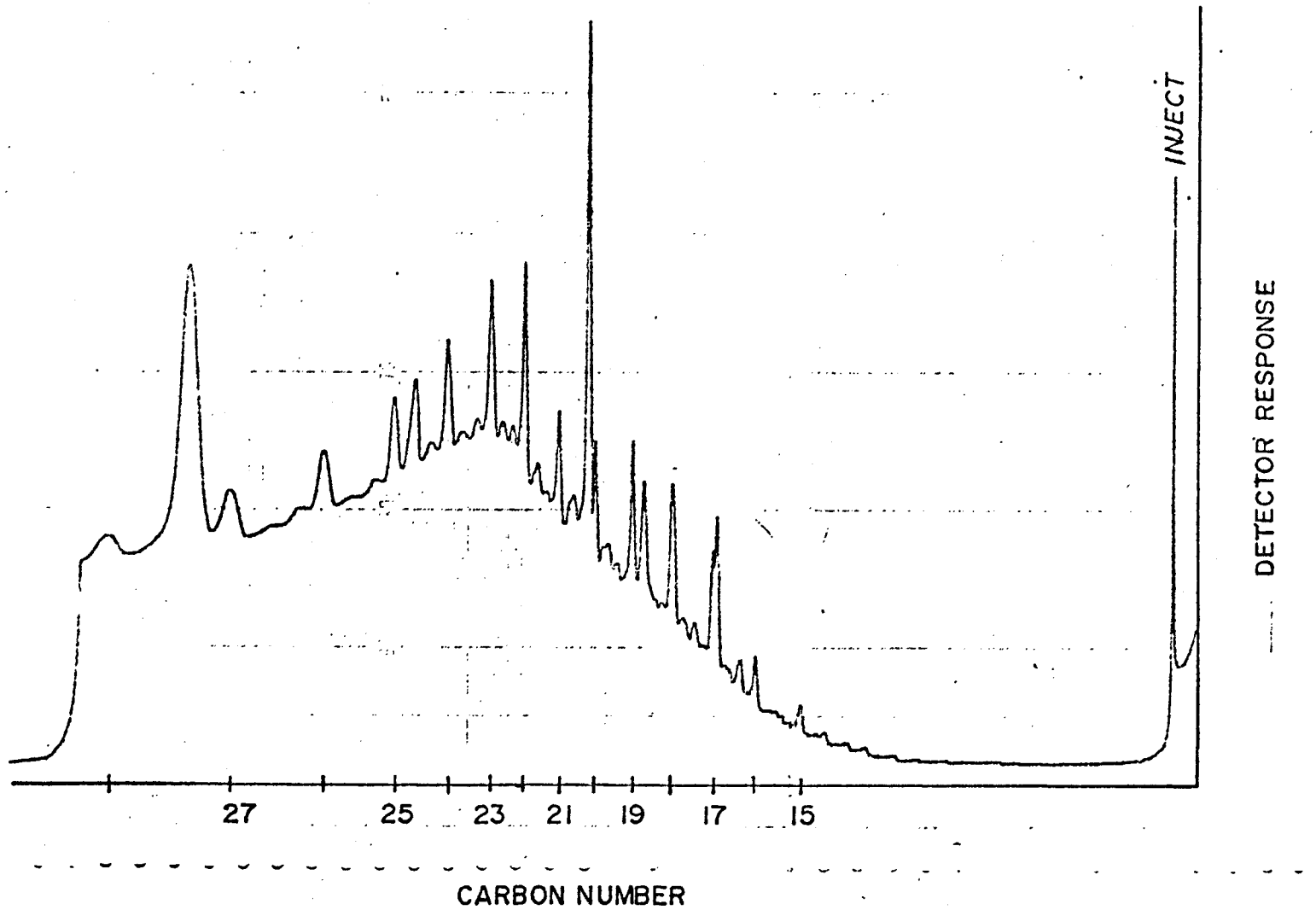
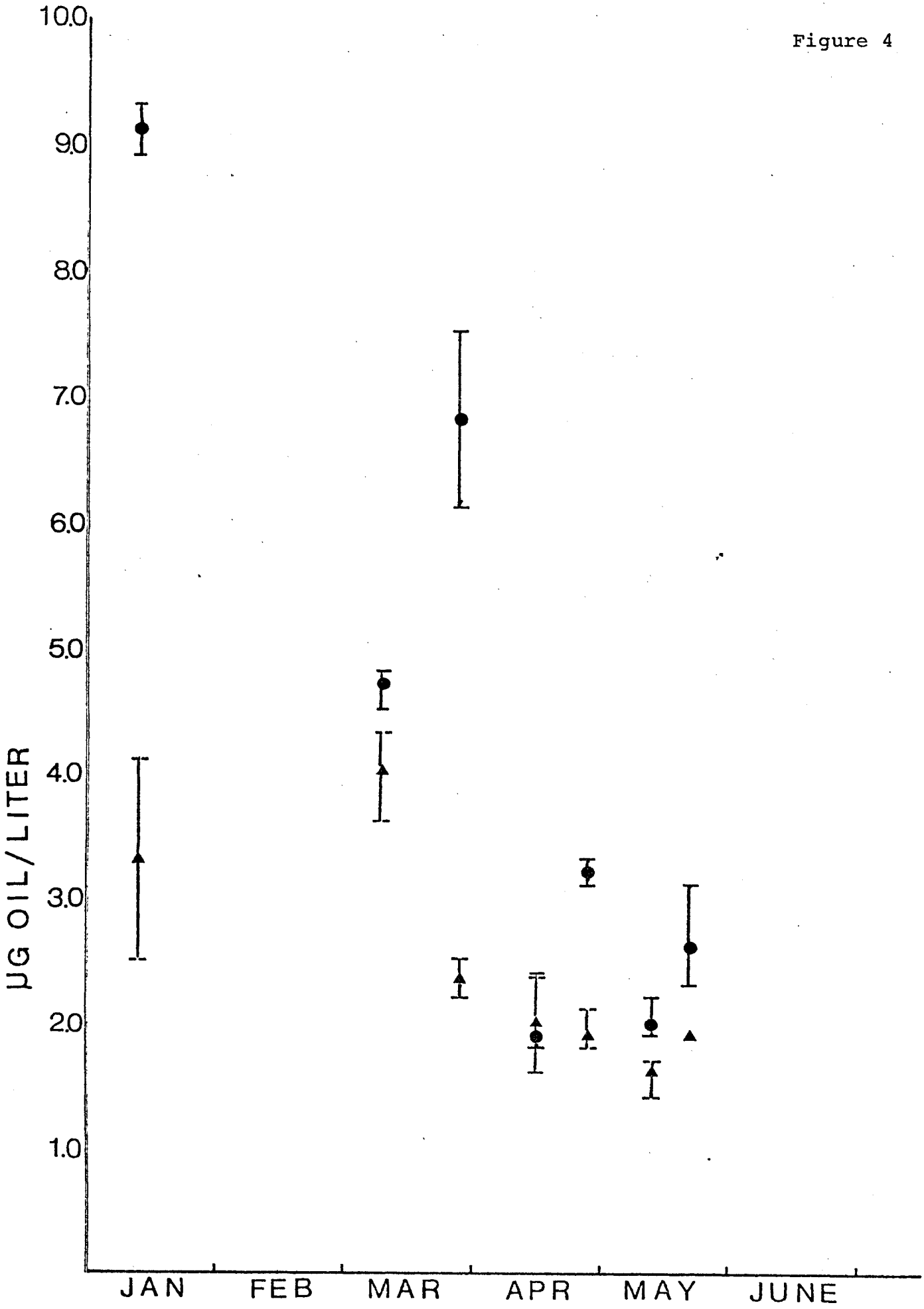


Figure 4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9.0
8.0
7.0
6.0
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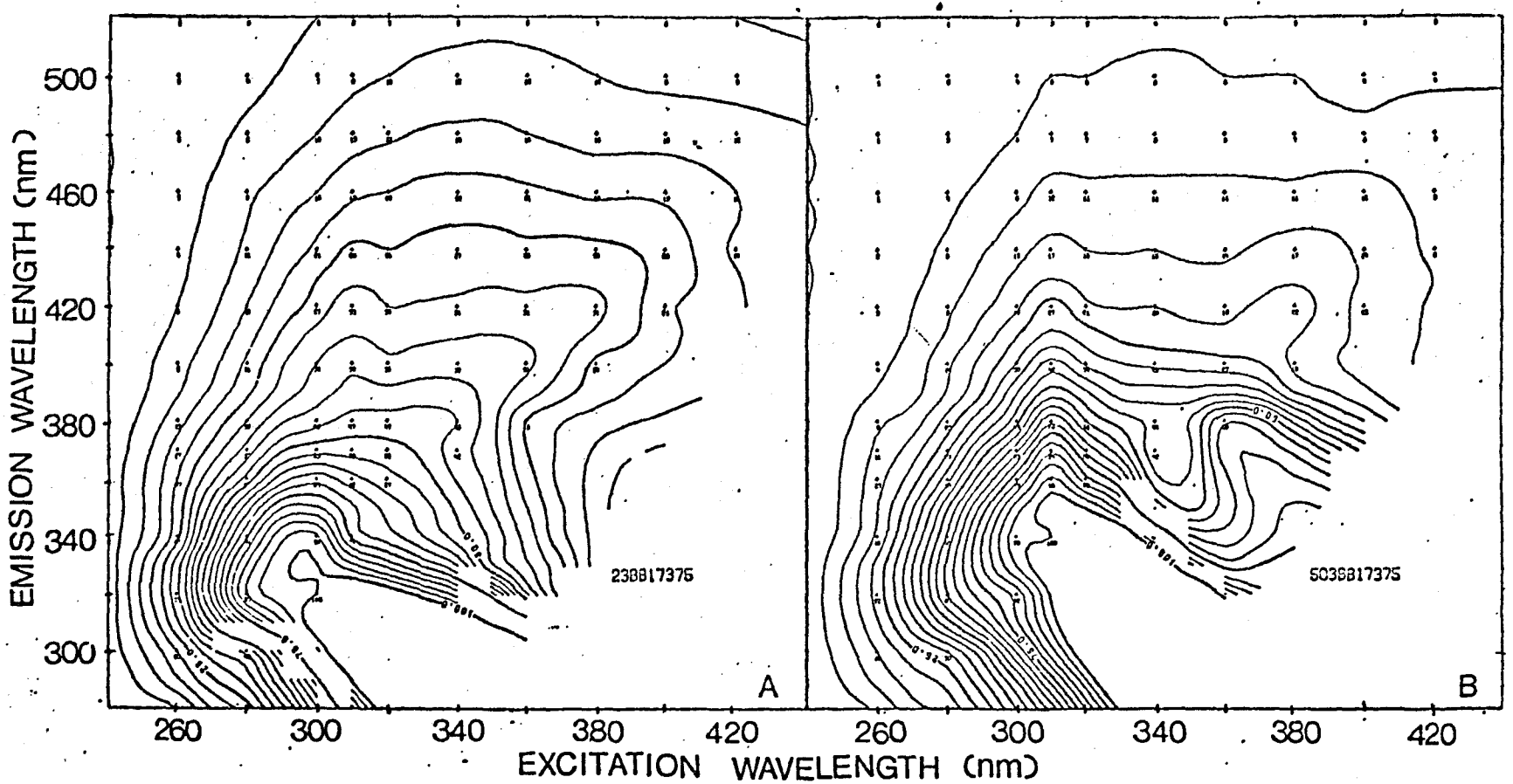
1.0
µG OIL/LITER
JAN
FEB
MAR
APR
MAY
JUNE

Figure 5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420
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340
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340
380
420
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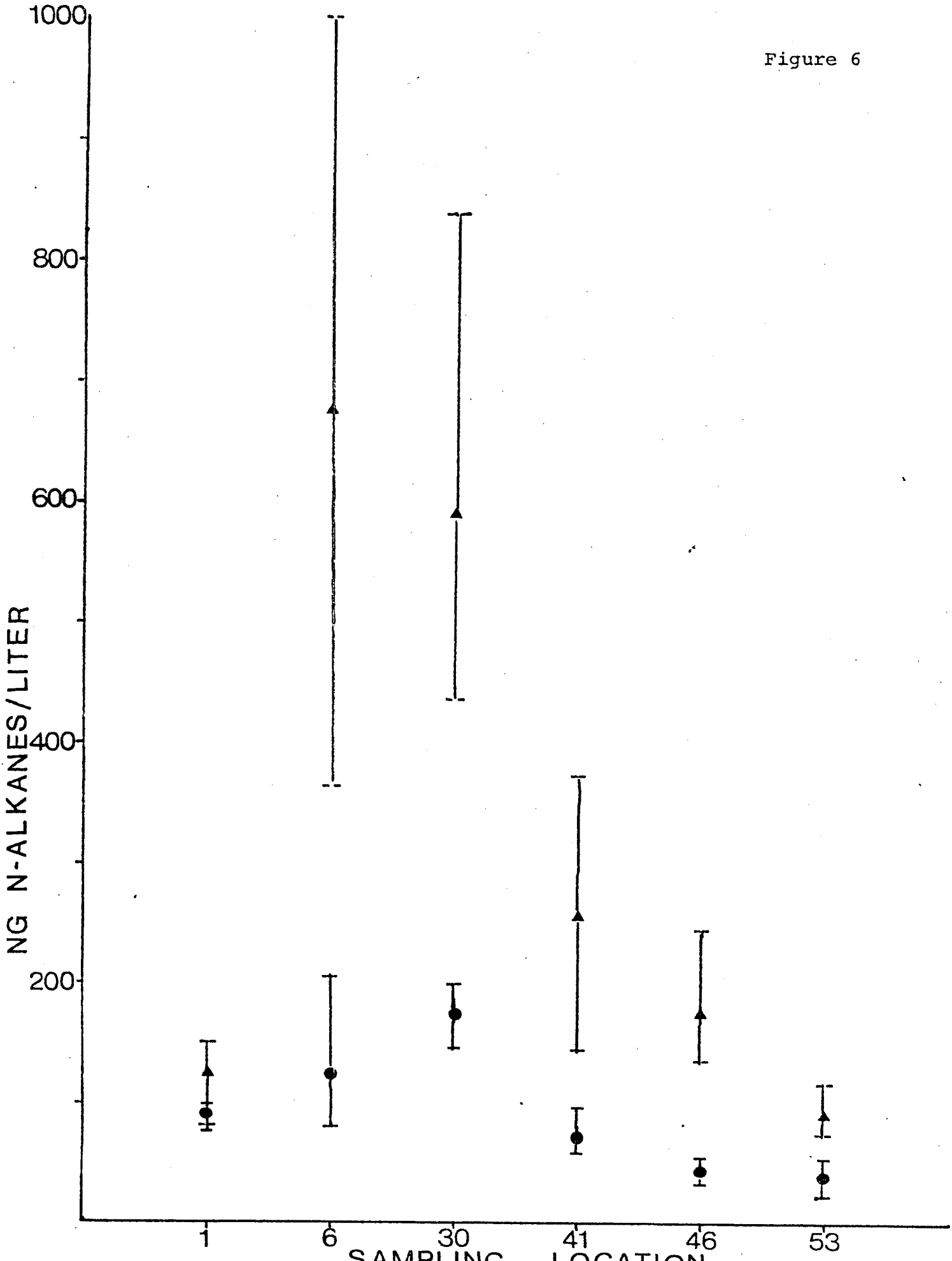
A
5038817375
B

Figure 6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600
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200
NG N-ALKANES/LITER
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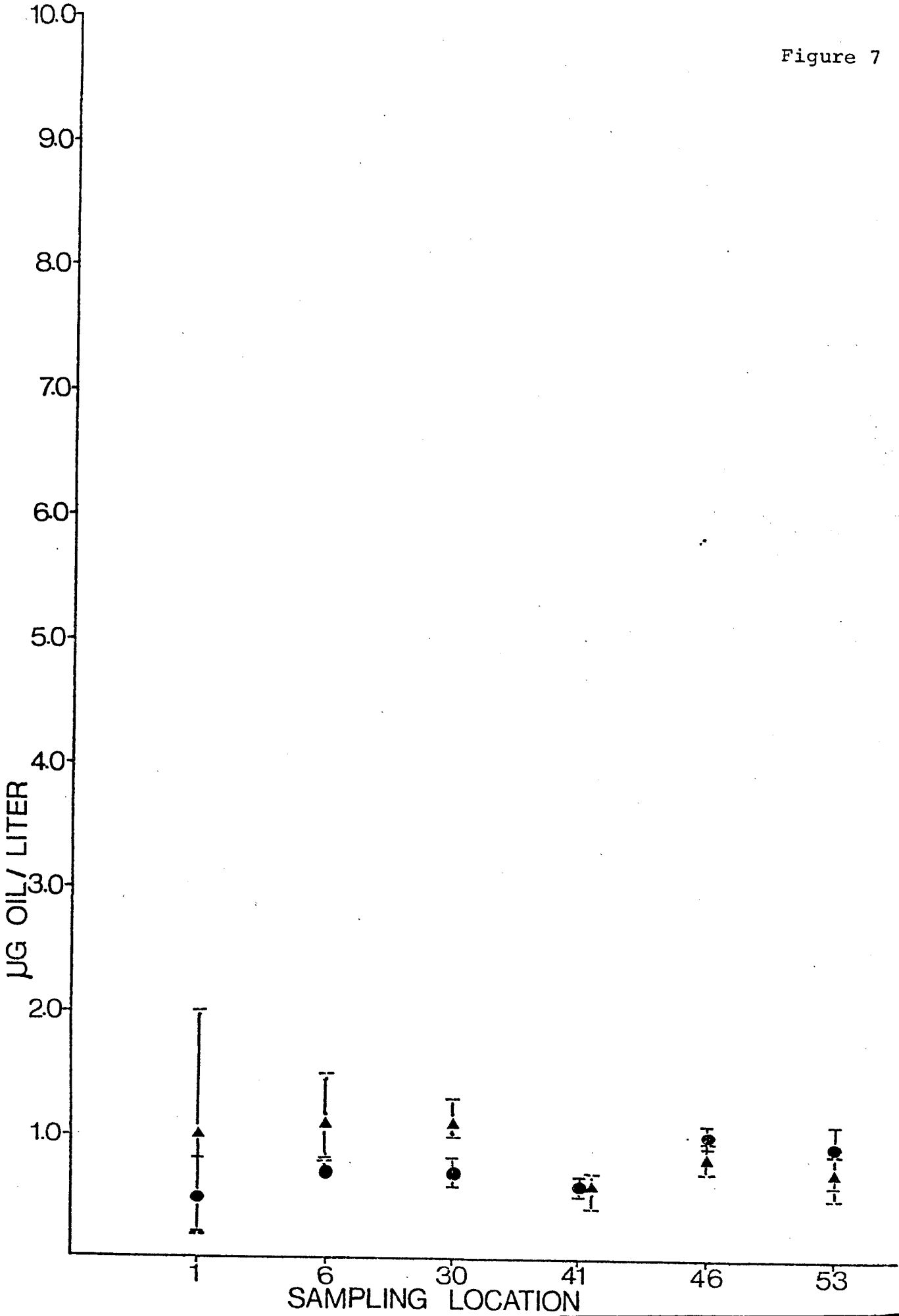
6
30
41
46
53
SAMPLING LOCATION

Figure 7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8.0
7.0
6.0
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4.0
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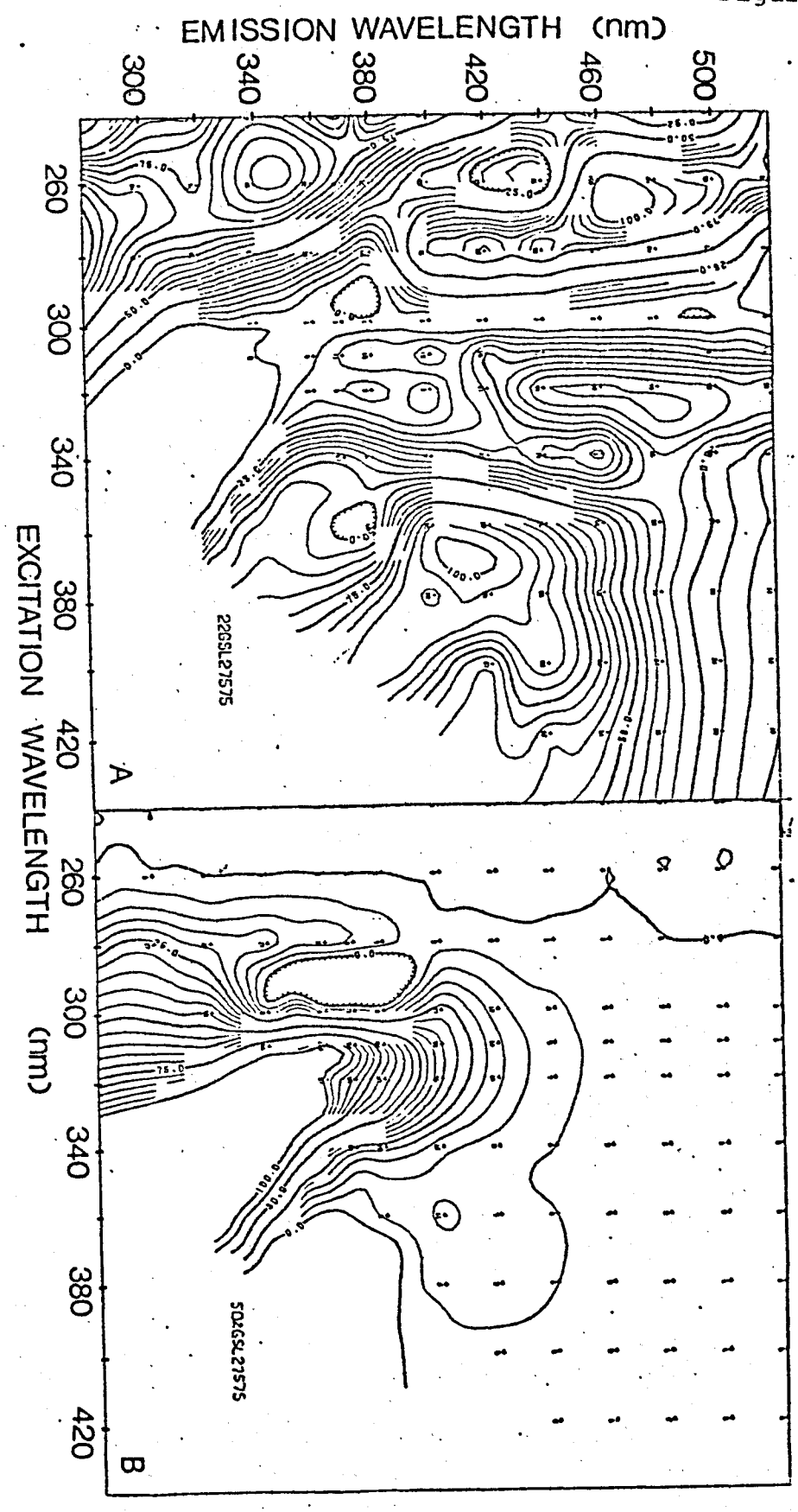
2.0
1.0
µG OIL/ LITER
1
6
30
41
46
53
SAMPLING LOCATION

Figure 8


EMISSION WAVELENGTH (nm)
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340
380
420
460
500
260
300
340
380
420
EXCITATION WAVELENGTH (nm)
A
B
22651 27575
50469 27575