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HYDROCARBONS IN THE MACKENZIE RIVER

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MANAGEMENT PERSPECTIVE

This survey of hydrocarbons in Mackenzie River water and suspended sediments was part of a broader and continuing study of the possible causes of fish liver impairment reported by local fisheries.

The survey, conducted in June, 1986, shortly after ice breakup, indicated diffuse hydrocarbon inputs by spring runoff from the river's drainage basin, which overwhelmed any inputs from the Norman Wells refinery or from natural oil seeps in the Norman Wells area.

The analyses were financially supported by the Northern Oil and Gas Action Program (NOGAP) through IWD, Yellowknife.

LES HYDROCARBURES DANS LES EAUX DU MACKENZIE

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PERSPECTIVE GESTION

On a dosé les hydrocarbures des eaux et des sédiments en suspension du fleuve Mackenzie dans le cadre d'une étude portant sur les causes possibles de l'altération du foie des poissons, phénomène qu'on a observé dans les pêcheries de la région; les travaux se poursuivent.

D'après les résultats d'un relevé effectué en juin 1986, peu après la débâcle printanière, les apports d'hydrocarbures diffus dus à l'écoulement des eaux de ruissellement printanier du bassin versant du fleuve sont plus importants que les apports attribuables à la raffinerie de Norman Wells ou aux infiltrations de pétrole naturelles dans la région.

La DGEI de Yellowknife a défrayé les analyses avec des fonds provenant du Programme d'initiatives pétrolières et gazières dans le Nord (PIPGN).

HYDROCARBONS IN THE MACKENZIE RIVER

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EXECUTIVE SUMMARY

Impaired fish liver quality has been reported on the lower Mackenzie River. This survey was part of a broader study on the possible impact on water quality by the Norman Wells refinery operations or by natural oil seeps in the Norman Wells area.

A June, 1986 survey along the river found higher alkane and polyaromatic hydrocarbon (PAH) concentrations in the system than a similar survey in August 1985. The concentration distributions along the river suggested diffuse inputs of these organics by the spring runoff from the river's drainage basin, which overwhelmed any inputs from the refinery or from the oil seeps.

The distribution of the organics between the suspended sediments and the water phase show the need for analyzing both phases for estimates of organic loadings in the river.

S.B. n°2270179

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On signale que les poissons du bas Mackenzie ont le foie altéré. Cette constatation est le résultat de travaux réalisés dans le cadre d'une étude sur les effets que pourraient avoir sur la qualité de l'eau les opérations de raffinage qui se font à l'usine de Norma Wells ou l'infiltration naturelle de pétrole dans la région.

En juin 1986, les concentrations d'alcanes et d'hydrocarbures polyaromatiques étaient plus élevées qu'en août 1985. D'après la distribution des concentrations dans le cours d'eau, les apports seraient diffus : la plus grande partie des composés organiques viendrait des eaux de ruissellement printanier s'écoulant du bassin versant du fleuve, la portion attribuable à la raffinerie ou à l'infiltration de pétrole étant moindre.

Comme les composés se trouvent dans les sédiments en suspension ainsi que dans l'eau, il faudrait analyser ces deux composants pour estimer la charge du fleuve.

LES HYDROCARBURES DANS LES EAUX DU MACKENZIE

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RÉSUMÉ

En juin 1986, on a dosé les n-alcanes et les hydrocarbures polyaromatiques des eaux et des sédiments en suspension du fleuve Mackenzie; on a constaté que les concentrations étaient plus élevées que lors du dosage effectué en août 1985. En raison de cette augmentation et des variations de concentration observées dans le cours du fleuve, on pense que les apports attribuables à la raffinerie de Norman Wells ou aux infiltrations de pétrole naturelles sont moins importants que ceux dus aux eaux de ruissellement printanier dans le bassin versant du fleuve. Comme les hydrocarbures se trouvent dans l'eau ainsi que dans les sédiments en suspension, il faudrait analyser ces deux composants pour être en mesure de déterminer la charge du fleuve.

HYDROCARBONS IN THE MACKENZIE RIVER

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ABSTRACT

A June, 1986 survey of n-alkanes and PAHs in Mackenzie River water and suspended sediments showed higher concentrations than a similar survey in August, 1985. The higher concentrations, and the concentration variations along the river suggested that any inputs from the Norman Wells refinery or from natural oil seeps were overwhelmed by diffuse inputs from spring runoff from the drainage basin. The distribution of the organics between the water phase and the suspended sediment showed the need for analyzing both phases if organic loadings in the river are to be calculated.

INTRODUCTION

Reports of impaired fish liver quality in the Mackenzie River had been made by subsistence fisheries on the lower reaches of the river during the early 1980's. Esso Resources Ltd. and the Northern Oil and Gas Action Program (NOGAP) have initiated several surveys on hydrocarbons in the river, and on the possible effects of the Norman Wells refinery operations and of natural oil seeps on river water quality (1-5).

This report presents the data of a 1986 survey of normal alkanes and polyaromatic hydrocarbons (PAHs) in the water and suspended sediments of the Mackenzie and Liard rivers and in Liard River bottom sediments. The survey was part of a broader program by NOGAP, and was a repeat of a 1985 survey under different flow conditions (6).

Normal alkanes, i.e. straight-chain aliphatic hydrocarbons, occur widely in natural water systems, often as a result of biological processes on land or in the water. The alkane distributions (profiles), and odd-carbon predominance may indicate biological or petroleum origins of this class of organic compounds. Their analysis is included in this report as they were found in significant amounts in the fractions containing the PAHs.

Polyaromatc hydrocarbons have been reported in freshwater environments in diverse geographic locations. They are regarded as significant environmental pollutants because of their potential carcinogenic or mutagenic properties (7-11). Although PAHs occur in petroleum, their main source is the combustion of various fuels in energy production, space heating, industrial processes and in the internal combustion engine. The PAHs thus produced are generally found on airborne particulates and are widely distributed before deposition on land or water surface by precipitation. Rivers may concentrate diffuse land-deposited PAHs from their drainage basins and deposit them in lakes or oceans.

EXPERIMENTAL METHODS

Survey area

The map in Figure 1 shows the location of the sampling sites along the Mackenzie River from Fort Simpson (205 miles or 328 km from Great Slave Lake) to Oniak Channel at Inuvik (at 992 miles or 1587 km). An additional site at Fort Simpson was in the Liard River before it entered the Mackenzie. The Liard, after flowing through an area of producing gas wells, empties a high sediment load into the Mackenzie River.

The surveys

While the 1985 survey was carried out from Aug. 10 to Sept. 12, the 1986 samples were collected between June 18 and July 1, i.e. shortly after the spring breakup. Thus, the two surveys allow comparisons between the major flow regimes of the river: low flow and low sediment loads sampled in late summer of 1985, and high flow with high sediment loads sampled in early summer of 1986. Although the sediment loads were not determined, the water turbidities, as shown in Figure 2, were significantly higher in 1986. It is noteworthy that Great Slave Lake contributed much less turbidity (sediment load) to the Mackenzie River than its tributaries in both flow regimes. The 1986 sampling sites are listed in Table 1.

In the fall of 1986, five bottom sediment samples were collected in the Liard River in relatively low flow areas to investigate the usefulness of such samples in a fast-flowing river and to obtain more information on the organics in one of the Mackenzie River tributaries.

Sample collection and handling

As described in the previous report (6), suspended sediment samples were collected with a Sedisamp System-II continuous-flow centrifuge, the centrifuging times varying from 25 minutes to 6.5 hours, depending on water turbidities. Water-soluble organics were sampled by passing 18 L aliquots of the centrifuged water through XAD-2 resin columns. The sediment samples were frozen, and the resin columns were refrigerated for transportation and storage prior to analysis.

Analyses

The extraction of the base/neutral organics, silica gel fractionation of the sediment extracts, and the analyses are described in the report cited above (6). The GC/FID quantitation was limited to normal alkanes in the C_{12} to C_{26} range and to 16 priority-pollutant PAHs listed in Table 2.

RESULTS AND DISCUSSION

Suspended sediments

The normal alkane and PAH concentrations on suspended sediments along the river are summarized in Table 3 and shown in Figure 3. The n-alkanes predominated at every site along the Mackenzie, with an average concentration ratio (C_{alkane}/C_{PAH}) of 2.85. At the single Liard River site, however, the PAH concentration was about three times greater than that of the alkanes (ratio = 0.38).

The concentration profiles of the alkanes and PAHs along the river showed similar patterns with high initial values followed by lower concentrations and then increases at Site 5, below Fort Good Hope. The initial high levels at the Fort Simpson site, which receives inputs from Great Slave Lake, were accompanied by low turbidities. This would suggest actual fluxes here would be lower, and possibly as low as those at the next two sites. As increasing water turbidities are only qualitative indicators of increasing sediment loads, measurements of suspended sediment concentrations and some estimation of sediment fluxes would significantly aid data interpretation in similar surveys. In the present study, knowledge of the organic fluxes along the river could indicate whether concentration decreases in the lower reaches of the river were due to sedimentation, dilution, or degradation processes.

The concentration maxima further downriver occur at a considerable distance from the Norman Wells refinery and from the natural oil seeps in the same area. This would indicate that PAHs from those sources were overwhelmed in this survey by inputs from the river's drainage area by the spring runoff. In the absence of industries and large population centers, these sources must be considered diffuse, the result of the precipitation of airborne PAHs in the drainage area.

River water

Alkane and PAH concentrations in the river water are shown in Table 4 and Figure 4. The measurable concentrations of both classes of hydrocarbons in the water in the 1986 survey, compared with no detectable amounts in 1985, indicates significant inputs into the river by spring runoff. The alkane/PAH concentration ratios vary from 0.32 to 4.05 along the river without a discernible pattern.

The concentrations along the river seem to vary in a similar fashion to those found on the suspended sediments: high initial values from Great Slave Lake, associated with low suspended sediment fluxes, and maximum concentrations at Site 5, below Fort Good Hope. The comments made for the suspended sediment results appear to be valid for the water samples.

Liard River sediments

The alkane and PAH concentrations in these bottom sediments, shown in Table 5, were higher than those found on the Mackenzie River suspended sediments, possibly as a result of gas production in the area. As the extent of these contaminated sediments is unknown, their influence on Mackenzie River water quality is uncertain.

Sediment-water partitioning of organics

The suspended sediment concentrations in the water were calculated from the reported water volumes that were centrifuged (12), and from the dry weights of the extracted sediment samples assuming an overall 90% recovery from centrifuging and sample handling. The results of these calculations are given in Table 6, with the reported water turbidities. The calculated solids concentrations show a linear variation with the measured turbidities in Figure 5, in agreement with the reported linear responses of nephelometric turbidimeters in the same concentration range (13).

The sediment-water partitioning constants were calculated for the n-alkanes and the PAHs from our data, using the formula:

$$K = \frac{\text{ug organics/g suspended sediment}}{\text{ug organics/mL water}}$$

The values, given in Table 7, are greatly scattered, but show a 100 to 1000-fold concentration of both alkanes and PAHs on the suspended sediments.

The distribution of these organics between the solid and water phases, <u>in a unit volume of water</u>, is given in Table 8, showing that the suspended sediments carry only a fraction of the total organic load in the river. Although this fraction may be as high as 70% of the total at high suspended solids loads, it drops significantly at low suspended solids concentrations. In the waters from Great Slave Lake, for instance, the suspended solids carried less than 5% of the total alkanes and PAHs in the river. Although the sediment-water partitioning of these organics favor the sediment phase, the low sediment concentrations produce the observed distributions. In addition to the water-volume effect, organics adsorbed on the non-settling or non-centrifuged fine particles have been reported to be significant factors in calculationg partitioning constants and distribution of organics. A recent paper by Gschwend and Wu (14) has suggested the consideration of three phases: water, suspended solids, and suspended but non-settling particulates in speciation studies of hydrophobic organic pollutants.

Alkane and PAH compositions

Alkane and PAH distributions were plotted only for the suspended sediment extract, since the concentrations of the water extracts were too low to allow GC/MS verification of individual components.

The distributions of the C_{12} to C_{26} normal alkanes are shown in Figures 6a to 6c. A strong C_{15} and C_{17} predominance, indicating recent biogenic alkanes, was seen at Site 1 only, in the inputs from Great Slave Lake. A bimodal alkane distribution, possibly suggesting a petroleum hydrocarbon input, was found only at the Liard River site.

The PAH distributions, given in Figures 7a to 7c, show that only a few of the 16 priority pollutant PAHs made up this class in most of the samples. The most common compounds found were naphthalene, fluorene, benzo(k)fluoranthene, and dibenzo(a,h)anthracene. The PAH profiles were similar along the whole length of the survey, including the Norman Wells area. In view of the probability that the spring runoff was the main source of these PAHs, the strong presence of naphthalene is intriguing.

PAHs that were not present in high enough concentrations to be quantitated, but were detected by GC/MS techniques, included some methyl homologues of Mass 178 (anthracene/phenanthrene) and of Mass 202 (pyrene/fluoranthene) as demonstrated by the ion chromatograms shown in Figures 8 and 9.

The n-alkane distributions in the Liard River bottom sediments, shown in Figures 10a and 10b, do not indicate a significant biogenic nature (e.g. C_{15} or C_{17} predominance). The PAH distributions, given in Figures 11a and 11b, show significant amounts of phenanthrene, which may be associated with a petroleum origin.

ACKNOWLEDGEMENTS

J. Tisdale and E. DuVal, of the National Hydrology Research Centre, conducted the sampling program. Technical and financial support was provided for the hydrocarbon analyses by Brian J. Olding, IWD, Yellowknife, and the Northern Oil and Gas Action Program (NOGAP).

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Table 1

Mackenzie River Sampling Sites, 1986

Site No.	Km from Great Slave	Sampling date	Turbidity N.T.U.	Details of site
1	329	June 21	11	Fort Simpson
2	577	June 23	53	Wrigley
3	847	June 26	288	Halfway Island
4	1044	June 27	336	Hardy Island
5	1142	June 28	288	Fort Good Hope
6	1444	June 29	156	Arctic Red River
7	1687	July 1	172	Inuvik
8	331	June 19	62	Liard River site

Table 2

Priority Pollutant PAHs

No.	Symbol	M.W.	Name
1	N	128	Naphthalene
2	AY	152	Acenaphthylene
3	AE	154	Acenaphthene
4	FL	166	Fluorene
5	PH	178	Phenanthrene
6	AN	178	Anthracene
7	F	202	Fluoranthene
8	PY	202	Pyrene
9	BaA	228	Benzo(a)anthracene
10	CH	228	Chrysene
11	BbF	252	Benzo(b)fluoranthene
12	BkF	252	Benzo(k)fluoranthene
13	BaP	252	Benzo(a)pyrene
14	IP	276	Indeno(123,cd)pyrene
15	DA	276	Dibenzo(a,h)anthracene
16	BP	276	Benzo(ghi)perylene

Table 3

Analysis of Mackenzie River Suspended Sediments - 1986

Site No.	N-alkanes[1] (micrograms / gram)	PAHs[2] (micrograms / gram)
1	1.523	0.418
2	0.791	0.196
3	0.125	0.052
4	0.205	0.076
5	0.255	0.147
6	1.116	0.391
7	0.773	0.289
8 (Liard R. sample)	0.994	0.264

Note: 1 - Sum of C_{12} to C_{26} normal alkanes

2 - Sum of 16 priority pollutant PAHs

Table 4

Analysis of Mackenzie River Water - 1986

Site No.	N-alkanes[1] - micrograms / L	PAHs[2] (ppb) -
1	0.591	1.824
2	0.147	0.303
3	0.239	0.111
4	0.410	0.414
5	0.505	1.234
6	0.168	0.261
7	0.219	0.054
8 (Liard R.)	0.284	0.292

Note: 1 - Sum of C_{12} to C_{26} normal alkanes

2 - Sum of 16 priority pollutant PAHs

Table 5

Analysis of Liard River bottom sediments

Sample No.	N-alkanes[1]	PAHs[2]
1	6.176	0.644
2	0.702	0.333
3	3.165	1.254
4	3.282	0.664
5	3.836	0.788

Note: 1 - Sum of C_{12} to C_{26} normal alkanes

2 - Sum of 16 priority pollutant PAHs

Table 6

Estimated concentrations of suspended sediments in Mackenzie River water

Site No.	Vol. of water centrifuged (L)	Dry sediment recovered (g)	Conc. of susp.sed. (mg/L)	Turbidity (N.T.U.)
1	1560	16.9	11	11
2	300	24.8	83	53
3	180	93.4	519	288
4	120	82.2	685	336
5	100	49.2	492	288
6	136	49.5	364	156
7	144	50.3	349	172
8 (Liard)	240	20.9	87	62

Table 7

Apparent partitioning constants* of n-alkanes and PAHs between suspended solids and water

Site No.	N-alkanes	PAHs
1	2576	229
2	5380	646
3	523	468
4	500	183
5	504	119
6	6642	1498
7	3529	5351
8 (Liard R>)	3500	904

$$* - K = \frac{\text{Mass of organics/g suspended solids}}{\text{Mass of organics/mL water}}$$

Table 8

Distribution of organics between the water phase and suspended sediments

Site No.	Amounts in micrograms/litre*			
	N-alkanes		PAHs	
	water	s.sed.	water	s.sed.
1	.591	.017	1.824	.005
2	.147	.066	.303	.016
3	.239	.065	.111	.027
4	.410	.140	.414	.052
5	.505	.125	1.234	.072
6	.168	.406	.261	.142
7	.219	.269	.054	.101
8 (Liard R.)	.284	.086	.292	.023

* - See text

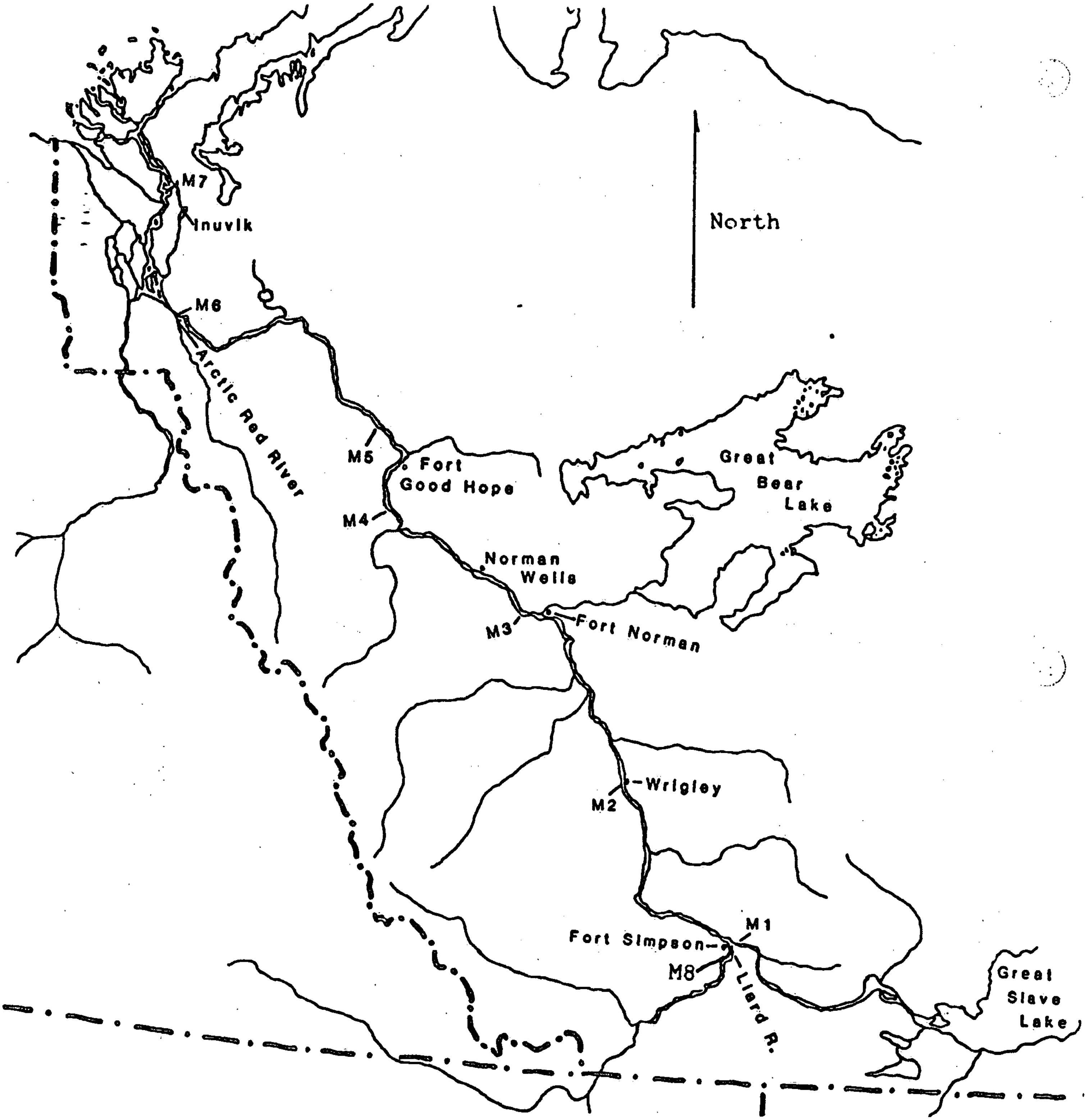


Figure 1

Mackenzie River Sampling Sites - 1986

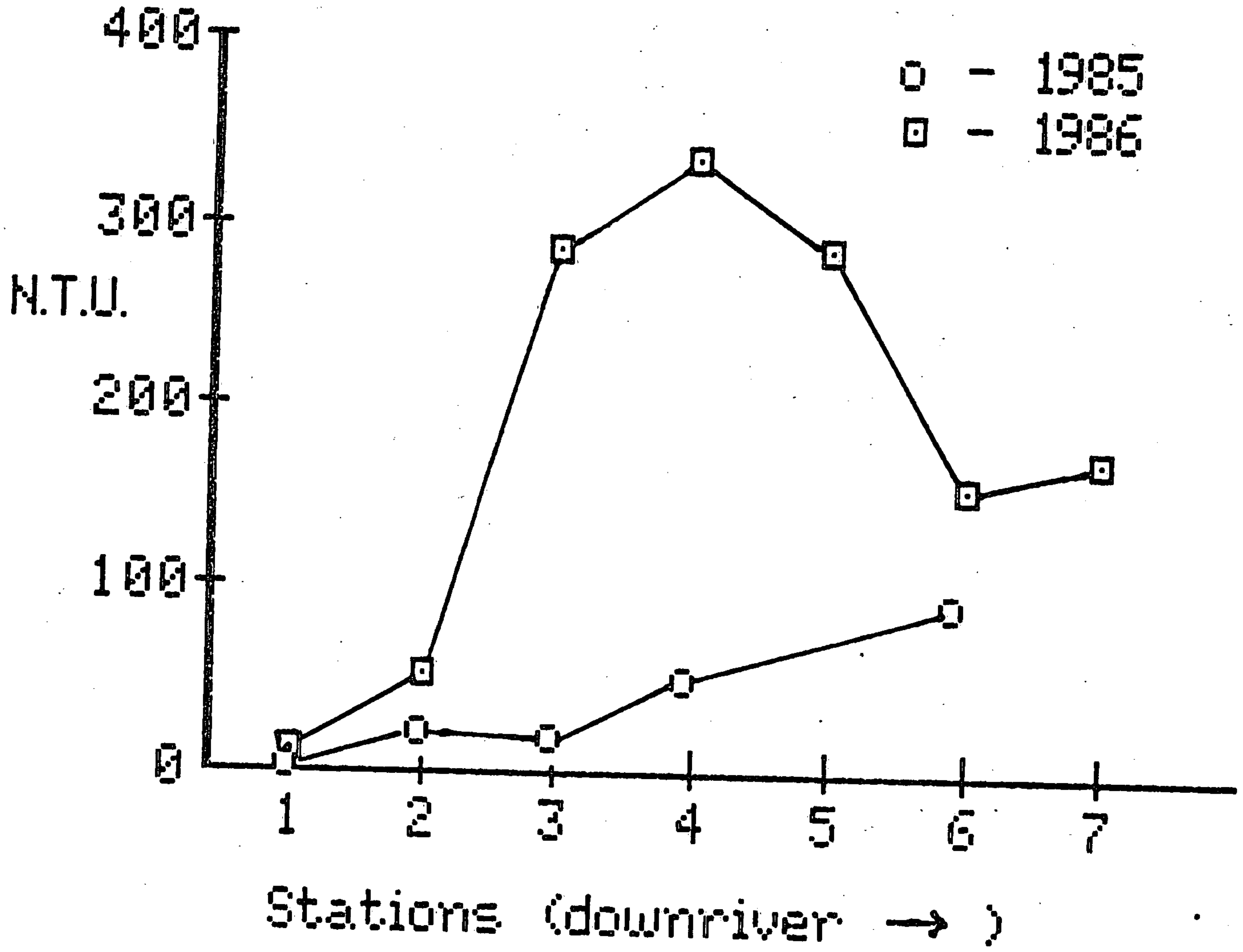
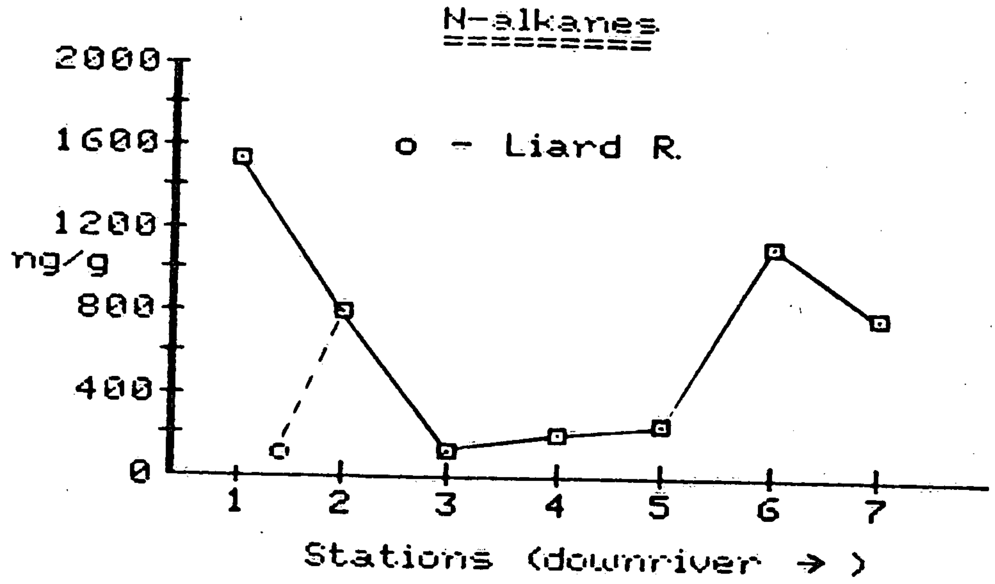


Figure 2

Turbidities in the Mackenzie River



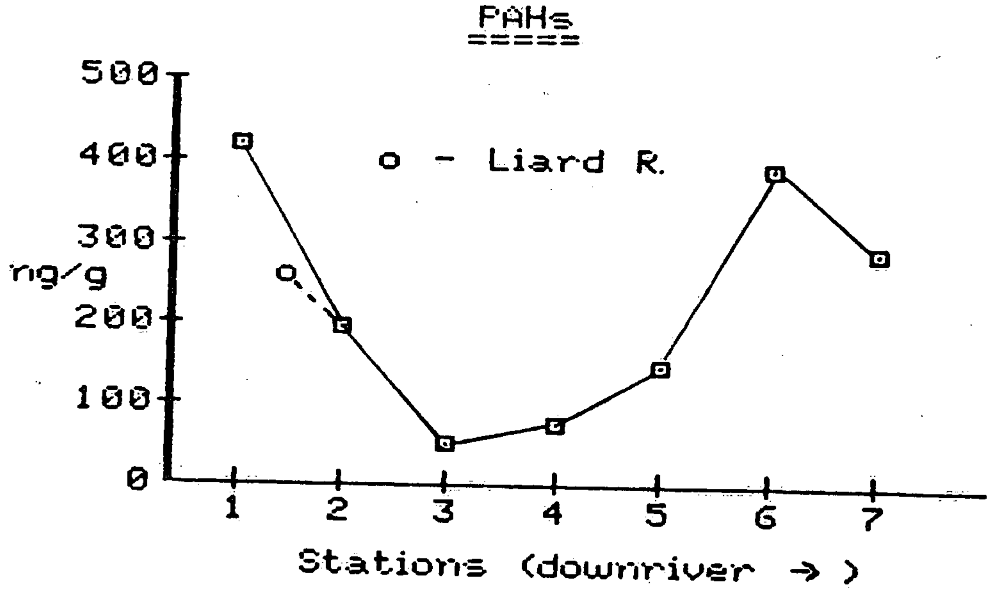


Figure 3

N-alkanes and PAHs in Mackenzie River
Suspended Sediments - 1986

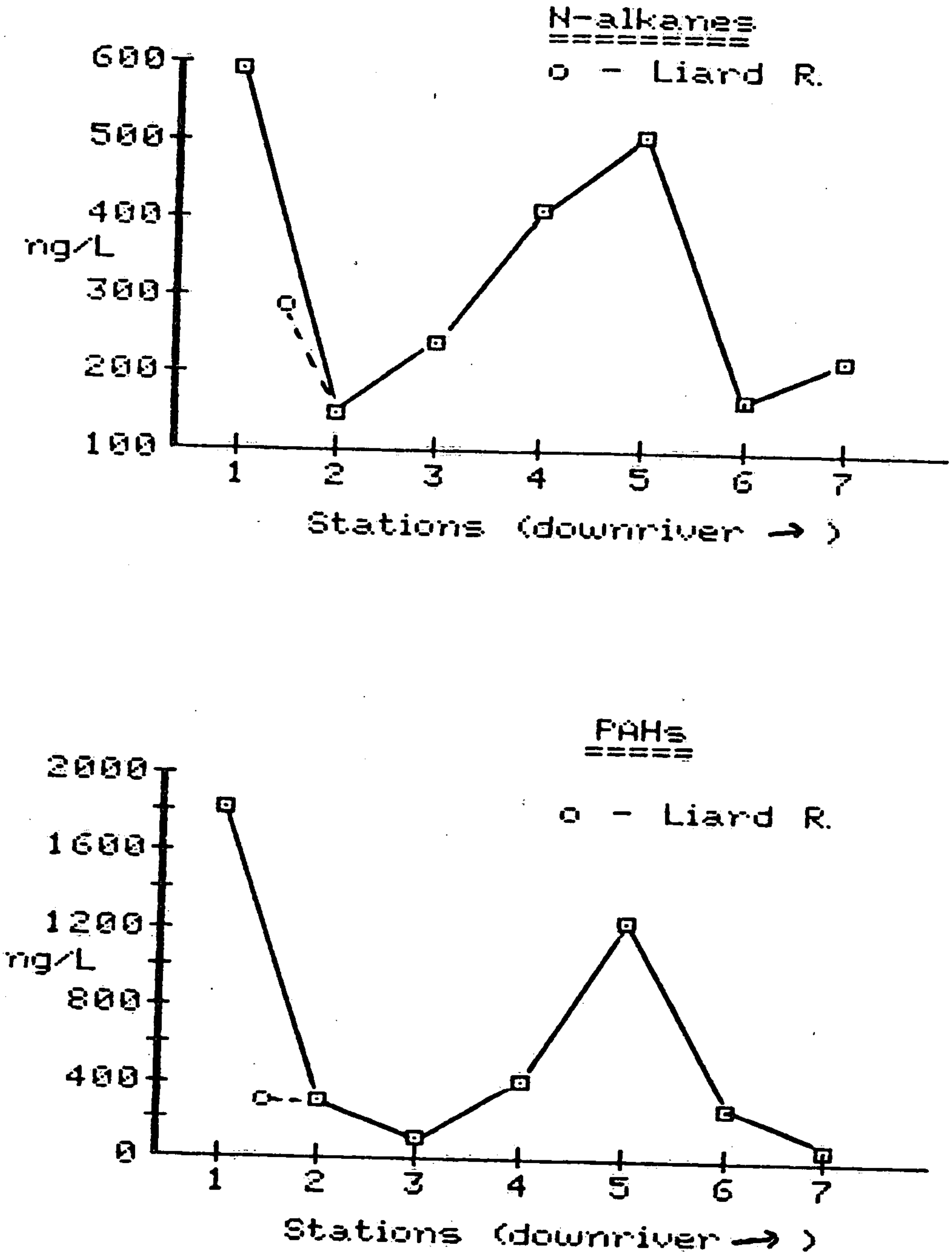


Figure 4

N-alkanes and PAHs in Mackenzie River Water - 1986

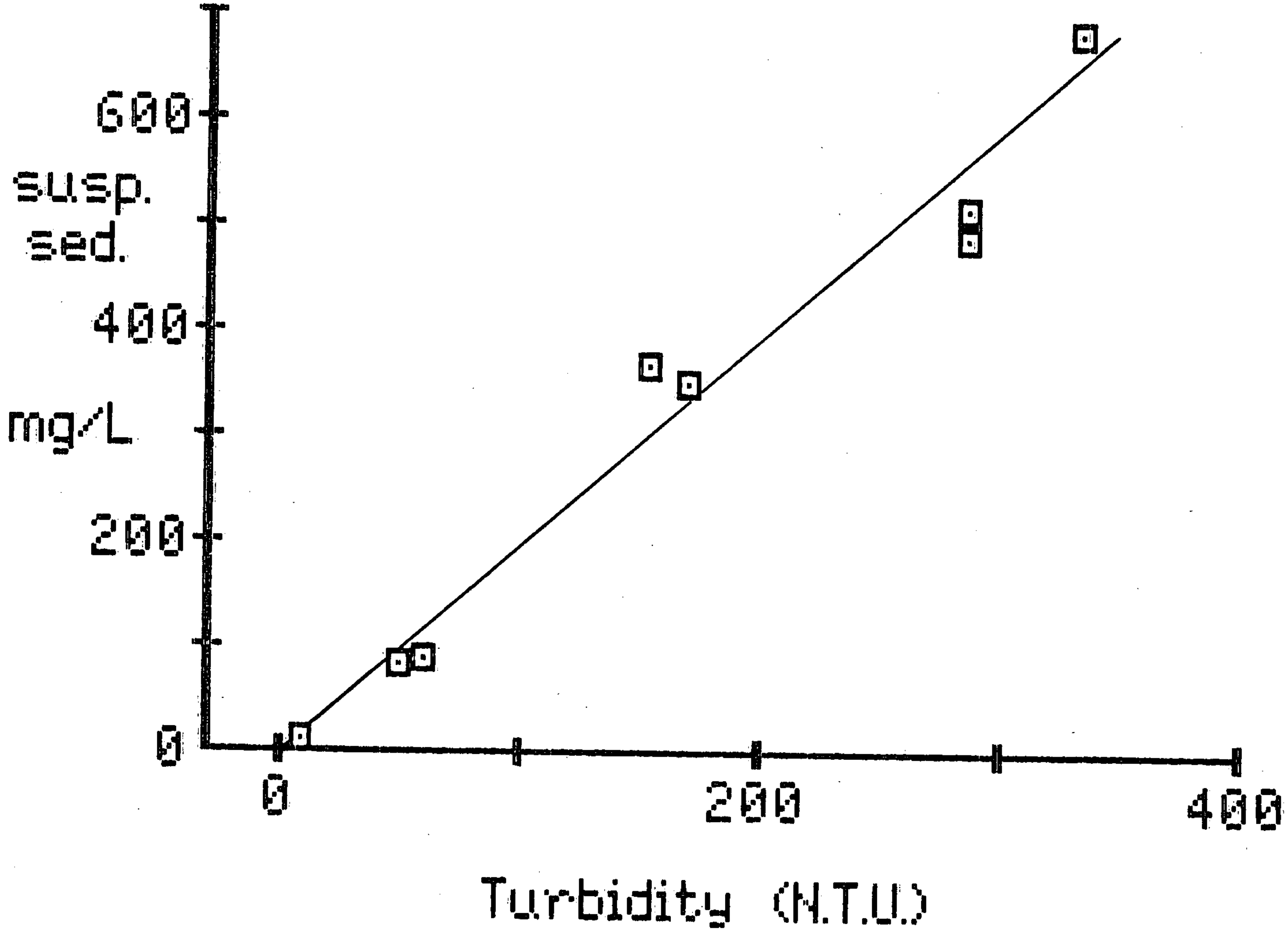


Figure 5

Turbidities and suspended sediments in Mackenzie River water

Figure 6a

N-ALKANES IN MACKENZIE RIVER SUSPENDED SEDIMENTS - 1986

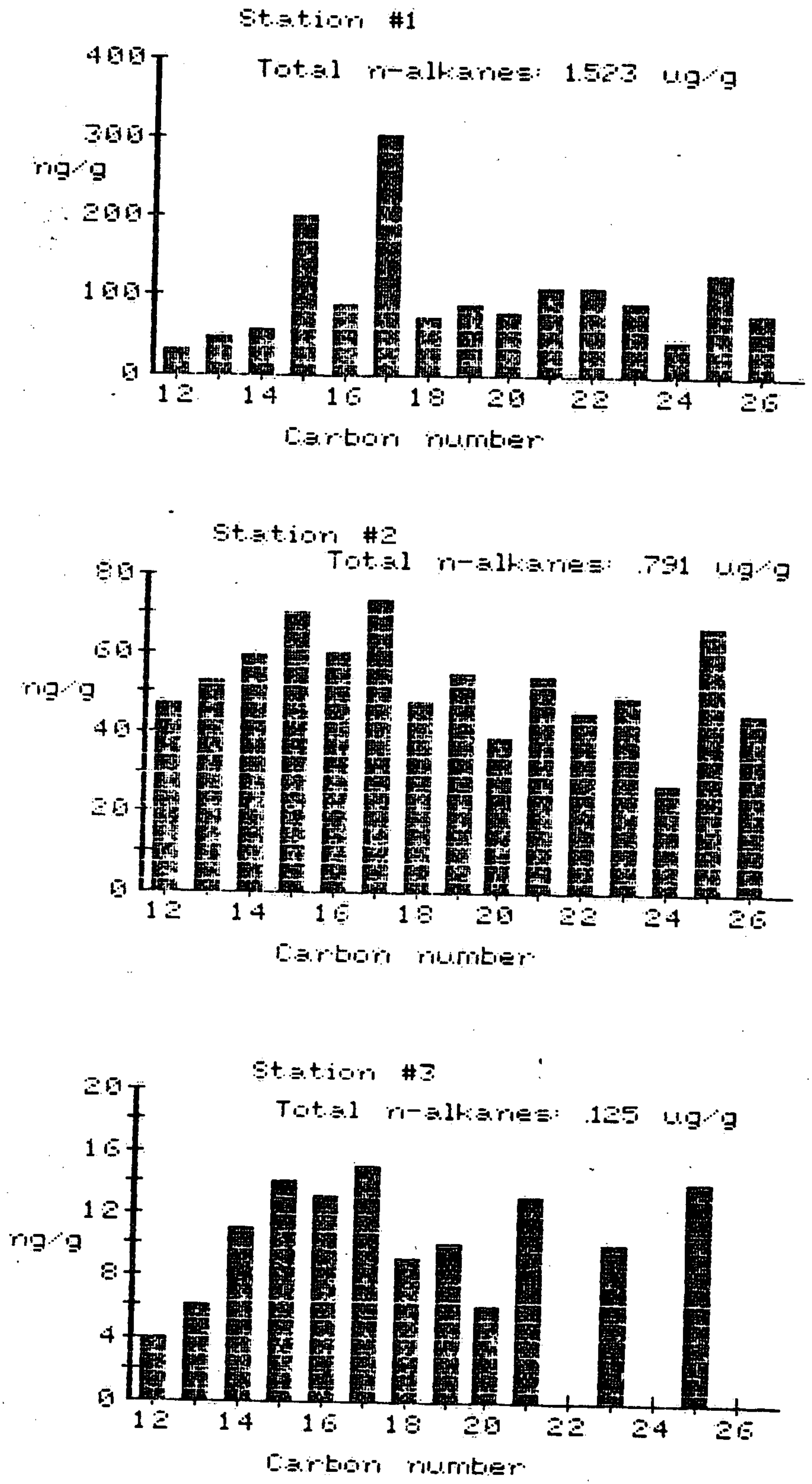
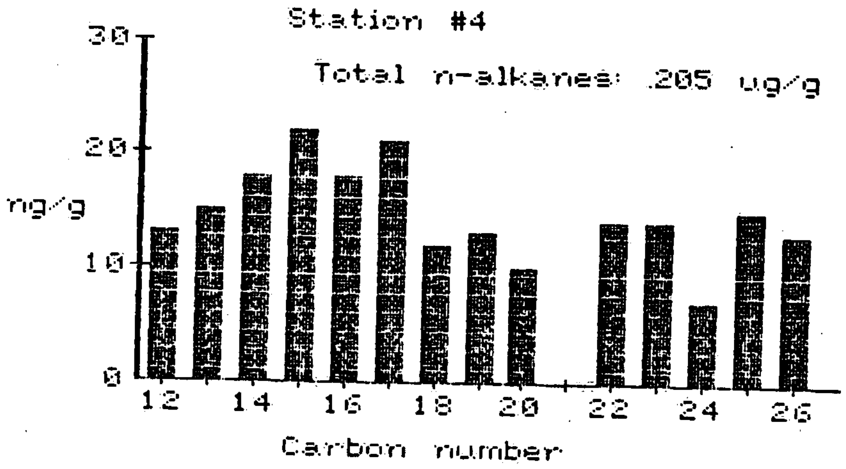
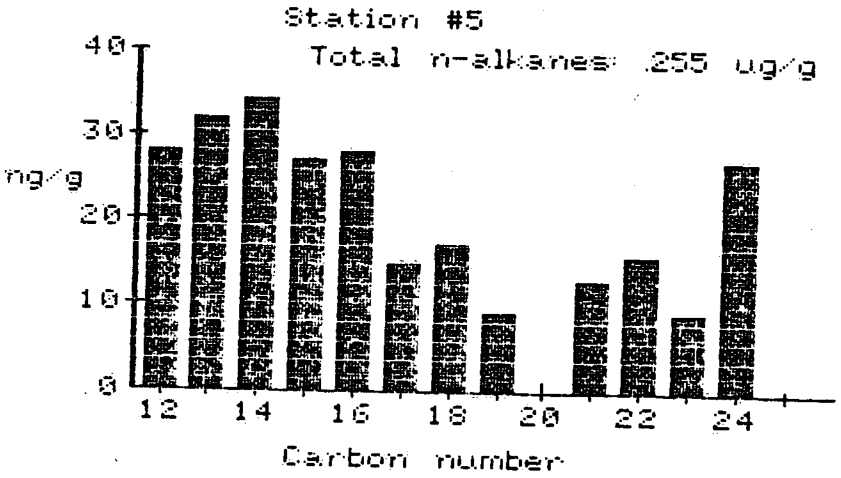


Figure 6b

N-ALKANES IN MACKENZIE RIVER SUSPENDED SEDIMENTS - 1986





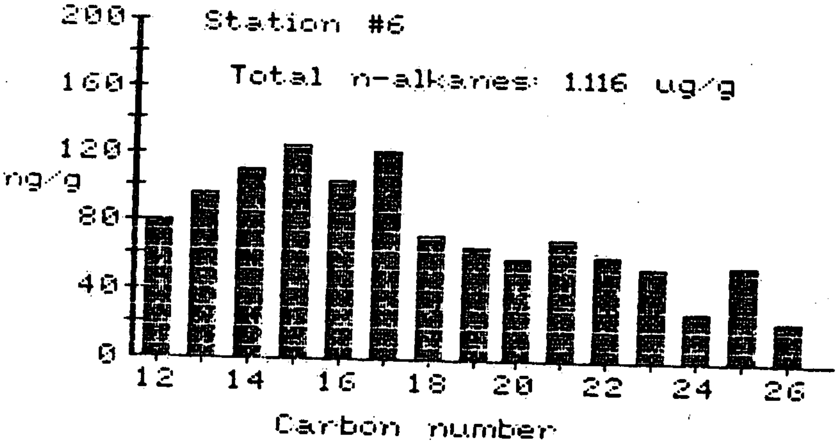
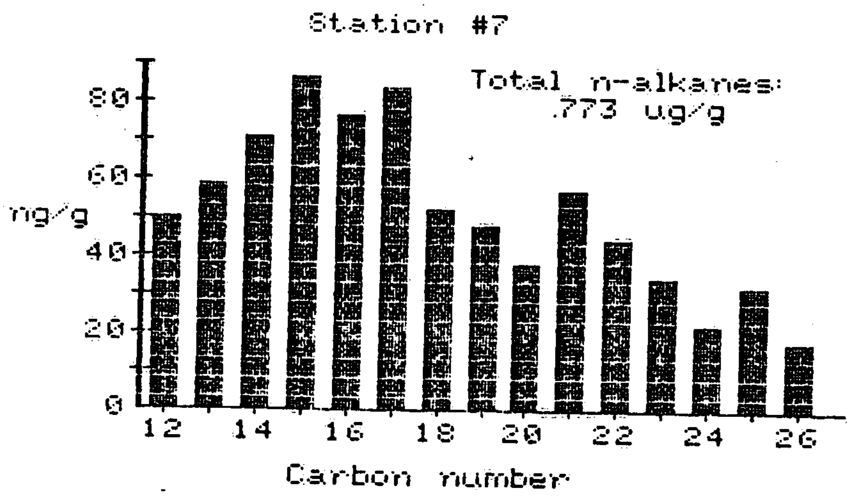


Figure 6c

N-ALKANES IN MACKENZIE RIVER SUSPENDED SEDIMENTS - 1986



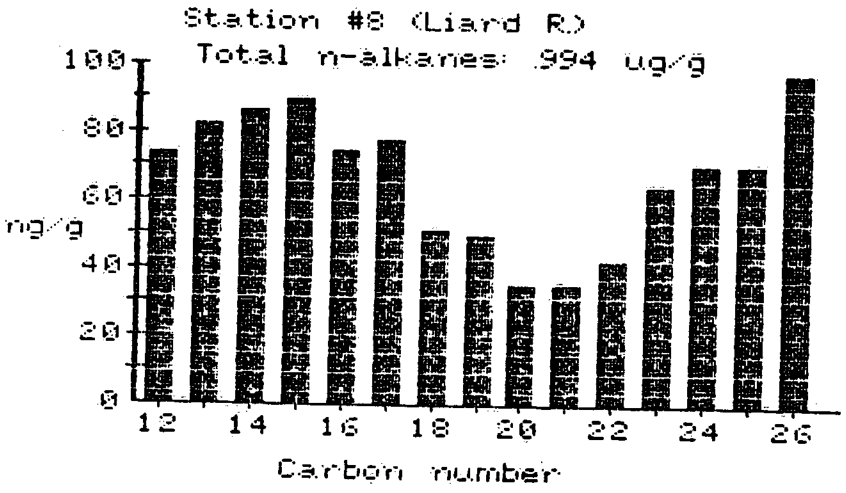


Figure 7a

PAHs IN MACKENZIE RIVER SUSPENDED SEDIMENTS - 1986

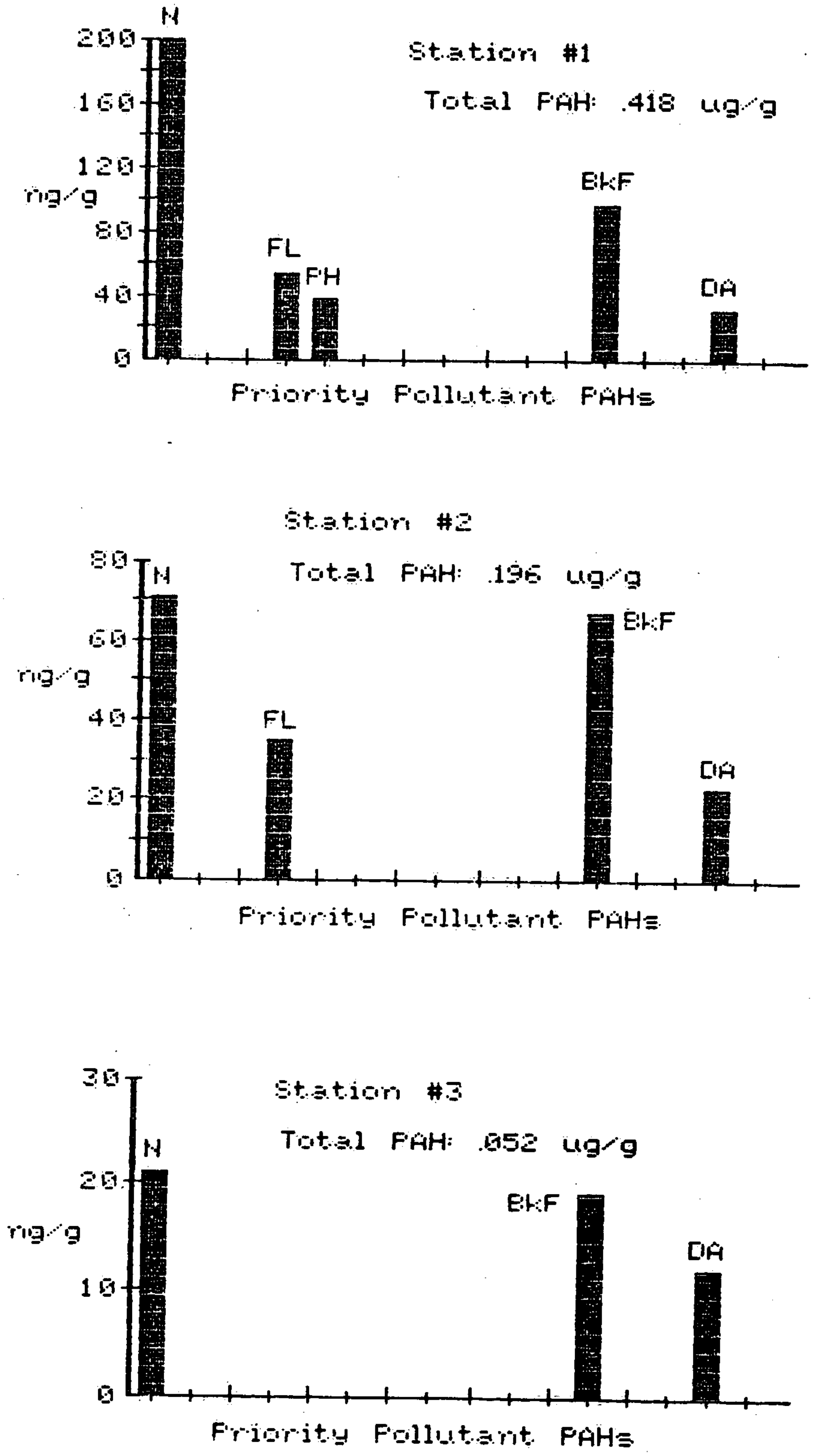


Figure 7b

PAHs IN MACKENZIE RIVER SUSPENDED SEDIMENTS - 1986

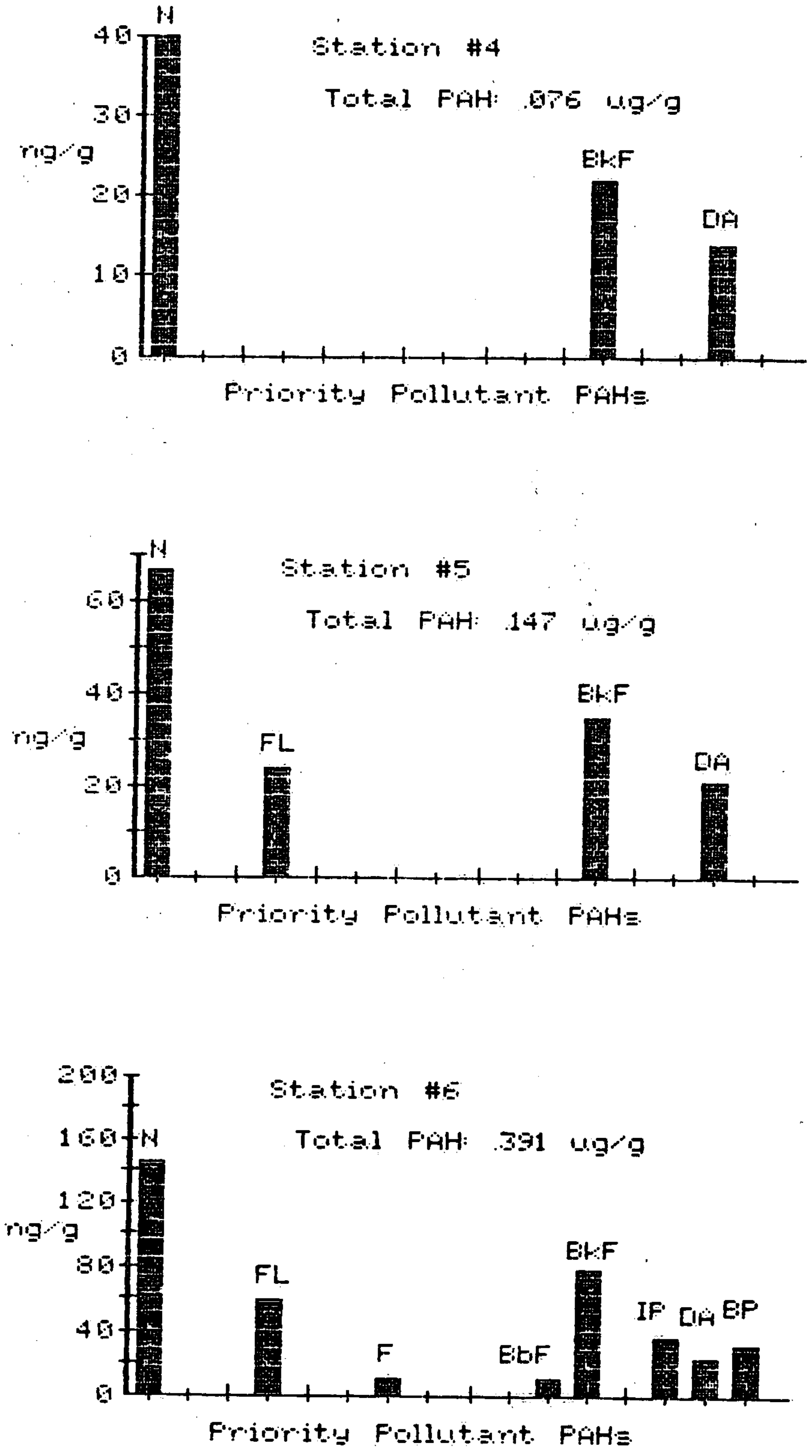
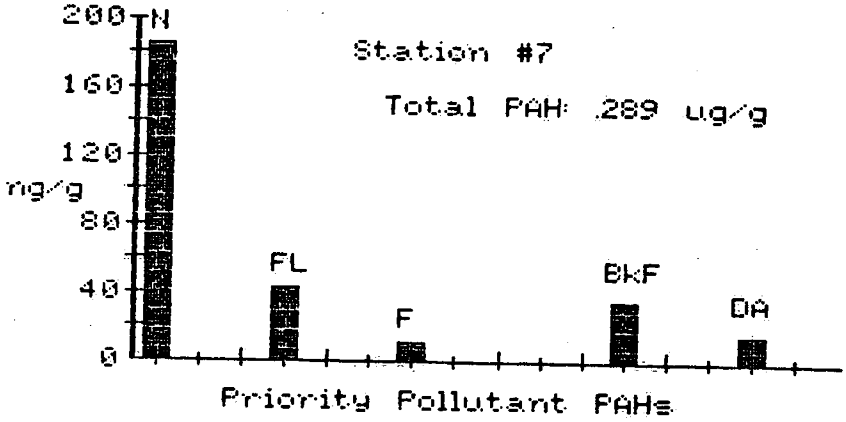
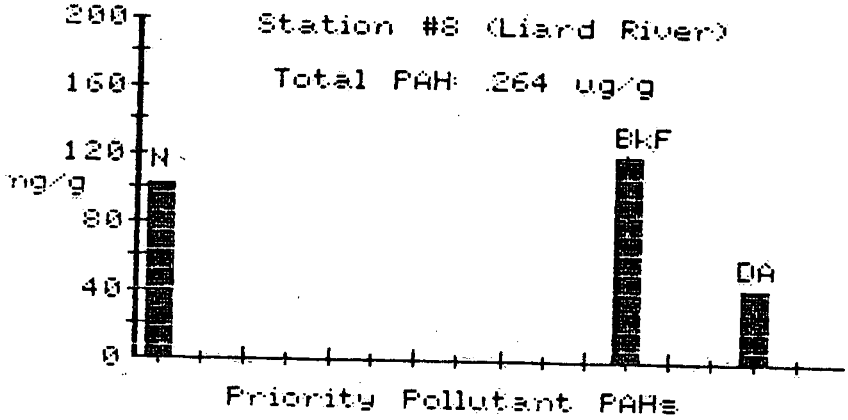


Figure 7c

PAHs IN MACKENZIE RIVER SUSPENDED SEDIMENTS - 1986





Priority Pollutant PAHs
(with molecular weights)

N - 128 - naphthalene
AY - 152 - acenaphthylene
AE - 154 - acenaphthene
FL - 166 - fluorene
PH - 178 - phenanthrene
AN - 178 - anthracene
F - 202 - fluoranthene
PY - 202 - pyrene

BaA - 228 - benzo(a)anthracene
CH - 228 - chrysene
BbF - 252 - benzo(b)fluoranthene
BkF - 252 - benzo(k)fluoranthene
BaP - 252 - benzo(a)pyrene
IP - 276 - indeno(123,cd)pyrene
DA - 276 - dibenzo(a,h)anthracene
BP - 276 - benzo(ghi)perylene

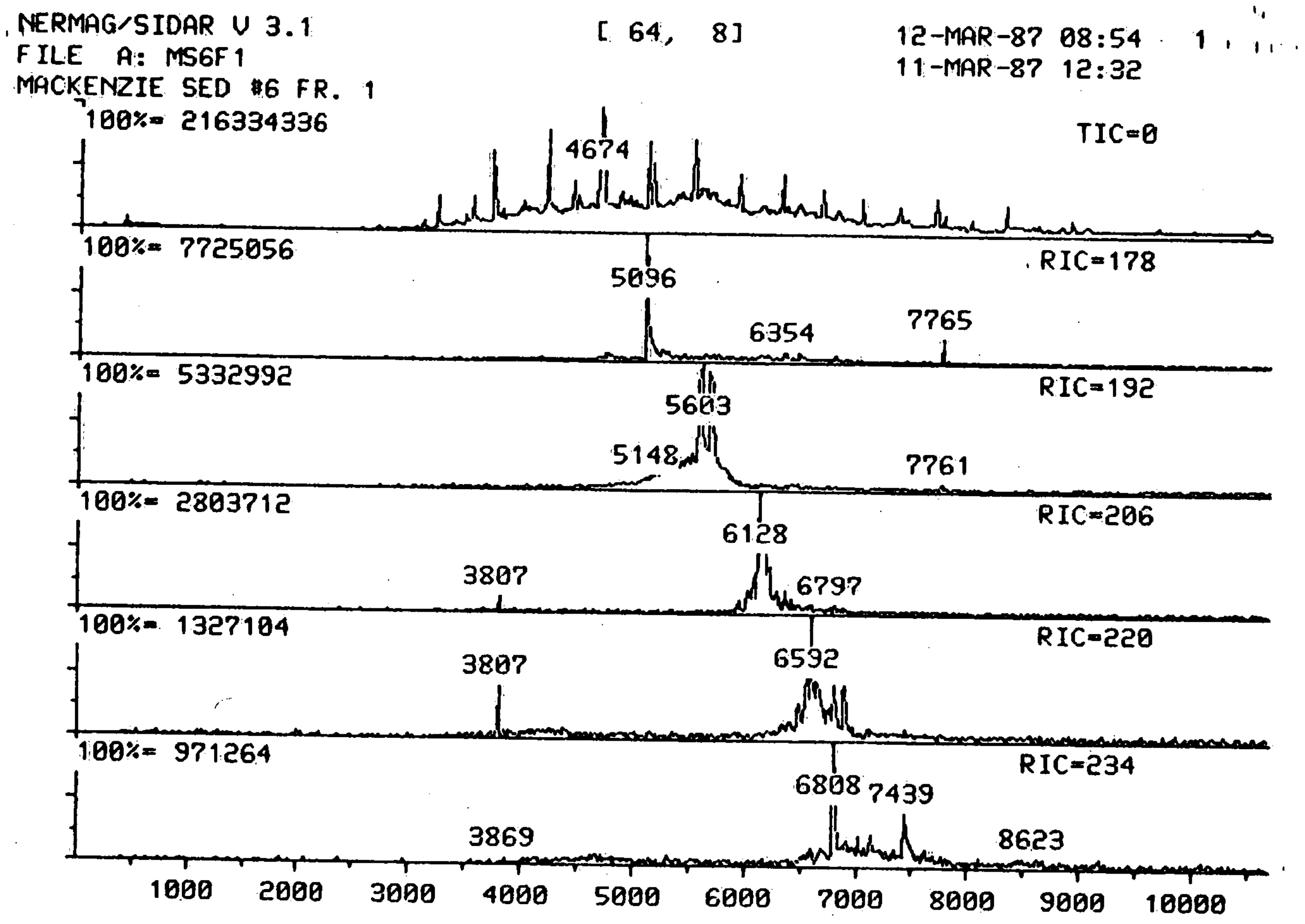


Figure 8

Methyl Homologues of Mass 178 PAHs

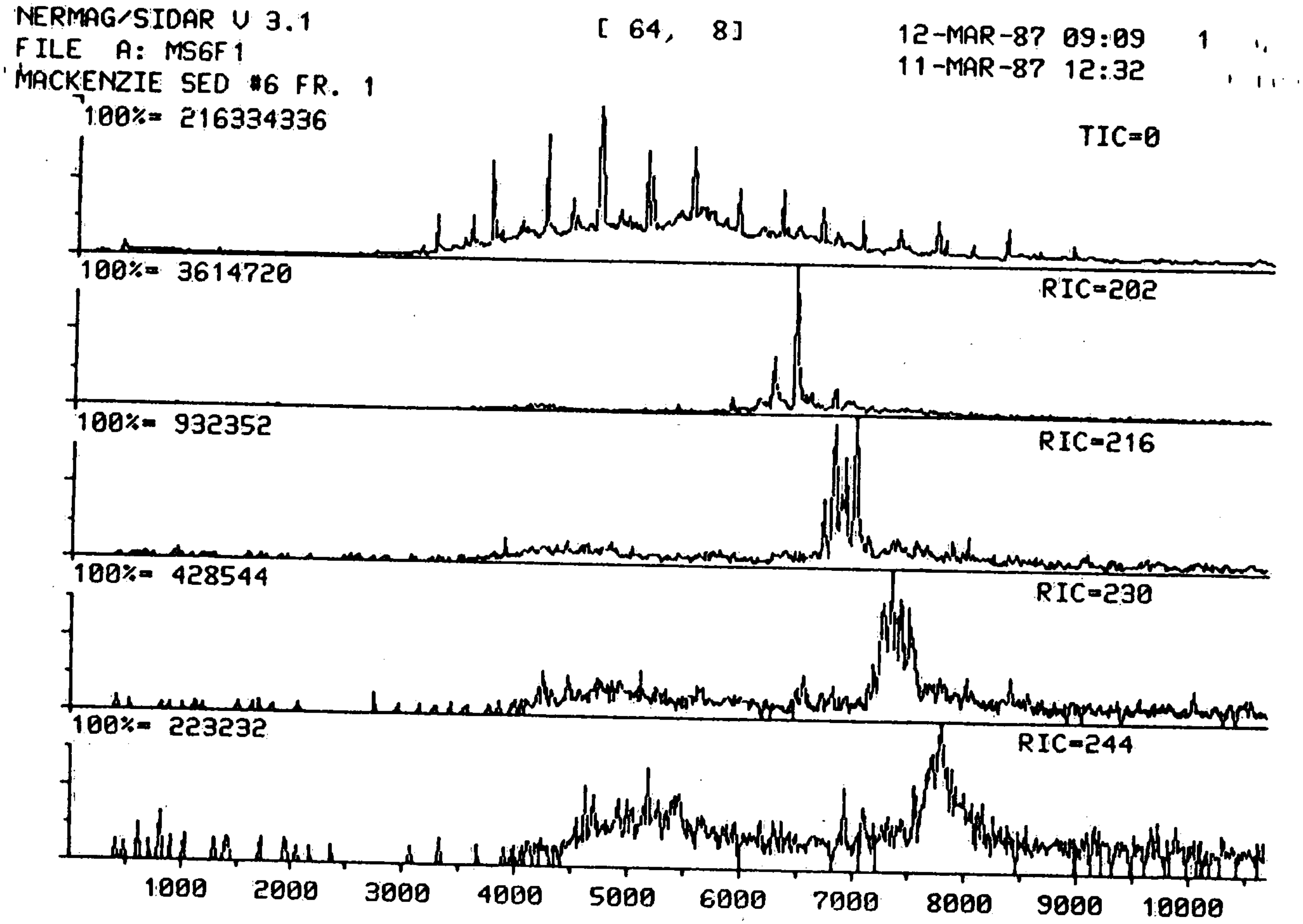


Figure 9

Methyl Homologues of Mass 202 PAHs

Table 10a

N-alkanes in Liard River sediments

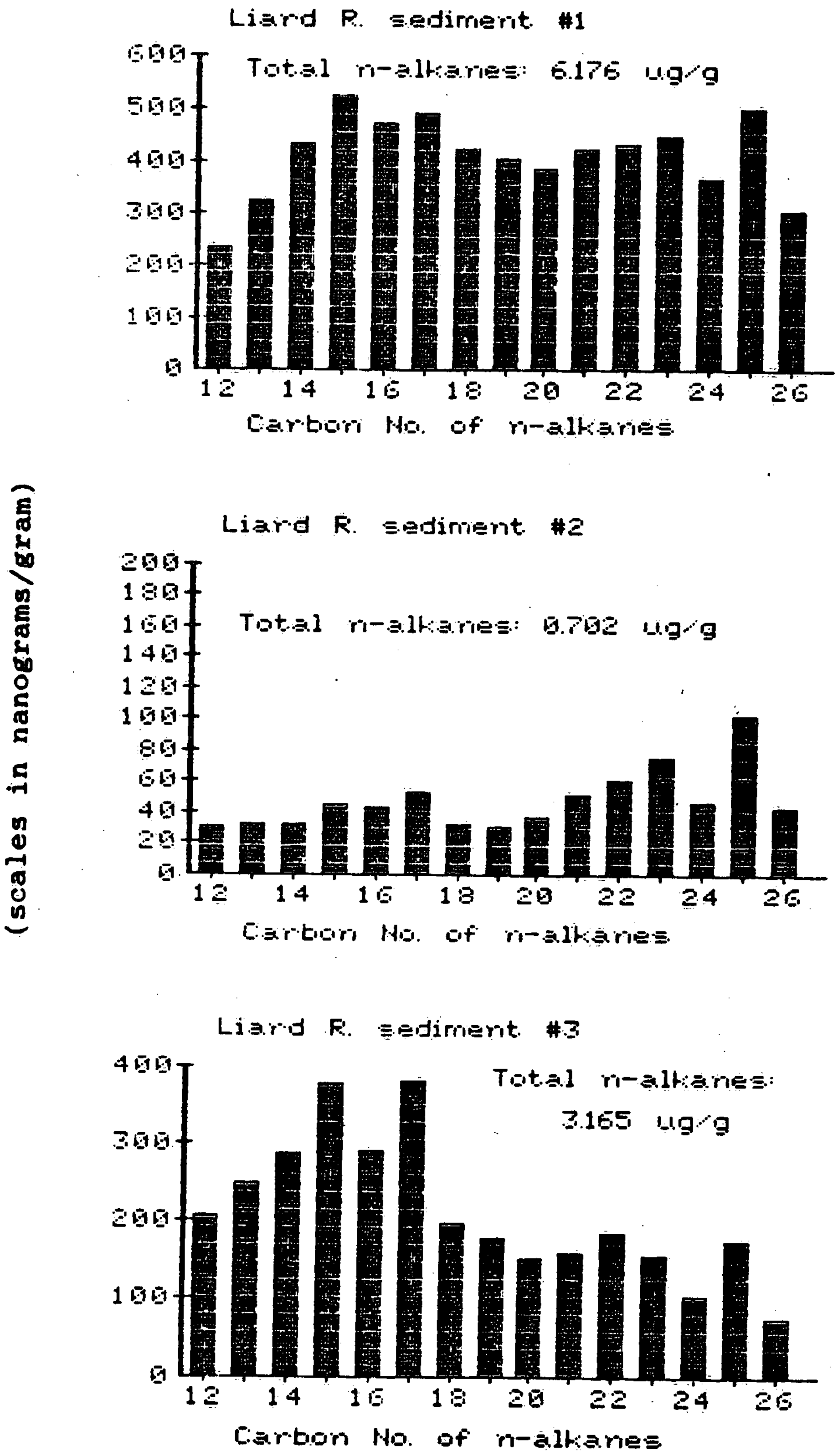


Table 10b

N-alkanes in Liard River sediments

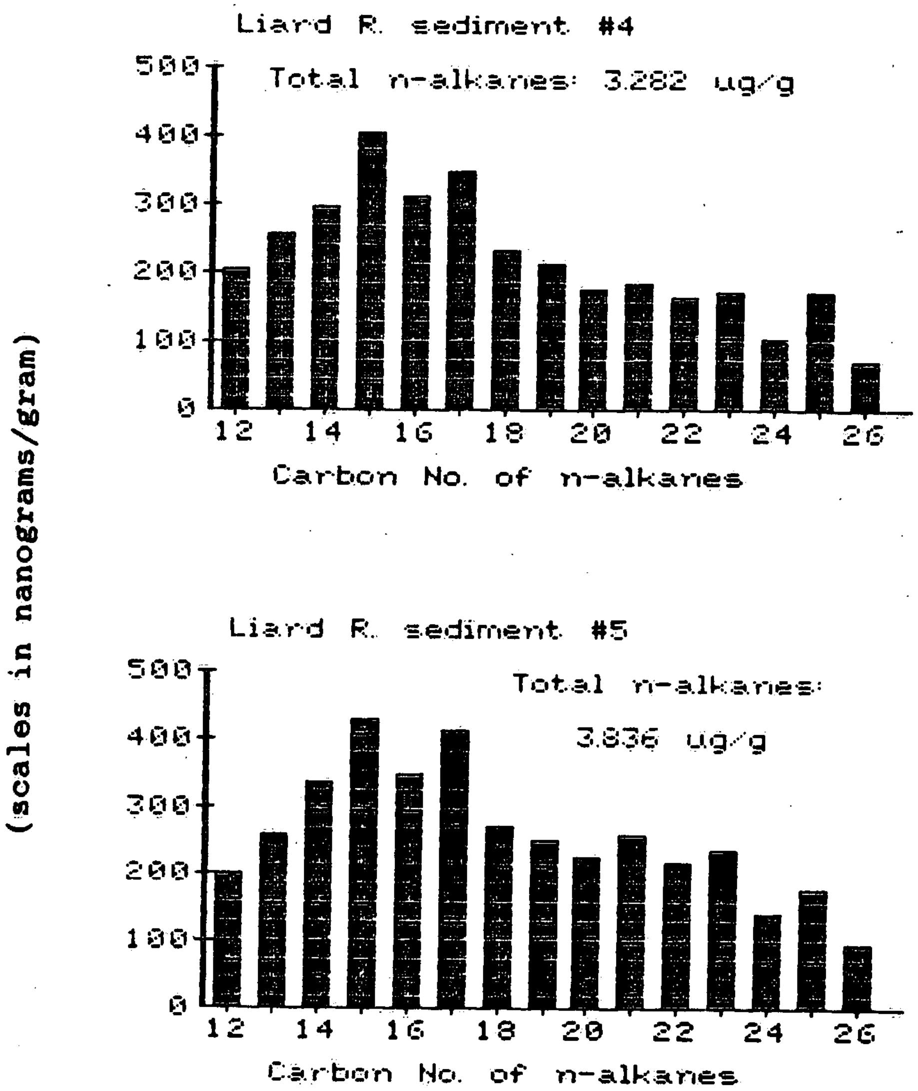
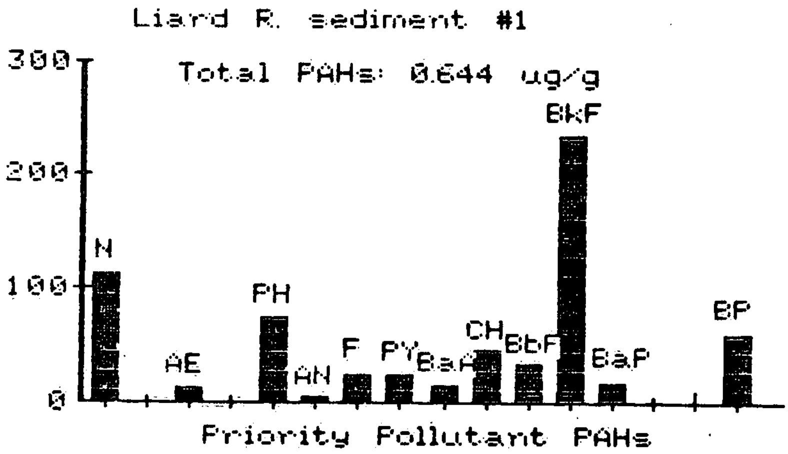
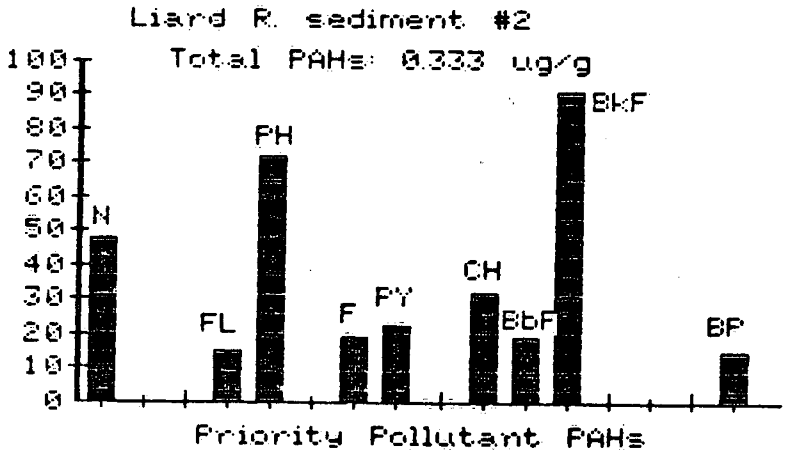


Table 11a

PAHs in Liard River sediments



(scales in nanograms/gram)



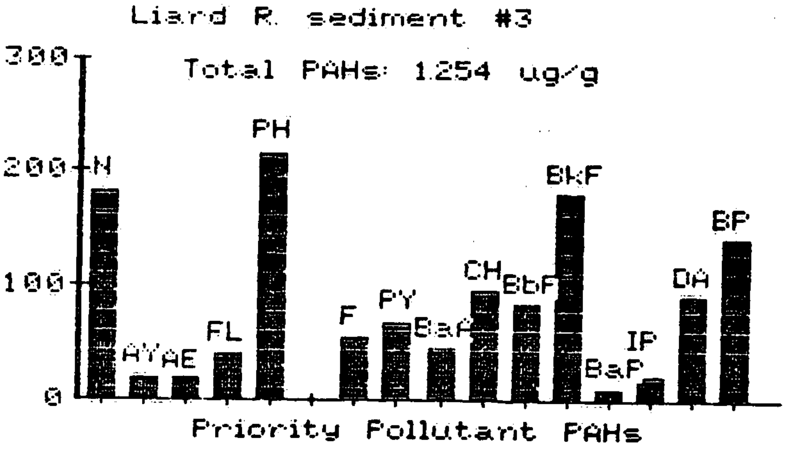


Table 11b

PAHs in Liard River sediments

(scales in nanograms/gram)