UNDER-ICE HYDROCARBONS IN THE MACKENZIE RIVER

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MANAGEMENT PERSPECTIVE

Reports of impaired fish liver quality in the Mackenzie River led to several studies of river water quality to establish baseline concentrations of various pollutants, and to detect possible effects of the Norman Wells oil refinery, and of are petroleum seeps on water quality.

Our three-year study of polyaromatic hydrocarbons and normal alkanes in the river, under varied flow conditions, showed no detectable effects of the Norman Wells refinery, and marginal effects of the natural oil seeps on water quality

This study was financially supported by the Northern Oil and Gas Action Program (NOGAP) through IWD, Yellowknife.

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EXECUTIVE SUMMARY

Our three-year study of hydrocarbons in the Mackenzie River was part of a wider study of various pollutants, and on the possible effects of the Norman Wells oil refinery and of area oil seeps on water quality.

PAH and n-alkane concentrations were found to vary with seasons and flow conditions. The largest inputs appeared to be diffuse and were related to spring runoff. The results of the study showed no detectable effects of the Norman Wells refinery, and marginal effects of the natural oil seeps on water quality.

This study was financially supported by the Northern Oil and Gas Action Program (NOGAP) through IWD, Yellowknife.

LES HYDROCARBURES SOUS LA GLACE DU FLEUVE MACKENZIE

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RÉSUMÉ

Notre étude sur les hydrocarbures dans le fleuve MacKenzie, d'une durée de 3 ans, s'inscrivait dans le cadre d'un vaste programme de recherche portant sur différents polluants ainsi que sur les effets possibles sur la qualité de l'eau de la raffinerie de pétrole de Norman Wells ainsi que des suintements de pétrole observés localement.

Il est observé que la concentration en HAP et en alcanes normaux varie selon les saisons et le débit. Les principales sources semblent être diffuses et sont associées au ruissellement printanier. L'étude montre que la raffinerie de Norman Wells n'a pas d'effet détectable sur la qualité de l'eau et que les suintements naturels de pétrole n'ont que des effets marginaux.

Cette étude a été subventionnée en vertu du programme d'initiatives pétrolières et gazières dans le Nord.

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PERSPECTIVE-GESTION

Des rapports indiquant une altération de la qualité du foie des poissons du fleuve MacKenzie ont conduit à la tenue de plusieurs études portant sur la qualité de l'eau afin que l'on puisse établir des concentrations de référence en différents polluants et afin de détecter les effets sur la qualité de l'eau de la raffinerie de pétrole de Norman Wells ainsi que des suintements de pétrole.

Notre étude, d'une durée de trois ans, sur les hydrocarbures polyaromatiques et les alcanes normaux du fleuve et selon différents débits, n'a pas permis de mettre en évidence des effets détectables que la raffinerie de Norman Wells aurait pu avoir sur la qualité de l'eau et a permis de montré des effets marginaux des suintements naturels de pétrole.

Cette étude a été subventionnée en vertu du programme d'initiatives pétrolières et gazières dans le Nord.

RÉSUMÉ

Les dosages effectués sur des échantillons d'eau prélevés dans le fleuve MacKenzie sous une couverture de glace, en mars 1988, ont révélé la présence de certains hydrocarbures polyaromatiques (HAP) et d'alcanes normaux en quantité mesurable. À l'instar d'études antérieures, c'est à la station d'échantillonnage la plus rapprochée du Grand Lac des Esclaves qu'ont été observées les concentrations les plus élevées de ces deux groupes de composés. Le naphtalène était la substance prédominante dans le groupe des composés polyaromatiques et il y avait seulement quelques-uns des 16 HAP jugés prioritaires qui pouvaient être observés en concentrations mesurables.

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ABSTRACT

Analyses of water samples from the ice-covered Mackenzie River, collected in March, 1988, showed that some polyaromatic hydrocarbons (PAHs) and normal alkanes were present in measurable quantities. As in earlier studies, the sampling site closest to Great Slave Lake yielded highest concentrations of both compound groups. Naphthalene was found as the predominant polyaromatic compound, and only a few of the 16 priority pollutant PAHs were present in quantifiable concentrations.

INTRODUCTION

This study of Mackenzie River water quality was initiated in 1985 in response to reports of fish tainting and impaired fish (burbot) liver quality from Mackenzie River communities. The specific aim of this study was to establish the "baseline" concentrations of some hydrocarbons, notably polyaromatics (PAHs) and normal alkanes in river water, and to investigate any measurable contributions by a small petroleum refinery in Norman Wells, or by natural oil seeps in the same area. Of the two compound classes, PAHs are known as fairly widespread pollutants with carcinogenic properties. The normal alkanes, or straight-chain paraffins, were conveniently available for analysis in the PAH matrix, and were expected to provide added clues to possible biological or anthropogenic sources of these hydrocarbons.

The sensitivity of this baseline study of river water quality was significantly enhanced by the use of a continuous-flow centrifuge (Sedisamp System-II) for the collection of suspended sediments for analysis.

Analyses of Mackenzie River water and suspended sediment in the fall of 1985 and the spring of 1986 showed important seasonal variations in PAH and normal alkane concentrations (1,2). The data suggested that a diffuse input of PAHs from the whole drainage area, especially high during the spring high flow, was probably greater than the hydrocarbon inputs from natural petroleum seeps in the river.

A third round of sampling of all river sites was made during the week of March 1 - 6, 1988, to investigate under-ice conditions. This completed the study of the various flow regimes and also to investigated the possible entrapment, under the river ice, of any oil from natural seeps. This report summarizes the results of analyses for PAHs and normal alkanes from the

March study.

EXPERIMENTAL METHODS

Sample collection

The location of the sampling sites is shown in Table 1. Unlike in the open water surveys, the water was not clarified by continuous-flow centrifugation. Two 20-L sample cans were filled at each site using an electric pump through a hole in the ice. Some of the water was used for the measurement of pH, conductivity, turbidity, and for seston filtration. The turbidity values are included in Table 1, and are shown in Fig. 1. For the hydrocarbon analyses, 36 L water was filtered through a GF-C glass fibre filter (2 micron pore size). This filtered water was then passed through an XAD-2 resin column under nitrogen pressure. The resin columns were refrigerated for storage and during transportation to Burlington.

In the laboratory, the resin was removed from the columns (stainless-steel tubes) and was Sohxlet extracted with a 1:1 acetone-hexane mix. After preconcentration, the extract was extracted three times with 0.1 M K_2CO_3. The organic phase, containing the base/neutral organics, was concentrated to 1 mL. The analyses were made on a Hewlett-Packard GC/MS system with the following operating conditions:

GC: Hewlett-Packard Model 5890
30 m fused silica capillary column, DB-5
Splitless injection
Inj. temp. 250°C - detector temp. 280°C
Program: 50°C to 140°C at 10°C/min - 2°C/min to 280°C - held at 280°C for 10 min

MS: Hewlett-Packard Series 5970 mass detector
Electron ionization, 70 eV
Select ion monitoring (SIM) mode

Normal alkanes (C_{12} to C_{26}) and 16 priority pollutant PAHs, listed in Table 2, were identified by retention times and by the presence of qualifying ions (m/e 57 and 71 for the alkanes, and the M, and M+1 ions for the PAHs).

RESULTS AND DISCUSSION

Water turbidities were found to be fairly low and uniform along the whole length of the river, consistent with conditions of zero runoff and low under-ice flow (Fig. 1).

The concentrations of PAHs and n-alkanes along the river are given in Table 3 and Figure 2. The PAH concentration was highest at the Fort Simpson station, i.e. in the water coming from Great Slave Lake. As the water and suspended sediment samples of this location had shown some special characteristics in the 1985 and 1986 studies as well, the water quality of Great Slave Lake, and its contribution to that of the Mackenzie, may deserve some attention. PAH levels were much lower in the Liard River, and remained low at all other stations in the Mackenzie. It is noteworthy that the Norman Wells area seeps did not appear to contribute to these background concentrations.

As shown by the statistics of Table 4, only a limited number of the 16 priority pollutant PAH list was detected in the majority of the samples. The PAH profiles are illustrated in Fig. 3a and 3b. The Hardie Island PAH pattern shown was representative of the PAH profiles of all sites except those at Fort Simpson and in the Liard River. While the Fort Simpson (Great Slave Lake) and Liard River samples contained a few extra compounds, naphthalene and phenanthrene were the dominant PAHs found in all of the samples. Although lower detection limits, such as obtainable by the extraction of much larger water volumes, or by centrifuging of suspended sediments, may allow the detection of additional PAHs, the relative concentrations would not be altered.

The possible origin of the PAHs is difficult to determine. Methyl naphthalenes were the only methyl homologs detected, at concentrations about two orders of magnitude lower than naphthalene. Their virtual absence normally precludes a petroleum origin. Combustion-derived PAHs, on the other hand, are low in methyl homologs, but are usually dominated by compounds in the 178-252 molecular-weight range (e.g. phenanthrene, fluoranthene and pyrene). The composition found here may be the result of the partitioning of the PAH compounds between the water phase and the suspended sediments, controlled by water solubility.

The n-alkane concentrations (Table 3 and Fig. 2) also start out high in the waters from Great Slave Lake, but show more high values in the middle range of the river (above and below Norman Wells). The alkane profiles, shown in Figures 4a and 4b, do not exhibit the C15 and C17 predominance, indicative of biogenic alkanes, that were seen in the 1985 and 1986 studies, especially in Fort Simpson samples (below Great Slave Lake). Since the source of these alkanes was presumably phytoplankton, this scene is probably normal for the season. The profiles of samples #4 and #7, coincident with somewhat higher concentrations, may indicate the presence of a narrow-cut petroleum product such as a fuel oil (heating or Diesel).

ACKNOWLEDGEMENTS

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Table 1

Mackenzie River sampling sites, 1988

Site No.	Location	km from Great Slave Lake	Date	Turbidity N.T.U.
1	Fort Simpson	329	March 1	74
2	Liard River	332	March 1	12
3	Wrigley	577	March 3	51
4	Halfway Island	848	March 3	27
5	Norman Wells[1]	900	Not sampled	
6	Norman Wells[2]	900	Not sampled	
7	Hardie Island	1044	March 4	48
8	Fort Good Hope	1094	March 4	51
9	Arctic Red River	1444	March 6	50
10	Inuvik	1587	March 5	48

(1) - upstream of refinery
(2) - downstream

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	278	Dibenzo(a,h)anthracene
16	BP	276	Benzo(ghi)perylene

Table 3

Alkanes and PAHs in Mackenzie River water

March, 1988

Site No.	N-alkanes[1]	PAHs[2]
	nanograms / L	
1	429	546
2 (Liard)	196	26.1
3	173	40.0
4	930	10.7
7	527	34.8
8	319	42.9
9	173	43.7
10	219	34.6

1 - sum of C12 to C26 n-alkanes
2 - sum of 16 priority pollutant PAHs

Table 4

Presence of measurable (+) and trace (T)
amounts of PAHs
in Mackenzie River water - March, 1988

Site	M128	M152	M166	M178	M202	M228	M252	M276/278
1	+	+	+	+	+	+	+	
2 (Liard)	+			+	+			T
3	+			+				
4	+			+				
7	+			+				T
8	+			+				T
9	+			+				
10	+			+				

Figure 1

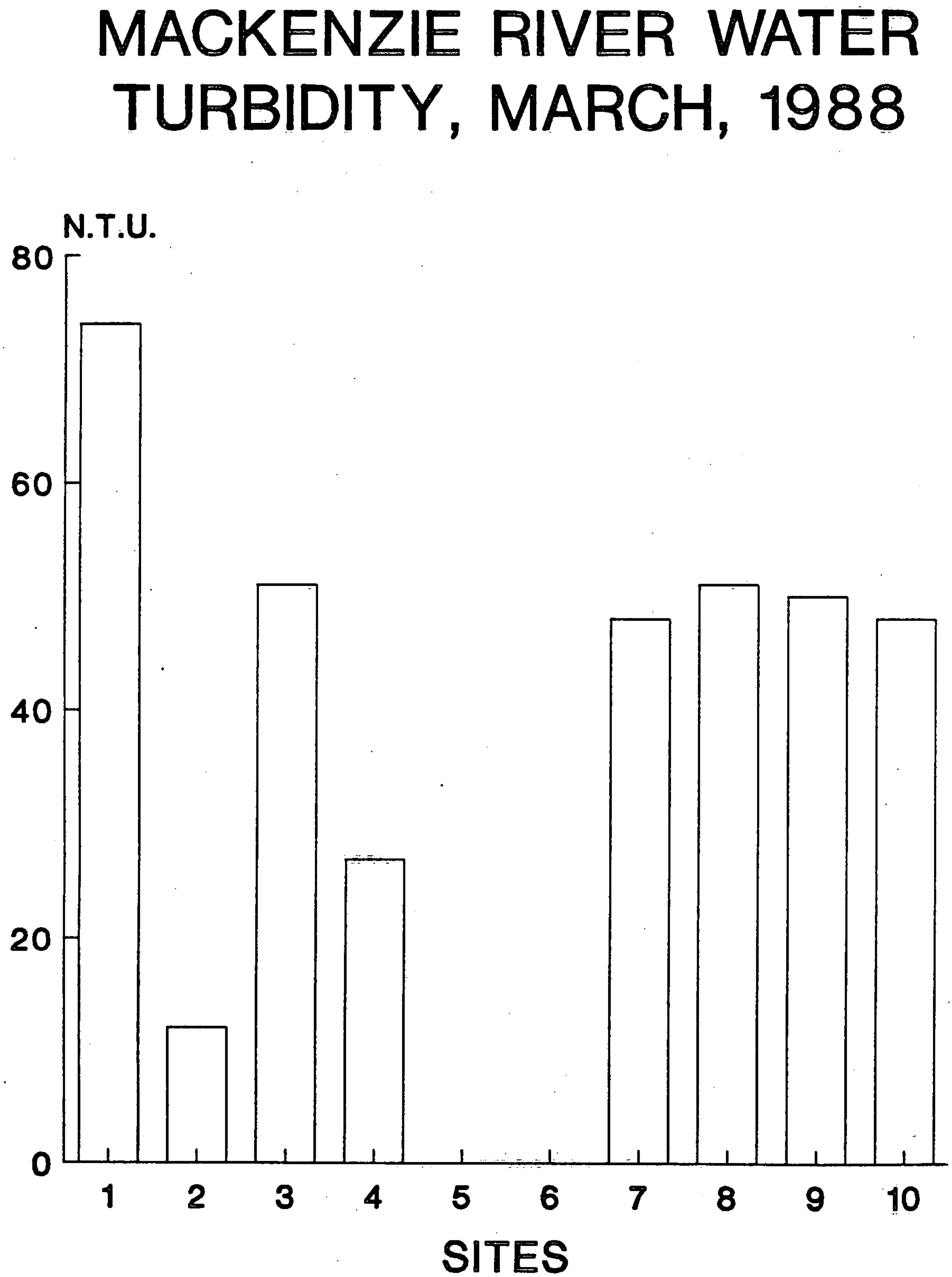
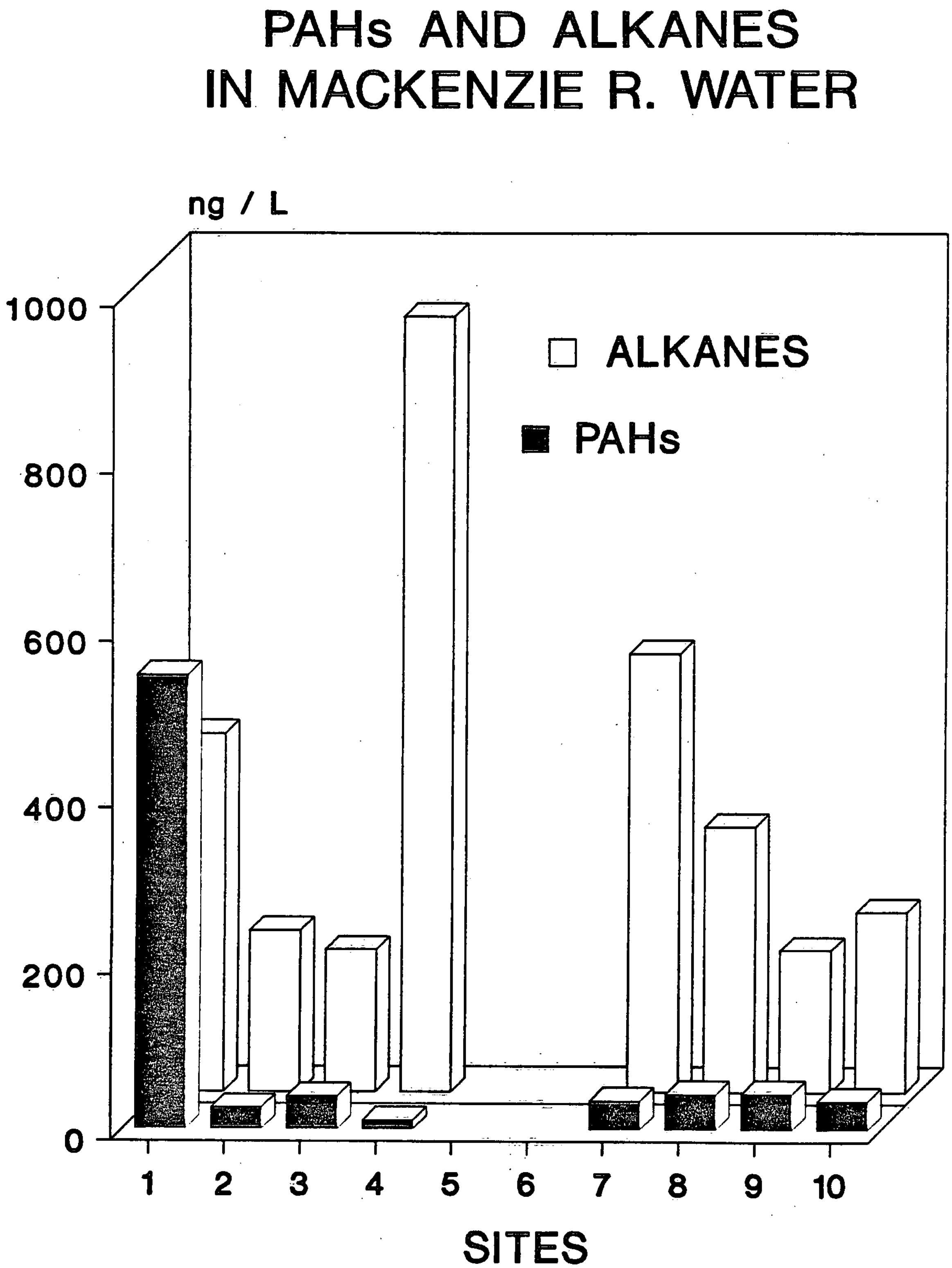

MACKENZIE RIVER WATER
TURBIDITY, MARCH, 1988
N.T.U.
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
SITES

Figure 2



PAHs AND ALKANES
IN MACKENZIE R. WATER
ng / L
1000
800
600
400
200
0
ALKANES
PAHs
1
2
3
4
5
6
7
8
9
10
SITES

Figure 3b

PAH profiles in Mackenzie River water
(note concentration scales)

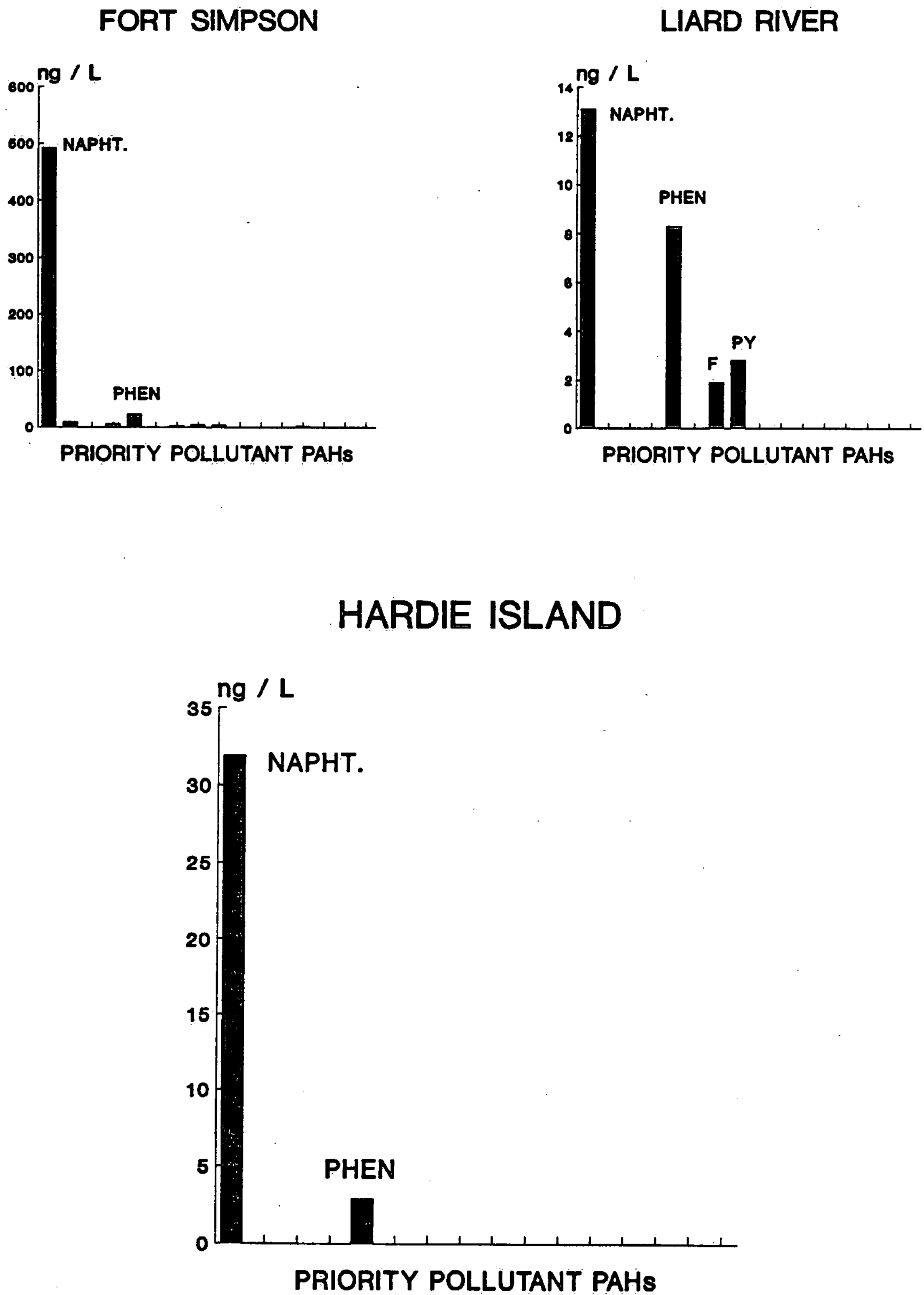
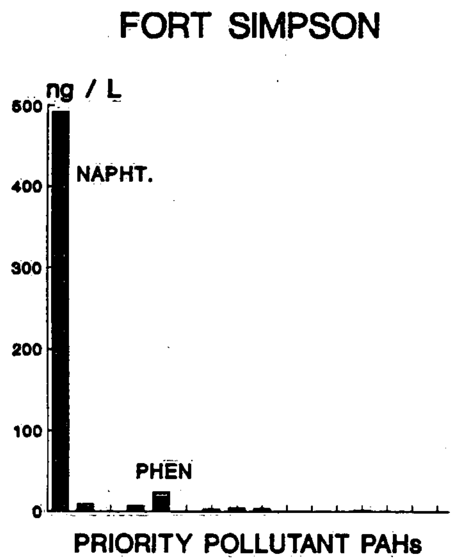
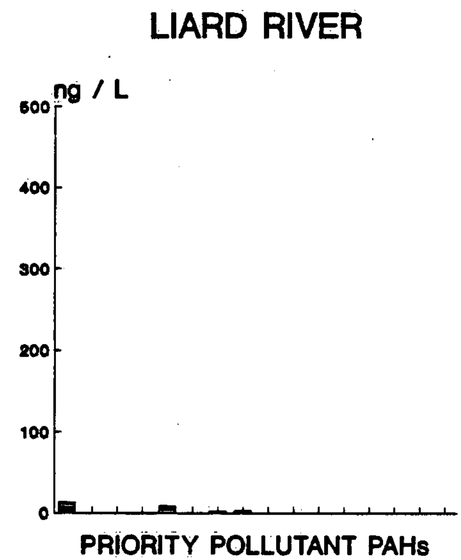


Figure 3a

PAH profiles in Mackenzie River water
(uniform concentration scale)





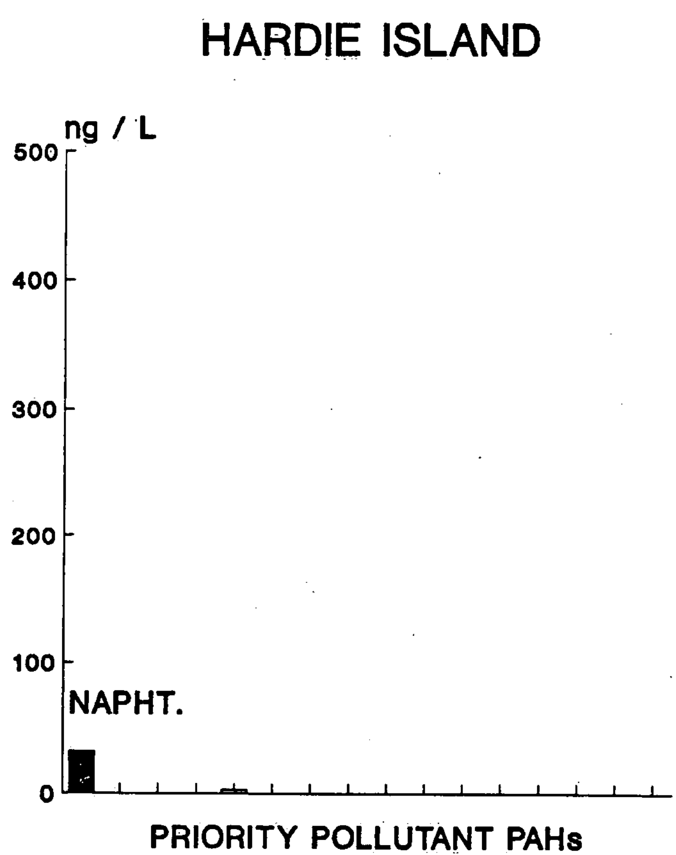


Figure 4a

N-alkane profiles in Mackenzie River water

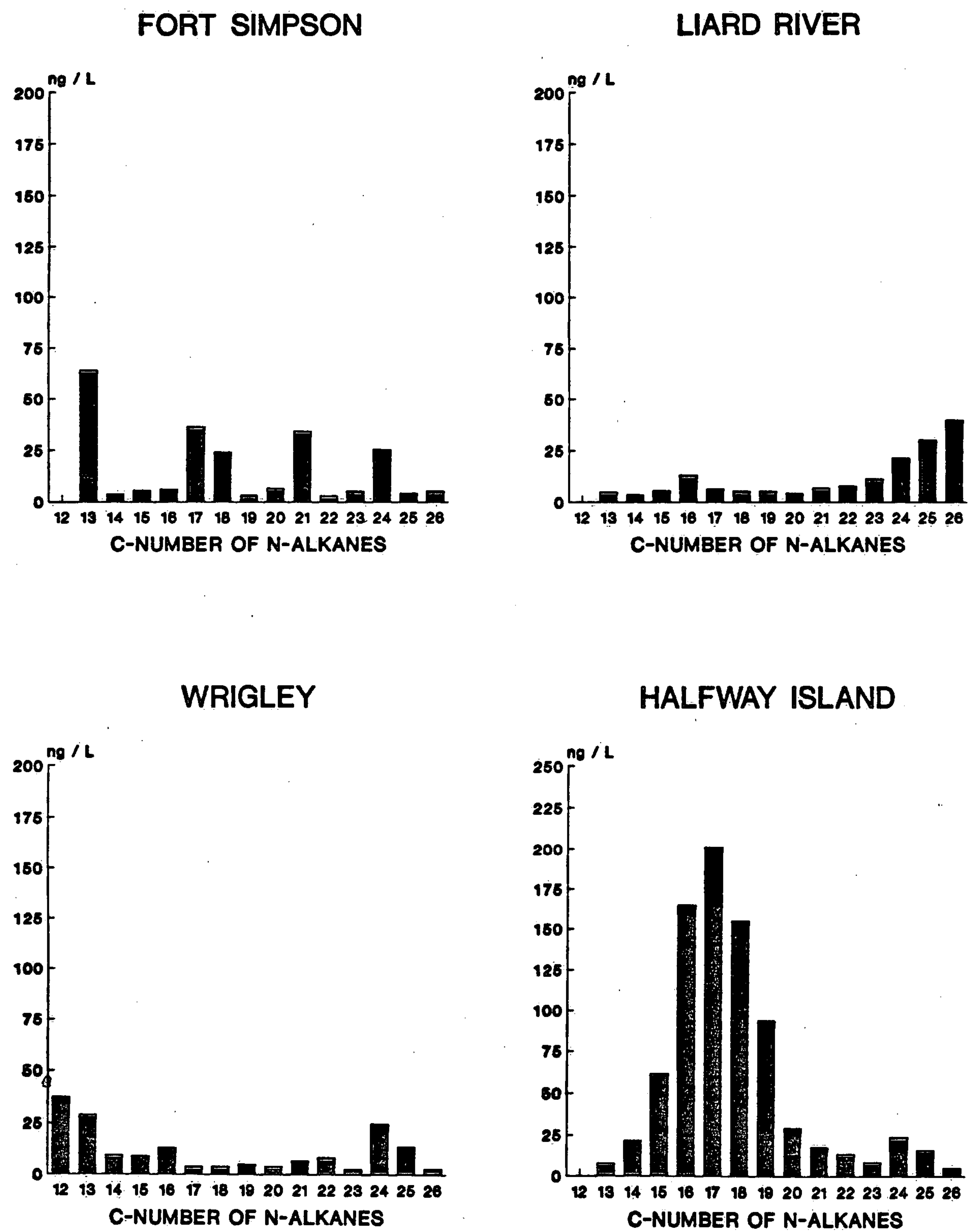


Figure 4b

N-alkane profiles in Mackenzie River water