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**HYDROCARBONS IN MACKENZIE RIVER
SUSPENDED SEDIMENTS**

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MANAGEMENT PERSPECTIVE

This survey of hydrocarbons in Mackenzie River suspended sediments, funded by the Northern Oil and Gas Action Program (NOGAP), was part of a broader effort to find the possible causes of fish tainting reported by local fisheries.

Increased concentrations of normal alkanes and polyaromatic hydrocarbons were detected in the Liard River entering the Mackenzie, and in the Mackenzie River at Norman Wells. These were probably related to natural gas wells in the Liard basin, and to oil seeps around Norman Wells. At the latter location, any effect on water quality may be produced by the natural seeps, rather than the local refinery.

The surveys are continuing in 1986 to establish the validity of the data under varied conditions (flow, turbidity, season).

La présente étude des hydrocarbures dans les sédiments en suspension du fleuve Mackenzie, financée par le Programme d'initiatives pétrolières

HYDROCARBURES DANS LES SEDIMENTS EN SUSPENSION DU FLEUVE MACKENZIE

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EN BREF

La présente étude des hydrocarbures dans les sédiments en suspension du fleuve Mackenzie, financée par le Programme d'initiatives pétrolières et gazières dans le nord, fait partie d'un effort plus global visant à trouver les causes possibles de la décoloration des poissons notée par les pêcheries locales.

Des concentrations croissantes de n-alcanes et d'hydrocarbures polyaromatiques ont été décelées dans la rivière Liard qui se jette dans le fleuve Mackenzie, ainsi que dans le fleuve Mackenzie à Norman Wells. Ces concentrations étaient probablement en rapport avec les puits des gaz naturels dans le bassin Liard, ainsi qu'avec les suintements d'huile autour de Norman Wells. A cet endroit, tout effet sur la qualité de l'eau peut être dû à des suintements naturels plutôt qu'à des déversements de la raffinerie locale.

Les études ont été poursuivies en 1986 afin d'établir la validité des données recueillies dans différentes conditions (écoulement, turbidité, saison).

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EXECUTIVE SUMMARY

Problems of fish tainting and of impaired fish liver quality have recently been reported by Mackenzie River fisheries. This survey, part of a broader effort in the area, concentrated on the presence of normal alkanes and polynuclear aromatic hydrocarbons (PAHs) in suspended sediments in a 1115 km stretch of the river.

Alkane concentrations were found to vary along the river in a discontinuous fashion, indicating a series of inputs and removal pathways. The alkane profiles in the samples showed both a biogenic source (e.g. algae) and some petroleum-derived compounds along the river. The aromatic hydrocarbons (PAHs) all came from a petroleum source and were apparently related to gas wells in the Liard River basin, and to natural oil seeps around Norman Wells.

Any effect of the Norman Wells refinery operations on the river water quality was indistinguishable from that of the oil seeps; our preliminary results indicate the latter as the major source of aromatic hydrocarbons in the river.

The survey is to be repeated in 1986 under different conditions of water flow, water turbidity, and time of the year.

LES HYDROCARBURES DANS LES SEDIMENTS EN SUSPENSION DU FLEUVE MACKENZIE

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SOMMAIRE

Récemment, les pêcheries du fleuve Mackenzie ont signalé des problèmes de décoloration des poissons, ainsi que de qualité amoindrie des foies de poissons. Cette étude, qui fait partie d'un effort plus vaste dans la région, a porté sur la présence de n-alcanes et d'hydrocarbures aromatiques polynucléaires (PAH) dans les sédiments en suspension prélevés sur une longueur de 1115 km de ce fleuve.

On a constaté que les concentrations d'alcanes variaient le long du fleuve d'une façon très discontinue, ce qui indique une série de voies d'apport et d'élimination. Les profils des alcanes dans les échantillons indiquaient des sources biologiques (p. ex. les algues) et la présence de certains dérivés du pétrole dans le fleuve. Les hydrocarbures aromatiques (PAH) provenaient tous d'une source pétrolière et étaient apparemment en rapport avec les puits de gaz du bassin de la rivière Liard, ainsi qu'avec les suintements naturels d'hydrocarbures autour de Norman Wells.

Il était impossible de distinguer tout effet des opérations de la raffinerie de Norman Wells sur la qualité de l'eau de la rivière de ceux des suintements naturels d'hydrocarbures; les résultats préliminaires indiquent que ces derniers constituent la principale source d'hydrocarbures aromatiques dans le fleuve.

RESUME

Une étude des n-alcanes et des hydrocarbures polycycliques aromatiques (PAH) dans le fleuve Mackenzie a montré que les puits de gaz du bassin de la rivière Liard et les suintements naturels d'hydrocarbures dans la région de Norman Wells du fleuve Mackenzie modifiaient de façon significative la concentration et la composition des hydrocarbures. Les profils des n-alcanes suggèrent la présence d'hydrocarbures d'origine biologique et dérivés du pétrole. La grande variété des méthyl-PAH indique que ces dérivés proviennent du pétrole plutôt que de la combustion à haute température. La concentration des hydrocarbures varie de façon discontinue le long de la rivière, ce qui suggère une série d'apports et de mécanismes d'élimination. Les résultats ont également montré l'utilité de l'échantillonnage et de l'analyse des sédiments en suspension dans des études de chimie des eaux des fleuves.

ABSTRACT

A survey of normal alkanes and polyaromatic hydrocarbons (PAHs) in the Mackenzie River showed that gas wells in the Liard River basin and natural oil seeps in the Norman Wells area of the Mackenzie River have significantly affected the concentration and composition of hydrocarbons. Normal alkane profiles suggested the presence of both biogenic and petroleum-derived hydrocarbons. The variety of methyl-PAHs indicated petroleum, rather than high-temperature combustion, as the probable source of the PAHs. The hydrocarbon concentrations varied in a discontinuous fashion along the river, suggesting a series of inputs and sinks. The results have also showed the usefulness of sampling and analyzing suspended sediments in studies of the water chemistry of rivers.

INTRODUCTION

Problems of fish tainting and of impaired fish liver quality have recently been reported by subsistence fisheries on the lower reaches of the Mackenzie River, and some surveys have been initiated on the possible effects of the Norman Wells refinery operation and of natural oil seeps on water quality in the river (1-5).

Polynuclear aromatic hydrocarbons (PAHs) have been reported to occur in airborne particulates, in soils, in freshwater and marine sediments in diverse geographic areas. Although their concentrations are generally lower than those of other organic classes, such as alkanes, they are regarded as significant environmental contaminants due to their carcinogenic or mutagenic potential (6-10). The main source of PAHs is the combustion of various fuels, such as coal in power plants, coal, oil, gas, or wood in space heating, coal coking, gasoline and diesel fuels. The PAHs produced by these processes are generally found on airborne particulate matter, and may be distributed widely before deposition on land or water surface in precipitation. River systems may concentrate the sediment-adsorbed PAHs in their drainage basins, and may produce some accumulations off river mouths in lakes and oceans. Petroleum is another potential source of PAHs, which may enter freshwater or marine environments from oil spills, refinery wastes, and from natural oil seeps.

This study of alkanes and PAHs in the Mackenzie River was part of a broader effort to establish background hydrocarbon levels and the possible impact of oil seeps and of the Norman Wells refinery on the water quality of the river.

EXPERIMENTAL METHODS

Survey area

The Mackenzie River drains an area of about 1.5×10^6 km² into the Beaufort Sea (4). It is characterized by large variations between summer and winter flows, and a high silt load. A note should be taken of the existence of gas fields along Liard River, of petroleum production and a small oil refinery at Norman Wells, and of natural oil seeps in the river in the Norman Wells area. The map in Figure 1 shows the location of the sampling sites over a 1115 km (696 mile) stretch of the river.

Sediment sampling program

The sampling strategy was that developed for the North Saskatchewan River. In that and other studies, riverine chemistry was found to depend on the discharge regime (high and low flow). In addition to anthropogenic influences, chemical regime responds to differences in water volume, amount of sediment in transit, differences in sediment provenance, in seasonal biomass, and to length of riverine transport. Organic pollutants and natural organic compounds both tend to be associated with suspended sediments in aquatic systems. The sampling program, therefore, focused both on water and on suspended sediments. The data reported here represent summer low flow conditions of 1985.

The Mackenzie River was sampled at six sites between Fort Simpson and Arctic Red River, plus at one site in the Liard River just before its confluence with the Mackenzie (Figure 1). Site selection reflects: background (Site #1); influence of the Liard River (Site #2); seeps of hydrocarbons in the reach below Fort Norman; oil extraction and refining activities at Norman Wells; and complaints of fish stock degradation at Fort Good Hope and Arctic Red River. The distance between the sites reflects a compromise between prior experience in determining downstream chemical changes, and field logistics for a study in such a remote area. The sampling program was carried out during a cruise of the launch "HMS Brock" which was dedicated to this program. Sites #1 and #2 were sampled on August 9 and 10, then all sites were sampled over the period August 25 (#1) to Sept. 12, 1985 (#8). The sites were sampled sequentially downstream to obtain an approximation of synoptic conditions.

Each site was sampled in the middle of the shipping channel; turbidity measurements indicated that the sites were well mixed across the section. Raw river water was pumped from a depth of approximately 0.3 m into a portable Sedisamp System-II continuous-flow centrifuge system at a rate of 4 L/min. The depth reflects prior experience in the vertical mixing characteristics of the silt-clay fraction of the suspended sediment load. Total centrifuging time was determined by river turbidity and varied between 2.5 and 9.0 hours. Each sample

represents a time-integrated material. The sediment recovered in the centrifuge was placed in acetone-rinsed aluminum foil and stored on ice during the cruise, then frozen and air-freighted to Burlington for analysis. A second centrifuge system was used to collect material for other physico-chemical determinations.

The samples (Table 1) were extracted and fractionated as shown in Figure 2. The base-neutral extract was cut into four fractions (/1 to /4), the first of which contained most of the alkanes and some of the PAHs. Fraction /2 contained more PAHs and some polar compounds. Fractions /3 and /4 contained few components that could be seen by gas chromatography. Fraction /5 was prepared by re-extraction of the dried and weighed sediments with dichloromethane (DCM) to test for any incompleteness of the acetone-hexane extraction.

Fractions /1 and /2 were analyzed by GC/FID for quantitation and by GC/MS for identification. Identification of n-alkanes and PAHs was based on their mass spectra and on retention times, whenever the latter were available.

Water samples

From the continuous centrifuge outflow 18 L aliquots were placed in stainless steel pressurized canisters and passed through stainless steel columns containing XAD-2 resin previously cleaned by acetone-hexane Soxhlet extraction. The tubes were then capped and refrigerated for storage and transportation. At the time of the analyses, the resin was removed from the tubes and Soxhlet extracted with acetone-hexane. The extract was then preconcentrated, and extracted three times with 0.1 M K_2CO_3 . The organic phase, containing the base/neutral organics was concentrated to 2 mL and used in the GC and GC/MS analyses. The aqueous phase was acidified to pH<2 and extracted with DCM to yield the acid fraction of the organics.

The equipment and operating conditions for the analyses were:

GC-Quantitative:

Perkin-Elmer Sigma 2000
Splitless injection
30 m fused silica capillary column (DB-5)
Inj. temp. 280°C - detector temp. 280°C
Program: 70°C for 2 min - 4°C/min to 280°C - 280°C
for 15 min

GC/MS:

Carlo-Erba system
On-column injection
30 m fused silica capillary column (DB-5)
Program: 70°C for 2 min - 5°C/min to 280°C - 280°C
for 15 min

MS:

Delsi-Nermag system
Electron ionization (70 eV)

RESULTS AND DISCUSSION

Suspended sediments

A) Alkanes and PAHs (/1 and /2 fractions):

Alkanes were the predominant organic compounds in the suspended sediment, and series of normal alkanes were well recognizable in all hexane fractions of the base-neutral extracts. All n-alkanes were independently identified by GC/MS, and their concentrations were determined by gas chromatography with FID, using individual response factors for each alkane. The concentrations, given in Table 2, ranged from undetectable to 2945 ng/g, with a detection limit of about 5 ng/g dry sediment.

The sums of n-alkane concentrations from C12 to C26 ranged from 0.141 to 3.759 ug/g sediment. The lowest values were found in the single bottom sediment sample (MS2c), the highest in the two samples collected just above the Liard River confluence (MS1a and MS1b). The suspended sediment from the Liard River contained much less alkanes. The downstream concentrations varied in a discontinuous fashion: dropping after the Liard confluence, increasing at Norman Wells, and dropping again in the lower reaches of the river (Fig. 3). This behaviour suggests a complex series of inputs (land runoff, tributaries, oil seeps) as well as removal mechanisms (degradation of organics, sedimentation of suspended sediments) in the river.

The n-alkanes were, on the average, dominated by the C15 and C17 members of the series, as shown in Figure 4. This strongly suggests a biogenic origin of these hydrocarbons. The preponderance of the C17 alkane is especially striking in the samples above Liard, where the freshly centrifuged sediments exhibited a strong fishy smell (11). The samples collected at Norman Wells showed, in addition to high C15 and C17 homologs, increased concentrations of the C22 to C26 alkanes. The appearance of these homologs may be a result of natural oil seeps in the area. The reconstructed ion chromatograms in Figure 5 show the two types of alkane distribution seen in the suspended sediment samples. The unimodal type (A) with the large C15 and C17 peaks was the more common one, while the bimodal distribution (B) was found only at Wrigley and just below the Norman Wells refinery, and may indicate mixtures of biogenic and petroleum hydrocarbons.

PAHs were present at readily detectable concentrations in

only two locations: in the Liard River just before its entering the Mackenzie, and in the Mackenzie River at Norman Wells, below the oil refinery. As shown in Figure 3, these occurrences were not related to the concentration of the organic matrix, or specifically to that of n-alkanes. The concentrations of individual PAHs were just below the FID limit of about 5 ng/g, and were estimated as about 1 ng/g dry sediment. The PAHs and other aromatics found at these two sites are listed in Table 3. The ion counts shown are normalized for 100 g dry sediment and may be used only to compare the relative amounts of given compound types between the samples.

The hexane fractions were then reduced in volume to about 100 μ L and were re-analyzed by GC/MS for PAHs that may be present in the samples at lower concentrations. The results, given in Table 4, show the occurrence of relatively low molecular weight PAHs in most of the samples. The presence of several methylated naphthalenes and phenanthrenes suggests a non-combustion source such as petroleum. The similarity of the compositions above and below the Norman Wells refinery indicates natural oil seeps as the likely source of these compounds. The tenfold concentration step needed to make many of these compounds detectable suggests that their concentrations were roughly one tenth of the 1 ng/g levels estimated for the three sites in Table 3, or about 0.1 ng/g.

In addition to alkanes and PAHs, some phthalate esters, substituted phenols and other oxygen compounds were detected but not identified in the /1 and /2 fractions.

B) Polar fractions:

Fractions /2 to /4 exhibited very few components detectable by GC/MS. Some oxygen compounds, primarily esters and acids were seen in most of the /2 fractions, but were not identified.

Water samples

The water extracts were all dominated by the presence of a large number of substituted benzenes, probable breakdown products of the XAD-2 resin, which were found in equal or greater numbers in the extracts of a "clean" resin sample. A single compound, benzothiazine, was absent in the blank, but was present in every one of the water extracts just above detection limits. This chemical is a breakdown product of rubber and is a common water pollutant.

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Table 1

Mackenzie River sites for suspended sediments

Site No.	Km from Great Slave Lake	Sampling Date(s)	Sample No.	Details
1	328.8	Aug. 10 Aug 25	MS1a MS1b	Fort Simpson, above Liard
2	332.0	Aug. 9 Aug. 26 Aug. 26	MS2a MS2b MS2c	Liard R. before Mackenzie (bottom sediment)
3	576.8	Aug. 28	MS3	Wrigley
4	848.0	Sep. 1	MS4	Halfway Island
5	900.8	Sep. 5	MS5	Above N.Wells refinery
6	(900)	Sep. 5	MS6	Below N.Wells refinery
7	1044.0	Sep. 8	MS7	Fort Good Hope
8	1444.0	Sep. 12	MS8	Arctic Red River

Table 2

N-alkanes in Mackenzie River suspended sediments
(nanograms/g dry sediment)

n C	MS1a	MS1b	MS2a	MS2b	MS2c	MS3	MS4	MS5	MS6	MS7	MS8
12			54	24	8	18	20			91	112
13			74	28	11	29	31			137	142
14			77	28	15	37	37		79	125	149
15	647	850	91	41	16	76	58	125	135	151	152
16	167	161	71	33	16	44	37	149	114	117	144
17	2945	1962	128	63	13	139	98	224	187	139	124
18		56	43	21	10	26	22	129	68	70	71
19		72	42	22	10	26	22	145	76	81	87
20		44	31	17	7	20	17	119		50	51
21		99	51	29	9	42	29	185	104	78	81
22			26	16	7	40	12	122	90	35	39
23		82	30	20	6	69	13	146	144	30	38
24		60	23		6	87		108	241	22	28
25		144	46	29	7	105	16	213	374	32	40
26		64	19			66		78	360		14
Total	3759	3594	806	371	141	824	412	1743	1972	1158	1272

Table 3

PAHs in Mackenzie River Suspended Sediments*

MS2a (Liard R., Aug.9):

methylnaphthalenes (2)	98,	163		
dimethylnaphthalenes (4)	26,	36,	54,	72

MS2b (Liard R., Aug.26):

naphthalene	291		
methylnaphthalenes (2)	240,	316	
dimethylnaphthalenes (2)	73,	124	
phenanthrene	248		
methylphenanthrene (anthr.)	57		
fluoranthene/pyrene	140		

MS6 (N.Wells, Sept.5):

benzene homologs (3)	361,	735,	1109
methylnaphthalenes (2)	310,	1161	
dimethylnaphthalenes (3)	155,	310,	581
phenanthrene	735		
M 252 PAHs (4)	155,	206,	942, 2000

- * The numbers are ion counts in thousands, normalized for 100 gram dry sediment weight. They may be used only to compare relative amounts of the same compound in the three sediments.

Table 4
PAHs Detected in Suspended Sediments

Compound	No. of isomers detected in...	...No. of samples (of max. 11)
naphthalene	(1)	10
2-methylnaphthalene	(1)	10
1-methylnaphthalene	(1)	9
dimethylnaphthalene	1	2
	2	5
	3	2
trimethylnaphthalene	1	1
acenaphthene	(1)	1
methyl-biphenyl	1	1
phenanthrene/anthracene	1	10
methylphenanthrene	1	2
	2	3
	3	1
dimethylphenanthrene	1	2
tetramethylphenanthrene	1	4
fluoranthene	(1)	6
methylfluoranthene	1	1

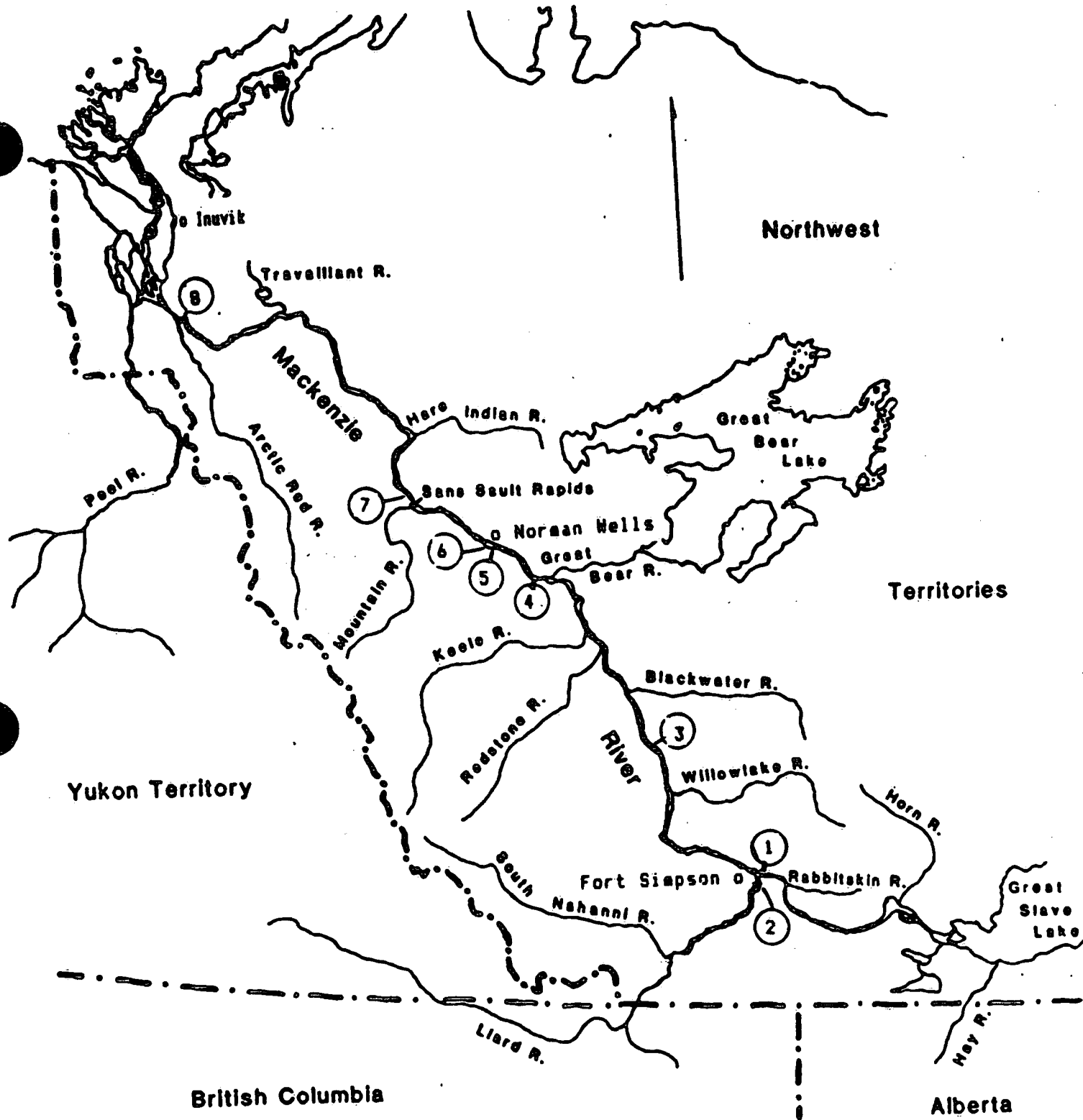
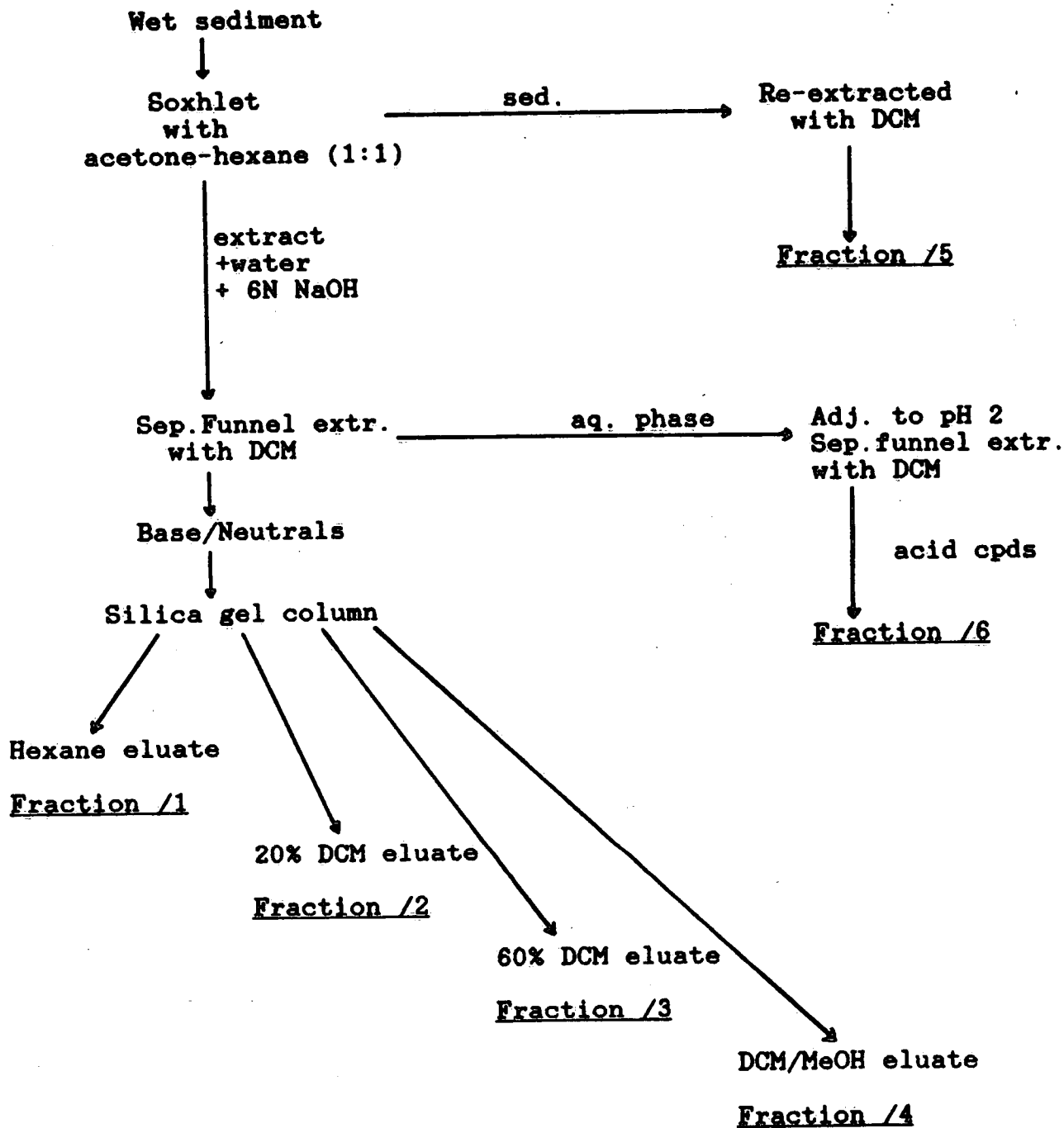


Figure 1

Mackenzie River sampling sites - 1985

Figure 2
Sediment Extraction Scheme



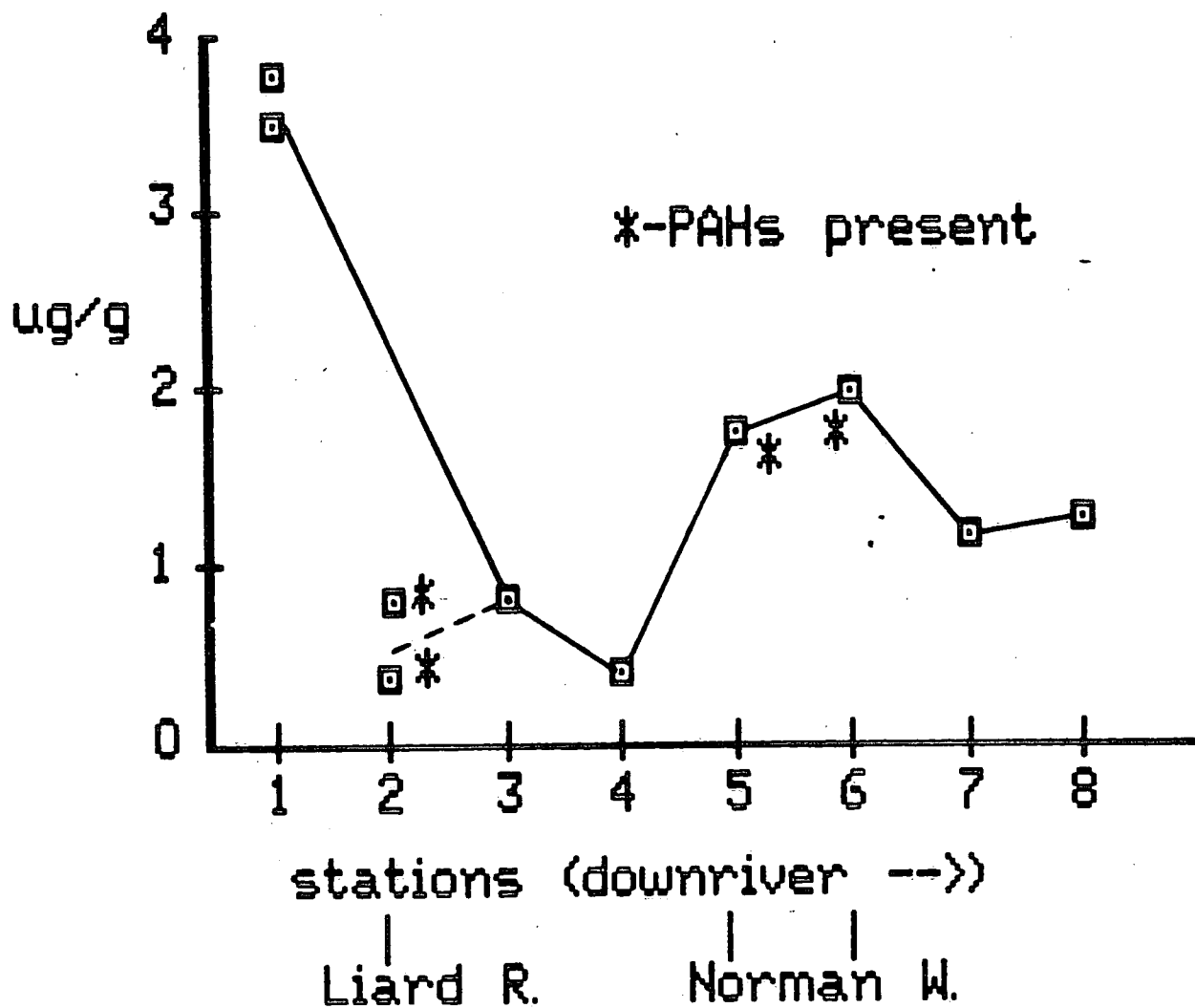


Figure 3
Normal alkanes in Mackenzie River suspended sediments

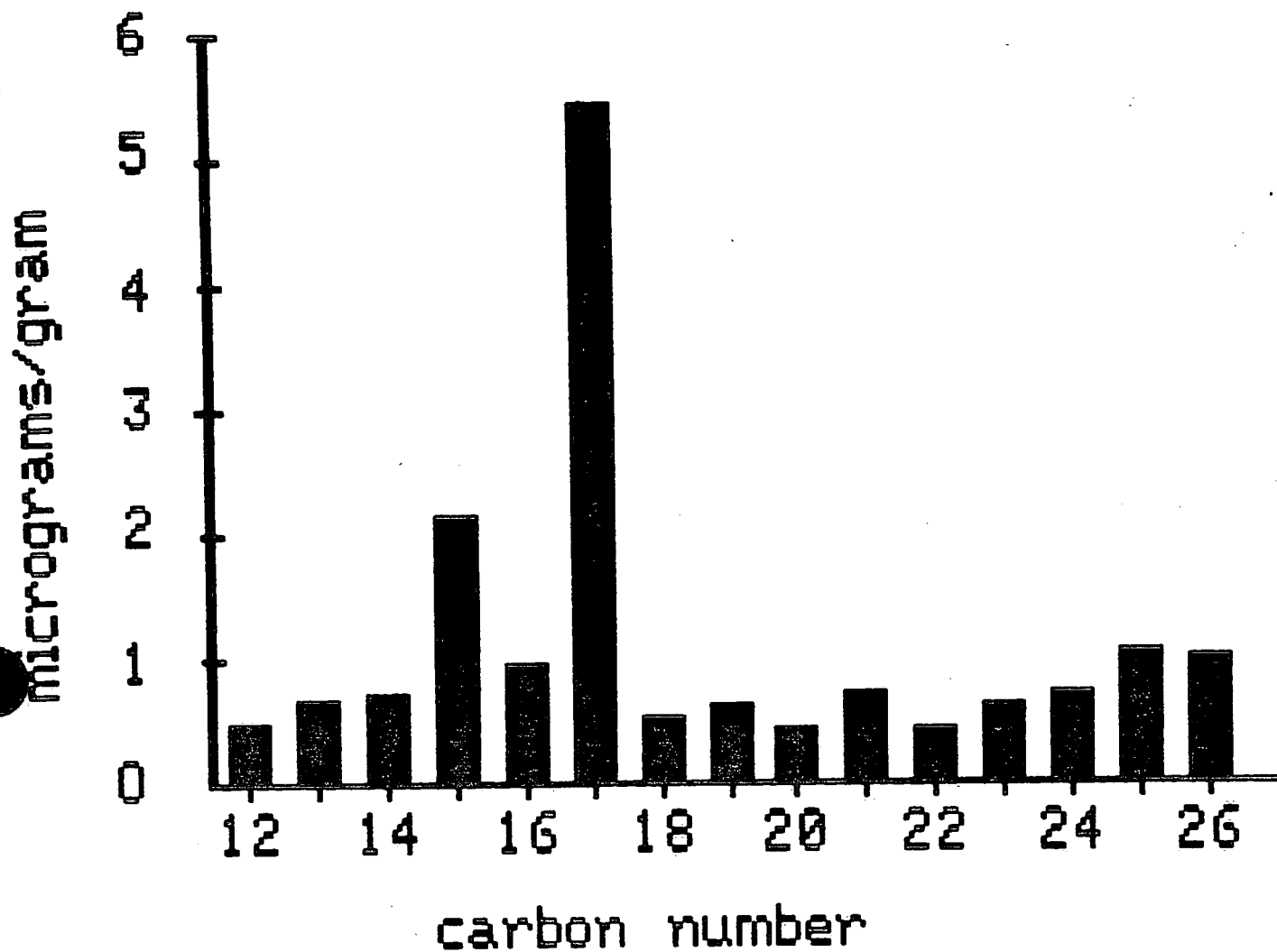


Figure 4
N-alkane profiles in Mackenzie River suspended sediments

Figure 5

Typical ion chromatograms of suspended sediment extracts

