FINAL REPORT ON HYDROCARBON PATHWAYS

IN THE MACKENZIE RIVER, NWT

by

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INTRODUCTION

Baseline assessment of water quality may reflect either (1) natural background chemistry, or (2) an operational baseline. In undisturbed environments the natural chemical background provides a measure against which subsequent chemical change may be assessed. Operational baseline is appropriate where, due to the anthropogenic activities, "natural" background has no practical meaning.

For major ions and most metals one can expect to find measurable levels in water and sediment samples arising from natural processes. In the general field of synthetic organic contaminants the natural background can be presumed to be zero. However, organic chemical investigations may include a variety of compounds, such as PAH's which, in addition to combustion from fuels may also be produced by natural processes such as fire.

The situation, especially for metals and organic compounds, is further complicated by atmospheric deposition of compounds. In remote areas, such as northern Canada deposition of heavy metals, pesticides

and other synthetic organic compounds is under active investigation. Metal enrichment, although evident in snowpack monitoring, is not usually noticeable in stream water or sediment samples due to natural background concentrations. However, even at trace levels, organic contaminants in aquatic biota or in water and sediments imply chemical enrichment from some combination of intra and extra basin sources. With limited exceptions, such as PHA's, organic contaminants are anthropogenic in origin.

Spatial and temporal changes commonly found in river data often make baseline assessment difficult. The chemistry of rivers is substantially influenced by hydrologic regime, especially for sediment-associated substances such as metals. In Canadian rivers, Ongley et al. (1981), Blachford and Ongley (1984) and Ongley et al., (in press) have found that river chemistry displays large seasonal differences reflecting presence (spring) or absence (summer) of erosion products supplied to the river during runoff events. Baseline must account, therefore, for seromolity. Our symoptic data for metal chemistry from prairie rivers illustrate systematic downstream changes caused by natural processes. Similar synoptic data for synthetic organic contaminants is not generally available, however, our work on the North Saskatchewan River (Ongley et al., in press) suggest an absence of systematic downstream trends. For data exhibiting downstream changes, therefore, baseline condition may be highly site dependent. In remote areas where data often reflect only one or two sites, baseline assessment for the purpose of defining temporal and spatial (i.e. downstream) states is particularly challenging.

The lower Mackenzie River (Figure 1), the largest northwards flowing river in North America, has received considerable attention in recent years due to oil and gas exploration in the Beaufort Sea of the Arctic Ocean. Although the Mackenzie Basin is still largely undeveloped, it drains agricultural lands of the northern prairies, lowlands of the Canadian Shield to the east, and mountains of British Columbia and the Yukon Territory to the west. The Basin is the site of: recent pipeline construction; urban communities such as Yellowknife on Great Slave Lake; current and abandoned mines with associated tailing ponds; producing oil wells, and a refinery at Norman Wells, just south of the Arctic Circle. Natural oil seeps occur in the bed of the Mackenzie River and of its major tributary, the Liard River. River traffic includes commercial barging upriver from the Beaufort Sea to Hay River on Great Slave Lake. As a northwards flowing river, the Mackenzie system transports the cumulative impacts of man's activities into the Arctic Ocean.

The Mackenzie River is one of the major rivers of the world. Discharge over period of record varies between 3000 and 25,000 cms. The Liard River produces much of the sediment load and, at times, may contribute up to 75% of the total water discharge. Upstream from the Liard, flow in the Mackenzie River is naturally controlled by Great Slave Lake which separates the Mackenzie River from major headwater rivers such as the Athabasca, Peace and Slave Rivers. The bed of the Mackenzie is mobile sand except where it cuts through bedrock.

This study addresses the following baseline concerns:

1. Characterize the hydrocarbon chemistry of water and suspended
    sediments.

2. Evaluate the use of water and suspended sediments for hydrocarbon
    monitoring.

3. Determine seasonal (high versus low flow) and downstream trends
    in hydrocarbon chemistry.

MATERIALS AND METHODS

Field Program

Study sites are located on the main stem of the Mackenzie and
lower Liard Rivers. The sites (Table 1, Figure 1) reflect: Liard at
its mouth (L) and Mackenzie (1) immediately upstream of the Liard
confluence; an intermediate site at Wrigley (2); upstream and
downstream of the Norman Wells oil field and refinery (3 and 4); an
intermediate site (5) well downstream of the confluence of Great Bear
River; immediately upstream of confluence of Arctic Red River (6); and
one site (7) near Inuvik on a major distributary of the Mackenzie
Delta.

The first sampling trip was in August, 1985 and the second in
June, 1986 immediately following spring breakup. Sampling dates,
turbidities, distances and discharges are noted in Table 1. Discharge

data are from gauges of the Water Resources Branch (Environment Canada) at Fort Simpson and upstream of Arctic Red River. The Fort Simpson gauge measures the combined discharge of the Mackenzie and Liard Rivers. The Liard, the major contributor of sediment to the Mackenzie River, can produce high turbidities at any time of the year in response to alpine rainfall events. The program was designed, however, to contrast on-snowmellt and low flow data of summer, 1985, with high flow and high turbidity conditions of snowmelt-generated runoff in spring of 1986.

The sampling program was operated from a 24 ft launch, commencing at Fort Simpson and working sequentially downstream over a two week period. The objective was to sample at approximate time of travel of the water mass, however, the sampling schedule was very dependent upon logistics and weather in this remote area. No independent measurement of hydrologic transit time was possible. At a mid-stream surface velocity of approximately 1 m/sec characteristic of the 1986 program, transit time should be approximately 15 days over the sampled distance of 1358 km. As we note below, the increase in turbidity downstream (Table 1, Figure 2) suggests that our objective, especially in 1986, was not achieved.

Sampling was at mid-stream as determined by bathymetry of the channel. Tributary plumes, especially of the Liard River, tend to remain distinct for long distances. Although sample sites were selected to reflect mixing, a turbidity profile was carried out at each section to ensure that the sampled point was characteristic of

the section. Following earlier studies (Blachford and Ongley, 1984; Ongley et al., in press) samples were taken from a depth of 0.3 m. For sediment samples we have found that the geochemically active fine-grained fraction (<62.5 μm) tends not to be depth dependent in turbulent rivers (Ongley, 19 , unpublished data).

Samples were pumped on board into a "Sedisamp" portable continuous-flow centrifuge at 4 L/min. Turbidity of pumped river water was measured with a Model DRT-15 turbidimeter (H.F. Instruments Ltd.). The de-watered bulk sediment samples were wrapped in acetone-cleaned aluminum foil and held on ice.

Sampling time for suspended sediments varied between <1 h to 8 h depending upon sediment concentration in the river. Centrifuge recovery efficiency, determined by comparing filter weights of filtered aliquots of raw and clarified water at 0.45 μm, generally exceeded 90%. Eighteen litres of the clarified water were collected in a stainless vessel and, under nitrogen pressure, passed through an XAD-2 resin column to recover water-soluble organics. The column was stored for subsequent analysis.

ANALYTICAL METHODS

The sediment samples were extracted and fractionated as shown in Figure 2. After the first batches of #5 fractions were found to contain no detectable hydrocarbons, the DCM re-extraction of the samples was discontinued. The acid compounds in fraction #6 were

stored refrigerated but were not analyzed: their removal was effected to simplify the analysis of the base-neutral fractions. Fractions #1 and #2 of the silica gel separation contained both the normal alkanes and PAHs. Only a few polar oxygen compounds (e.g. aldehydes and ketones) were detected in fractions #3 and #4.

The XAD-2 resin was removed from the absorption columns and was Soxhlet extracted with the acetone-hexane mix. The extract was then washed with 0.1 M K_2CO_3: the organic phase, containing the base-neutrals, was then analysed without a silica gel separation step.

The base-neutral extracts or the silica gel column fractions were concentrated in a rotary evaporator, followed by nitrogen blow down to 2 mL. Quantitative analysis was performed on a gas chromatograph with a flame ionization detection, calibrated by standards of C_{12} to C_{26} normal alkanes, and of 16 priority pollutant PAHs, listed in Table 2. Mass spectra were obtained on a Delsi-Nermag system with electron ionization at 70 eV. The alkanes and PAHs were identified by their retention times and their mass spectra. The chromatographic conditions were:

System: for GC/FID:

Perkin-Elmer Sigma 2000 (splitless injection), or HP-5700 (10:1 split injection)

for GC/MS:

Carlo-Erba system (on column injection)

Column:	30 m fused silica capillary, DB-5
Injection temp:	280°C - Detector temp.: 280°C
Program:	70°C for 2 min, then
	4°C/min to 280°C (GC/FID), or
	5°C/min to 280°C (GC/MS), then
	280°C for 15 min.

The mass spectra were obtained on a Delsi-Nermag system with electron ionization (70 eV). The n-alkanes and the priority pollutant PAHs were identified by their mass spectra and retention times.

RESULTS

Suspended Sediments

The downstream variation in turbidity (Figure 2) suggests that time-of-travel criteria for sampling were not achieved during spring discharges of 1986. Although a moderate amount of floating debris (trees, etc.), associated with rising and peak discharge conditions on the Liard, occurred at Sites 1 and 2, major increases of debries at Sitres 3, 4 and 5 suggest that vessel transit time exceeded time-of-travel. Sampling at Sites 6 and 7 probably preceeded the crest; these latter sites had very little debris and reduced turbidity.

Mixing of Liard and Mackenzie water occurs very slowly; the Liard River plume may be visible for many hundreds of kilometers. Turbidity measurements were made across each section in 1985. Comparison of turbidity values across the Section at Site 2 (Table 1) in 1986 indicate considerable mixing at the sample point. In 1986, the position of floating ebris at Site 2 occupied two-thirds of the channel width indicating that Liard River water had mixed across at least two-thirds of the channel.

Analyses of the centrifuges suspended sediments in the two sampling periods are summarized in Table 3 and Figure 3.

Normal alkanes were present at all sites in both sampling periods. Their concentrations varied along the river in a discontinuous fashion suggesting a series of inputs and removal mechanisms. The alkane concentrations were highest at Site 1, in the flow from Great Slave Lake. This location also showed a consistent odd-carbon predominance of the C_{15} and C_{17} alkanes, suggesting a biogenic origin (possibly algae). The alkanes at the Liard River site and at the sites of the oil seep area showed some bimodal distributions, indicating a mixed alkane input from biogenic and petroleum sources.

PAH concentrations were too low for quantitation in the 1985 samples. Their levels were estimated at least an order of magnitude below that of the alkanes at the Liard and the Norman Wells sites. In the rest of the sampling area, their concentrations were estimated to be another order of magnitude lower.

In the 1986 samples, PAHs were found in measurable quantities at all sites, at concentrations similar to those of the alkanes.

Although direct comparisons are difficult between the qualitative observations in 1985 and the quantitative data of 1986, some observations may be made. The PAH assemblages in 1985 appeared to contain most of the priority pollutant PAHs in the molecular weight range of 128 to 252, with several methyl homologs. The 1986 PAH suites consisted mainly of three or four dominant compounds (napthalene, fluorene, benzo(k)fluoranthene and dibenzo(a,h)anthracene), and appeared to contain fewer methyl homologs.

The observed variation of PAH composition in the two sampling periods, their intermediate concentrations at the Liard and Norman Wells sites in 1985, and their presence along the whole length of the river at significantly higher levels in 1986 indicate different PAH sources in the two sampling periods.

The 1985 inputs, although small, were probably affected by petroleum sources in the Liard River and in the Norman Wells area. The similarity of PAH compositions above and below the Normal Wells refinery suggest natural oil seeps, rather than the refinery operations, as a possible source.

The inputs in 1986 probably arose from combustion-produced PAHs deposited in the river drainage basin from local or outside sources, and washed into the river system by the spring runoff. Such an event of significantly increased concentrations was probably short lived,

but apparently overwhelmed possible local PAH inputs in the Liard River and in the oil seep area. It had been suggested that entrapment of seep oil under the winter ice may produce localized "oil spills" during the spring breakup. The PAH compositions in the lower reaches of the river in 1986 were similar to those found upriver, and did not appear to be affected by the spring release of trapped oil.

Water Samples

Analysis of river water samples showed no measurable or detectable alkanes or PAHs at any of the sites in 1985. The 1986 samples, on the other hand, showed the presence of both compound classes at all sites. As indicated by the data in Figure 3 and Table 4, concentration variations along the river were similar to those seen on the suspended solids.

DISCUSSION

Results of the two year study showed significant variations in the concentration and composition of the two compound classes and showed the importance of the timing of such studies. Recognition of river flow regimes appears mandatory in data interpretation.

Concentration and composition variations along the river indicate the importance of recognizing inputs and removal mechanisms of organics and suspended particulate matter that appears to carry a significant portion of those organics.

The analysis of fine suspended material collected by centrifuging large volumes of river water enhances the sensitivity of the analytical methods and is thus useful in the study of low-level organic loadings in rivers.

The sediment-water partition coefficients of alkanes and PAHs were calculated from the 1986 data as

$$K = \frac{\text{µg organics/g centrifuged dry sediment}}{\text{µg organics/mL water}}$$

The values were greatly scattered but showed a 100 to 1000-fold concentration of both alkanes and PAHs on the suspended sediments. It must be recognized that these values do not describe partitioning between solids and water, but between the fraction of the suspended sediment that is removed by the centrifuge, and the water phase that will contain non-settling and non-centrifuged fine particles.

In addition to the partition coefficients, the significance of the suspended sediments in carrying the organic load of the river must depend on magnitude of the sediment load itself. The suspended sediment concentrations at the sampling sites were calculated from the centrifuged water volumes and dry sediment weights, assuming a 90% recovery from the centrifuging and sampling ɩ handling. The distributions of the alkanes and PAHs between a unit volume of water and suspended sediment recovered from that unit volume are given in

Table 4. These calculations show that the centrifuged suspended solids carried a fraction of the organic load that varied from less than 5% in the waters from Great Slave Lake (Station 1, centrifuged suspended sediments 11 mg/L) to about 70% in the lower reaches of the river (Stations 9 and 10, suspended solids about 350 mg/L).

The above calculations show that estimates of organic loadings in rivers must be based on their concentrations in suspended sediments and in the water phase (including colloidal particulates). The study also shows the need for an assessment of the seasonal variation of both flows and concentrations in the river.

ACKNOWLEDGEMENTS

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TABLE 1. Mackenzie River sampling sites.

Site	Km from Great Slave Lake	Discharge m^3s^{-1}	Date	Turbidity NTU	Location
				- 1985 -	
1	329	10,500	Aug 10	8.5	Fort Simpson
		9,550	Aug 25	6.7	(repeat)
2	332	3,490	Aug 9	41	Liard River
		3,260	Aug 26	42	(repeat)
			Aug 26	NA	(bottom sediment)
3	577		Aug 26	22	Wrigley
4	848		Sep 1	18	Halfway Island
5	900		Sep 4	56	N. Wells (upstream)
6	900		Sep 4	50	N. Wells (downstream)
7	1044		Sep 8	55	Hardie Island
8	1094		-	-	Fort Good Hope
0	1444	12,300	Sep 12	84	Arctic Red River
				- 1986 -	
1	329	14,700	June 21	11	Fort Simpson
2	332	5,930	June 19	62	Liard River
3	577		June 23	53	Wrigley
4	848		June 26	288	Halfway Island
7	1044		June 27	336	Hardie Island
8	1094		June 28	288	Fort Good Hope
9	1444	21,100	June 29	156	Arctic Red River
10	1587		July 1	172	Inuvik

TABLE 2. Priority Pollutant PAHs used for Calibration.

No.	Symbol	Molecular Weight	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(1,2,3,-c,d)pyrene
15	BP	276	benzo(g,h,i)perylene
16	DA	278	dibenzo(a,h)anthracene

TABLE 3. N-alkanes and PAHs in Mackenzie River suspended sediments.

Site No.	1985			1986	
	N-alk[1]	PAH[2]		N-alk	PAH
1	3.759	ND		1.523	0.418
	3.594 (3)	ND			
2	0.806	TR		0.994	0.264
	0.371 (3)	TR			
	0.141 (4)	ND			
3	0.824	ND		0.791	0.196
4	0.412	ND		0.125	0.052
5	1.743	TR		NS	NS
6	1.972	TR		NS	NS
7	1.158	ND		0.205	0.076
8	NS	NS		0.255	0.147
9	1.272	ND		1.116	0.391
10	NS	NS		0.773	0.289

Note: 1 – sum of C_{12} to C_{26} normal alkanes
       2 – sum of 16 priority pollutant PAHs
       3 – repeat sample
       4 – bottom sediment sample
    TR – trace
    ND – not detected
    NS – not sampled

TABLE 4. Analysis of Mackenzie River water (1986).

Site No.	N-alkanes[1] (micrograms/L)	PAH[2]
1	0.591	1.824
2	0.284	0.292
3	0.147	0.303
4	0.239	0.111
7	0.410	0.414
8	0.505	1.234
9	0.168	0.261
10	0.219	0.054

1 - sum of C_{12} to C_{26} normal alkanes
2 - sum of 16 priority pollutant PAHs

TABLE 5. Analysis of Mackenzie River water (1986).

Site No.	N-alkanes[1]		PAH[2]	
	Water	Suspended Sediment	Water	Suspended Sediment
1	.591	.017	1.824	.005
2	.284	.086	.292	.023
3	.147	.066	.303	.016
4	.239	.065	.111	.027
7	.410	.140	.414	.052
8	.505	.125	1.234	.072
9	.168	.406	.261	.142
10	.219	.269	.054	.101

* Amounts are given in micrograms/L of centrifuged water, and in micrograms/suspended sediment found in 1 L of water.
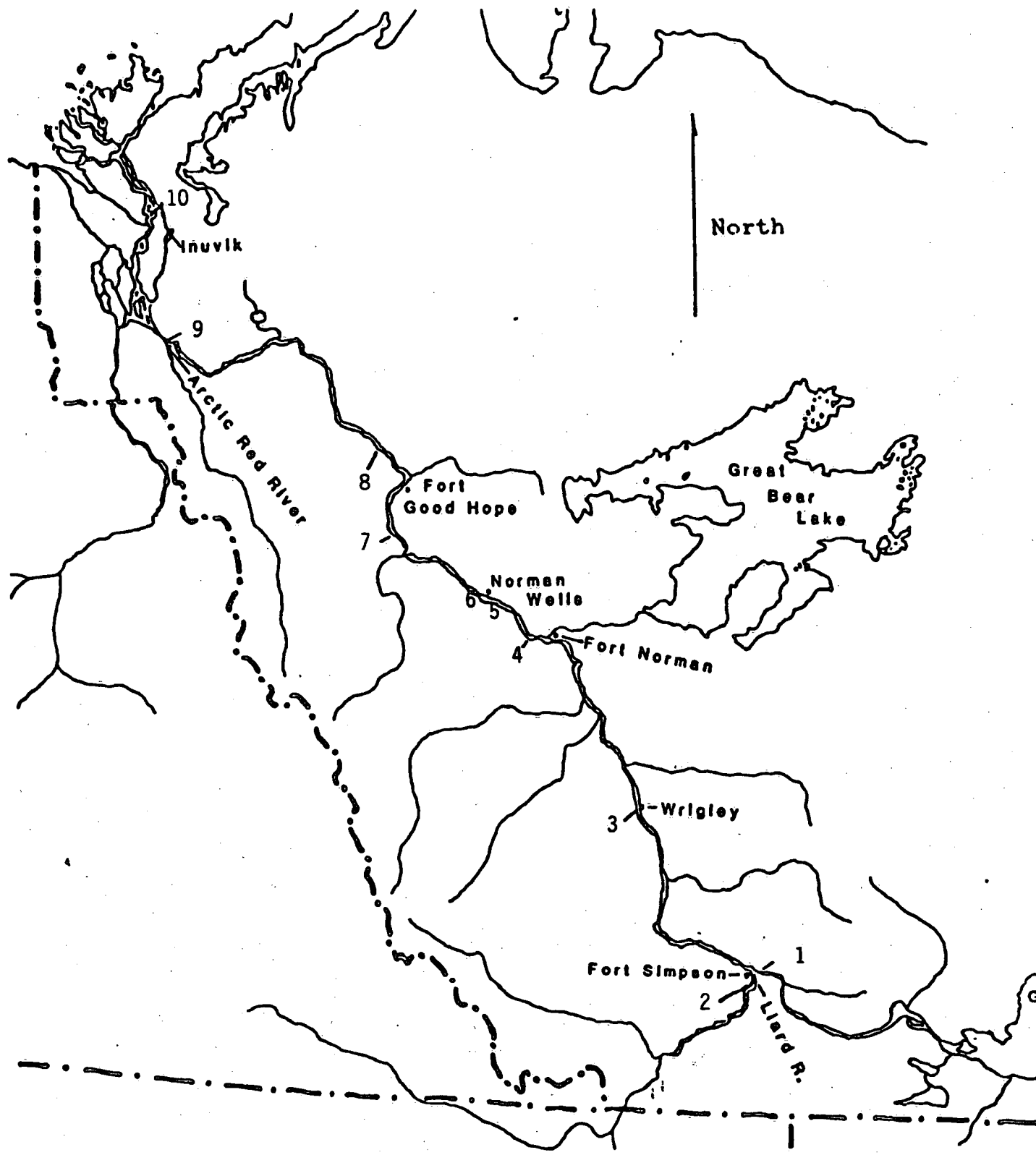
Figure 1

Mackenzie River Sampling Sites - 1986
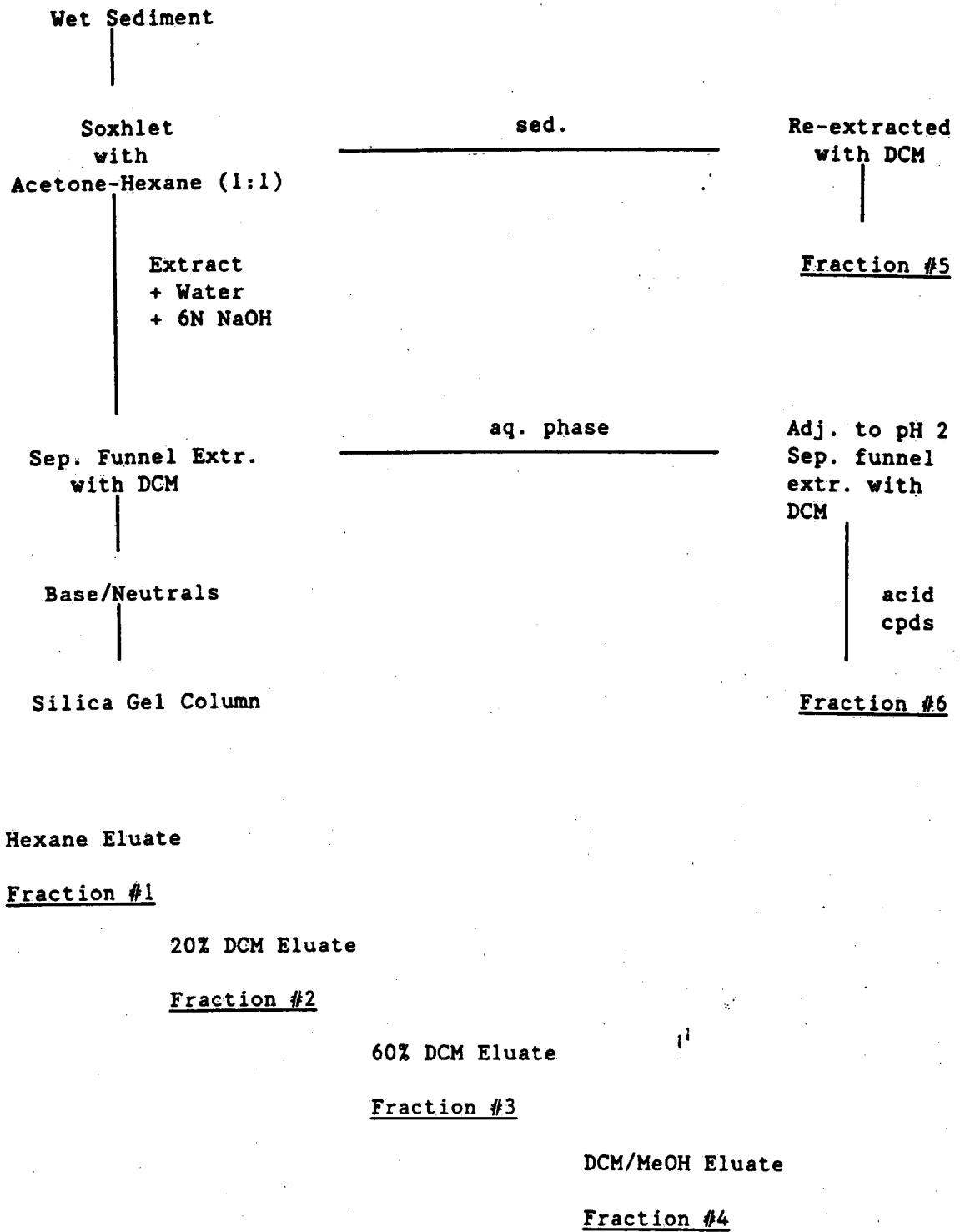
FIGURE 2.   Sediment Extraction Scheme

Wet Sediment
|

Soxhlet   sed.   Re-extracted
with   ―――――――――――――――――――   with DCM
Acetone-Hexane (1:1) |

                                                        Fraction #5
Extract
+ Water
+ 6N NaOH

                                 aq. phase   Adj. to pH 2
Sep. Funnel Extr.   ―――――――――――――――――――   Sep. funnel
with DCM   extr. with
| DCM

Base/Neutrals   acid
| cpds

Silica Gel Column   Fraction #6

Hexane Eluate

Fraction #1

            20% DCM Eluate

            Fraction #2

                        60% DCM Eluate

                        Fraction #3

                                    DCM/MeOH Eluate

                                    Fraction #4

Figure 3

N-alkanes and PAHs in the Mackenzie River

SUSPENDED SEDIMENTS, 1985
  ▣ – n-alkanes
  o – PAHs

SUSPENDED SEDIMENTS, 1986
  ▣ – n-alkanes
  o – PAHs

CENTRIFUGED RIVER WATER, 1986
  ▣ – n-alkanes
  ◆ – PAHs

site number