

# Composition and Origins of Polycyclic Aromatic Hydrocarbons in the Mackenzie River and on the Beaufort Sea Shelf

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**ABSTRACT.** Polycyclic aromatic hydrocarbon (PAH) concentrations in suspended particulate samples from the Mackenzie River delta and shelf sediments from the Beaufort Sea are higher than expected for a pristine area. Low concentrations of combustion PAHs indicate that anthropogenic inputs are low. Alkyl PAH distributions indicate that a significant component of the lower molecular weight parent (unsubstituted) PAH fraction is petrogenic. The majority of the high molecular weight PAHs, together with the petrogenic PAHs, have a principal source in the Mackenzie River. Despite the high PAH content, we consider the area still to be pristine. Although PAH concentrations are below the concentrations believed to induce toxic effects on biota, the high natural concentrations may make this region of the Arctic sensitive to additional PAHs from human activities.

**Key words:** polycyclic aromatic hydrocarbon (PAH), Arctic, baseline, sediment, effects threshold, principal components analysis

**RÉSUMÉ.** Les concentrations d'hydrocarbures aromatiques polycycliques (HAP) dans des échantillons de particules en suspension venant du delta du Mackenzie et de sédiments du plateau continental de la mer de Beaufort sont plus élevées qu'on pourrait s'y attendre pour une zone vierge. Les faibles concentrations de HAP de combustion suggèrent que l'apport anthropique est faible. La distribution des HAP alkyles indique qu'une composante importante de la fraction de HAP-mère (non substitué) à bas poids moléculaire est pétrogénétique. La majorité des HAP à haut poids moléculaire, ainsi que les HAP pétrogénétiques, ont leur source principale dans le fleuve Mackenzie. Malgré la teneur élevée en HAP, la région est toujours considérée comme vierge. Bien que les concentrations d'HAP soient inférieures aux valeurs qui pourraient avoir des effets toxiques sur le biote, les fortes concentrations naturelles peuvent rendre cette région de l'Arctique sensible aux HAP supplémentaires venant des activités humaines.

**Mots clés:** hydrocarbure aromatique polycyclique (HAP), Arctique, données de base, sédiment, seuil des effets, analyse des principaux composants

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## INTRODUCTION

The ends of the earth are now generally perceived to be contaminated by chemicals discharged in lower latitudes. For many years polar regions were thought to be the last pristine refuge from contamination. By the late 1960s and early 1970s, organochlorines had been measured in both Arctic and Antarctic biota, establishing beyond doubt that compounds produced by human activities were being transported at global scales (e.g., Holden and Marsden, 1967; Tatton and Ruzicka, 1967; Risebrough, 1992).

A wide variety of evidence has since demonstrated that the Arctic is no longer pristine. Organochlorines (PCBs, dioxins/furans and pesticides), polycyclic aromatic hydrocarbons (PAHs) and metals (Hg, Cd, Pb) are transported from temperate latitudes either in the vapour phase or on aerosols (Patton et al., 1991; Barrie et al., 1992). For the organochlorines, global transport coupled with biomagnification into simple, fat-dominated food chains has led to concentrations in traditional arctic foods sufficient to raise public concern about the

health of humans and the ecosystem (Oemhe and Ottar, 1984; Twitchell, 1991; Kinloch et al., 1992; Norstrom and Muir, 1994). These contaminants have recently been upstaged by the discovery of both deliberate and accidental discharges of radioactive waste and industrial contaminants by the former Soviet Union to north-flowing rivers and the Russian Arctic shelves (Green, 1993; Yablokov et al., 1993). In the Canadian Arctic, concerns have arisen over PCB, petroleum and metal contamination measured in the vicinity of DEW (Distant Early Warning) Line sites (Thomas et al., 1992).

PAHs are among the most widespread contaminants in the marine environment. In the Arctic, however, PAHs have received less public attention than organochlorines or radionuclides despite known PAH sources which include natural inputs, petroleum exploration and production, and long-range atmospheric transport (Daisey et al., 1981; Thomas et al., 1986; Patton et al., 1991; Lockhart et al., 1992; Steinhauer and Boehm, 1992; Yunker et al., 1993). The environmental significance of PAHs is founded in their potential to form carcinogenic and mutagenic diols and

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epoxides that react with DNA (Zedeck, 1980; Malins and Hodgins, 1981; Stein et al., 1990). Studies in the coastal zones of industrial regions have described elevated PAH concentrations in surface sediments (Hites et al., 1980; Bouloubassi and Saliot, 1991) and documented biological effects as a consequence (Malins et al., 1984). The emphasis during the last decade on organochlorines (e.g., Loganathan and Kannan, 1991) has resulted in progress toward limiting or curtailing their production and discharge. Meanwhile, the input of anthropogenic PAHs to the world's oceans continues, albeit at a reduced level (Gschwend and Hites, 1981; Jones et al., 1989).

Several factors suggest that a further evaluation of PAHs within the Arctic is warranted at this time. 1) Recoverable reserves of oil have been found on the Russian, Canadian and American shelves; production has already taken place at Prudhoe Bay and we can anticipate pressure to produce oil within a few years — particularly from the Russian shelves. 2) Modern analyses (on-column injection, fused-silica columns, the use of perdeuterated standards) suggest that much of the work done in the 1970s probably underestimated concentrations of the higher PAHs (Wakeham, 1993). 3) A full assessment of the environmental significance of individual PAH metabolites has proved elusive because the analysis of PAH metabolites in marine organisms has been restricted to semiquantitative analysis of groups of compounds (Krahn et al., 1986; Varanasi et al., 1987; Stein et al., 1990; Collier and Varanasi, 1991). 4) In the course of studying the hydrocarbon geochemistry of the Canadian Beaufort shelf, we have found much higher concentrations of PAHs than expected for a pristine area (Yunker et al., 1993).

Unlike the organochlorines, PAHs have both natural (oil seeps, bitumens, forest fires) and anthropogenic (fossil fuel and combustion) sources. These sources overlap, particularly for combustion, and processes such as diagenesis can modify sedimentary PAH distributions over time. This has two important consequences. 1) The environmental fate and effects of anthropogenic PAH must be evaluated against a site-specific background of natural PAH. 2) It is difficult to distinguish sources based on PAH data alone, and one must consider a broad range of hydrocarbon indicators to define inputs, transport and sedimentary persistence of PAHs. Multivariate pattern recognition techniques provide an efficient tool to address both aspects.

The Canadian Arctic has been extensively explored for oil and gas. Between 1973 and 1987 close to 100 wells were drilled on the Canadian Beaufort shelf to delineate oil fields (Environmental Sciences Limited, 1991). There are sufficient proven oil reserves in a single large reservoir (Amauligak—estimated at 700 to 800 million barrels) to justify production, but for economic reasons drilling has all but ceased since 1987. In 1986, we initiated studies to establish the natural hydrocarbon geochemistry prior to oil production in the Canadian Beaufort Sea.

This paper provides an overview of hydrocarbon results for the Mackenzie River and the Beaufort Sea with emphasis on both an oil-spill baseline and the concentrations, sources and potential impact of PAHs.

## METHODS

Mackenzie River suspended particulate samples were collected in the three principal channels of the delta during the June and July freshet in 1987 (Fig. 1; Yunker et al., 1990, 1991, 1992). Water was pumped from 1 m depth to obtain samples both by direct filtration using precombusted GF/D and GF/F glass fibre filters (Whatman, 293 mm) and by integrated collection over one to three days using a continuous flow centrifuge. All wetted surfaces were Teflon or stainless steel and were well cleaned with organic solvents. Beaufort Sea shelf and shelf edge sediment samples were collected in July and August 1987 by Smith-McIntyre (0.12 m<sup>2</sup>) and Ponar (0.06 m<sup>2</sup>; Station 1 only) grab samplers. Shoreline peat samples from representative geological environments along the Beaufort Sea coast were also obtained in 1987; locations and descriptions have been given in detail in Yunker et al. (1991).

Prior to extraction, samples were spiked with an internal surrogate standard mixture containing 13 perdeuterated *n*-alkanes and PAHs. The parent PAH standards used for quantification spanned the range of PAHs quantified and included [<sup>2</sup>H<sub>8</sub>]naphthalene, [<sup>2</sup>H<sub>10</sub>]acenaphthene, [<sup>2</sup>H<sub>10</sub>]anthracene, [<sup>2</sup>H<sub>10</sub>]pyrene, [<sup>2</sup>H<sub>12</sub>]chrysene, [<sup>2</sup>H<sub>12</sub>]benzo(k)-fluoranthene, [<sup>2</sup>H<sub>12</sub>]benzo(a)pyrene and [<sup>2</sup>H<sub>14</sub>]dibenz(a,h)-anthracene. Sample extracts were separated into fractions on a 1 × 10 cm silica gel column (F1—alkanes, hopane triterpenes; F2—PAHs). Samples were analyzed using a Finnigan Incos 50B GC/MS coupled to a Varian 3400 GC with a CTC A200S autosampler and a 30 m DB-5 capillary column (J & W Scientific, 0.25 mm i.d./0.25 μm film) that was inserted directly into the ion source. Quantification of the parent PAHs and the alkyl PAHs cadalene (4-isopropyl-1,6-dimethylnaphthalene), pimanthrene (1,7-dimethyl phenanthrene), simonellite (1,1-dimethyl-1,2,3,4-tetrahydro-7-isopropylphenanthrene) and retene (1-methyl-7-isopropylphenanthrene) has been described (Yunker et al., 1991, 1993).

The alkyl-substituted PAH identified as tetramethyl octahydrochrysenes (4MeOHC; three tetramethyl isomers of 1,2,3,4,4a,11,12,12a-octahydrochrysene; with most likely the 3,3,7,12a- and 3,4,7,12a-isomers, plus one other isomer), trimethyl tetrahydrochrysenes (3MeTHC; the 3,4,7- and 3,3,7-isomers of 1,2,3,4-tetrahydrochrysene) and trimethyl tetrahydropicenes (3MeTHP; the 1,2,9- and 2,2,9-isomers of 1,2,3,4-tetrahydropicene) fit the retention time and mass spectral characteristics published by Wakeham et al. (1980a; a mass spectral correction for one of the octahydrochrysenes was subsequently published by Simoneit, 1986). Response factors for these compounds were corrected for the abundance of the quantifying ion relative to the total ion current of each compound.

All hydrocarbon data presented in this paper are above the statistical limit of detection (3 σ above the mean of six procedural blanks); most results exceed the limit of quantitation (10 σ above the mean blank). Potential interferences, perdeuterated standard recoveries and closeness to the limit

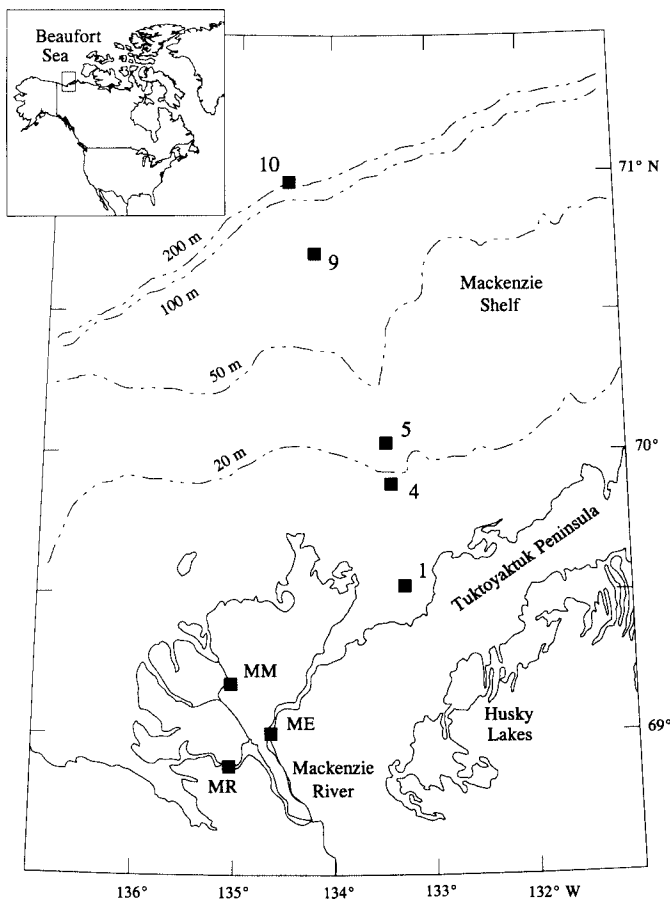


FIG. 1. Suspended particulate sampling locations in the Mackenzie River delta (Stations ME, MM and MR in the East, Middle and Reindeer channels) and sediment sampling locations on the Mackenzie shelf (Stations 1-9) and at the shelf edge (Station 10). Only those stations shown were sampled for hydrocarbons.

of detection were assessed for each PAH measurement before data were used for geochemical interpretations.

For organochlorine analysis, sediments were spiked with PCB 209 internal standard and extracted on a shaker table, first with dichloromethane/methanol (1:1) and then twice with dichloromethane. The combined extracts were washed twice with solvent-extracted distilled water, dried over sodium sulphate, concentrated to 1 mL by rotary evaporation, and blown down to 200  $\mu$ L with a gentle stream of nitrogen. After removal of sulphur with activated copper, sample extracts were separated into fractions on a  $1 \times 10$  cm florisil column using hexane (F1), dichloromethane/hexane (15:85; F2) and dichloromethane/hexane (1:1; F3). Samples were analyzed by GC/ECD using a Hewlett Packard 5890 GC and a  $30 \text{ m} \times 0.25 \text{ mm}$ ,  $0.25 \mu\text{m}$  DB5 Durabond fused silica column. Selected samples were confirmed by quadrupole GC/MS.

For coplanar PCB analysis, fractions F1 and F2 were recombined, spiked with  $^{13}\text{C}$ -labeled PCBs 80, 77, 126 and 169 and applied to a 5% carbon/celite 545 column (2 cm bed in a 7 mm diameter glass column) using hexane. The column was washed with 5 mL cyclohexane/dichloromethane (1:1) and 5 mL ethyl acetate (both discarded) and the coplanar PCBs were eluted with 25–30 mL of toluene/ethyl acetate (1:1). This eluate was reduced just to dryness, redissolved in

hexane (1 mL) and loaded onto an alumina column (10 g, 100% activated). The column was washed with hexane (discarded) and the PCBs eluted with dichloromethane/hexane (5:95). The sample was concentrated under a stream of nitrogen and spiked with  $^{13}\text{C}$ -PCB 153 recovery standard. Samples were analyzed by Finnigan Incos 50B GC/MS coupled to a Varian 3400 GC and a  $60 \text{ m} \times 0.25 \text{ mm}$ ,  $0.10 \mu\text{m}$  DB5 fused silica column.

Unsupervised principal components analysis (PCA) was performed using the nonlinear iterative partial least squares (NIPALS) algorithm in a program which allowed a detailed examination of both sample and variable projections (respectively scores and loadings, Yunker et al., 1991; software was provided by the Chemometrics Clinic, Seattle, WA). Undetected “zero-values” were replaced by a minimum area value as described in Yunker et al. (1989). Because different units were used for sedimentary particulate (ng/g) and atmospheric aerosol samples ( $\text{pg}/\text{m}^3$ ; Patton et al., 1991), each sample was normalized before PCA. To avoid spurious negative correlations in the normalizing variables arising from closure, a normalization factor derived from a subset of variables with mid-range standard deviations and means was used (Johansson et al., 1984). Data were then log-transformed and mean-centered before PCA.

Methods used to calculate annual fluxes of individual hydrocarbons to the Beaufort Sea have been detailed in Yunker et al. (1991). Suspended particulate fluxes from the Mackenzie River represent the integrated total of ng/L concentrations from both spring freshet and summer/fall flow regimes. Peat fluxes from coastal shoreline erosion represent the integrated total of 776 coastal segments which have been classified into upland and lowland ng/g concentration ranges.

## RESULTS AND DISCUSSION

The major source of terrestrial material to the Canadian Beaufort shelf is the Mackenzie River. It is the fourth largest river draining into the Arctic in terms of discharge ( $3.0 \times 10^{11} \text{ m}^3/\text{a}$ ) and the largest in terms of sediment supply (ca.  $2.2 \times 10^{11} \text{ kg}/\text{a}$ ; Milliman and Meade, 1983; Macdonald and Thomas, 1991). River discharge and suspended particulate matter (SPM) concentrations are both low from November to May (respectively  $3500 \text{ m}^3/\text{s}$  and  $3\text{--}4 \text{ mg}/\text{L}$ ). In late June river flow and SPM increase dramatically (to  $25,000 \text{ m}^3/\text{s}$  and  $> 250 \text{ mg}/\text{L}$ ); flow and SPM both remain high over the summer with only a gradual decrease to the end of October. Almost all of the annual flux of terrigenous detritus from the river to the adjacent Mackenzie shelf occurs during summer. Since the river is the major source of PAH, alkane and hopane hydrocarbons to the shelf (Yunker et al., 1991, 1993), we begin our discussion by comparing the hydrocarbon composition of the shelf sediments to what the river supplies at freshet.

In the following discussion we rely on several different ways of determining PAH sources. These can be summarized as follows:

- *PAH alkyl homologue series*. The relative amounts of

the alkyl-substituted PAHs (e.g., a dimethylphenanthrene such as pimanthrene; Fig. 2) to the parent PAHs (e.g., unsubstituted phenanthrene) can be used to distinguish a petroleum or petrogenic source from a combustion source.

- *PAH stability.* The relative amounts of the unstable or kinetic PAHs (e.g., fluoranthene with a five-membered ring; Fig. 2a) compared to the more stable or thermodynamic PAHs (e.g., pyrene with all six-membered rings) can indicate combustion or anthropogenic input.
- *Source-specific PAH.* In general PAHs such as acenaphthene and acenaphthylene are specific for a combustion source and cadalene and retene are specific for a plant source (Fig. 2b).
- *Principal components analysis.* By using a complete series of PAHs in a multivariate approach, we incorporate all of the above source characteristics into a single, robust test.

### PAH Concentrations and Distributions

Total PAH concentrations (PAHs of molecular-mass 178 to 278, perylene excluded; Table 1; Fig. 2a) for Mackenzie River delta suspended particulates and shelf sediments are higher than expected for a pristine area (Hites et al., 1980). PAH molecular-mass profiles for samples from the Mackenzie River, the Mackenzie shelf and Beaufort Sea coastal peat have the same dominant molecular-mass constituents: 178 and 252 (Fig. 3a to 3c). These PAH profiles are distinctive and differ from the commonly observed marine particulate or sediment profile that has a predominance of compounds with mass 202 and 252 (Hites et al., 1980; Bates et al., 1984; Lipiatou and Saliot, 1991).

While peat does contain substantial amounts of hydrocarbons (particularly the higher plant-derived *n*-alkanes), PAH concentrations are significantly lower in peat than they are in the river and in shelf sediments (Fig. 3). The direct flux of PAHs to the Beaufort Sea from shoreline erosion of peat is also only a minor process (Fig. 3a and 3c). Yunker et al. (1991) have estimated that peat erosion contributes substantially less than 1% of the river particulate flux for most of the PAHs.

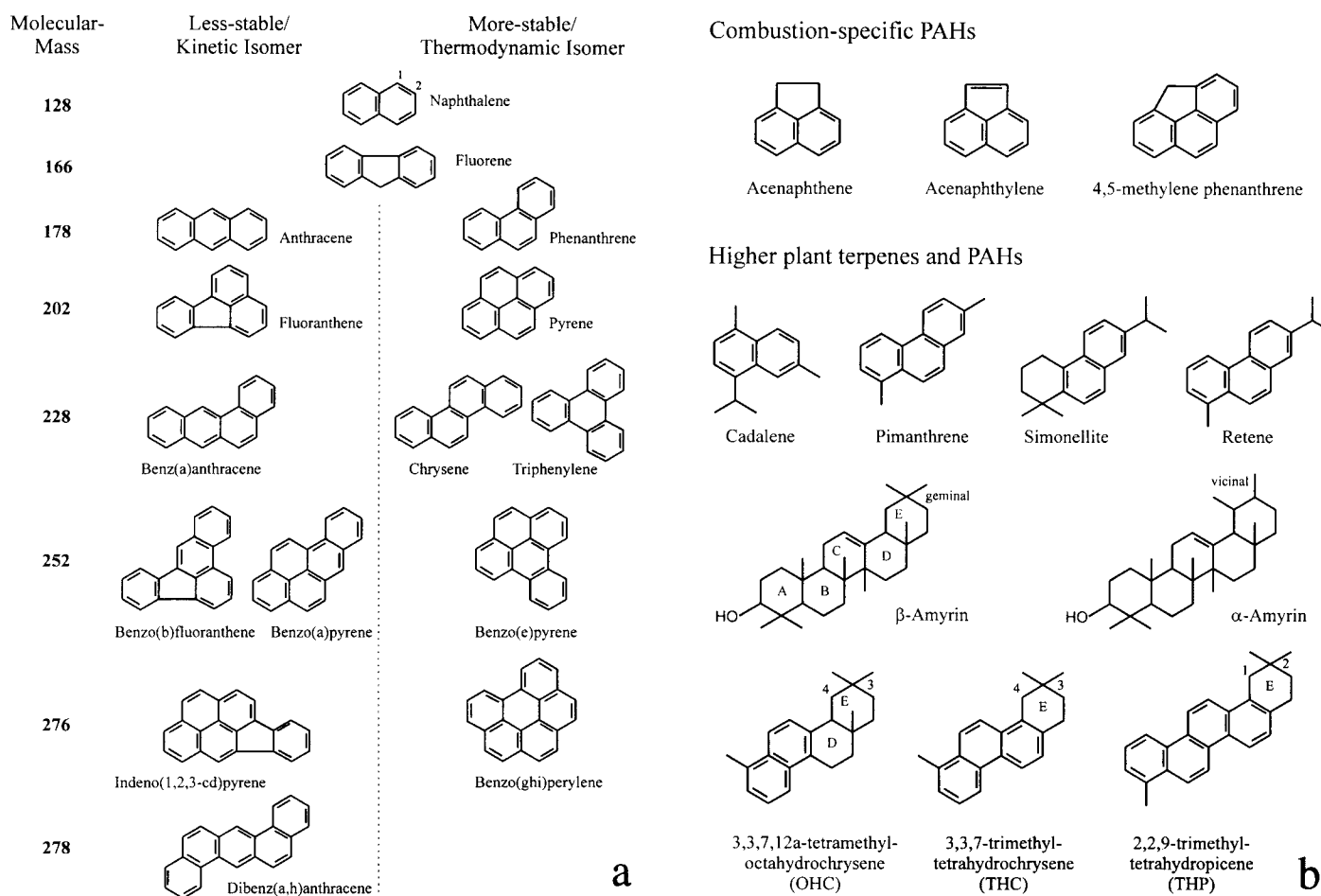


FIG. 2. Structures of key compounds mentioned in the text. In (a) parent PAHs for each molecular mass are shown. Compounds are separated into two groups to differentiate between the less stable or kinetic PAH isomer(s) and the more stable or thermodynamic PAH isomer(s). Because the b, j and k isomers of benzo(b)fluoranthene differ only in the location where the outlying benzene ring is joined, only benzo(b)fluoranthene is illustrated. In (b) combustion-specific PAHs and higher-plant terpenes are shown. The methylated chrysenes and picones include isomers with both geminal (two substituents on the same carbon) and vicinal (substituents on adjacent carbons) methyl substitution patterns on the E-ring, but only geminal isomers are shown. Full names for the OHC, THC and THP alkyl-substituted PAHs are given in the methods section.

TABLE 1. Alkane, PAH and organochlorine concentrations in suspended particulate collected from the Mackenzie River at freshet and in sediment from the Mackenzie shelf.

Parameter	River particulate <sup>a</sup> ng/g (mean ± SD)	Shelf sediment <sup>b</sup> ng/g (mean ± SD)
<i>n</i> C <sub>13</sub> -C <sub>36</sub> alkanes	12 400 ± 4300	9800 ± 1700
Isoprenoids <sup>c</sup>	1980 ± 680	950 ± 279
Total naphthalene, fluorene, 178 and 202 <sup>d</sup>	520 ± 120	400 ± 130
178-278 PAH total <sup>d</sup>	970 ± 110	850 ± 230
Benzo(a)pyrene	47 ± 20	42 ± 25
Non-coplanar PCBs <sup>e</sup>	< 0.16	< 0.15
PCB 79, 78, 81, 77, 126 or 169	< 0.01	< 0.01
PCB Total <sup>f</sup>	< 4.7	< 4.3
p'p'-DDE	< 0.11	< 0.11
Hexachlorobenzene	0.15 ± 0.05	0.43 ± 0.22
Hexachlorocyclohexanes	0.60 ± 0.50	1.3 ± 1.2

<sup>a</sup> n = 36 for alkanes, n = 10 for PAH and n = 3 for PCBs and organochlorines.

<sup>b</sup> n = 6.

<sup>c</sup> Total of 2,6-dimethyl undecane, norfarnesane, farnesane, 2,6,10-trimethyl tridecane, norpristane, pristane and phytane.

<sup>d</sup> The parent PAH of molecular-mass 178 to 278 are defined in the caption for Fig. 3.

<sup>e</sup> An average detection limit for the 29 major trichloro- to nonachloro-substituted congeners is given. These congeners are 31/28, 52, 49, 61/94/74, 66/80/95, 60, 101, 97/86, 87, 151, 118, 114, 153, 105, 141, 137, 138, 129/126, 182/187/159, 183, 128, 156, 180, 191, 199, 196/203, 208/155, 194 and 206.

<sup>f</sup> The upper limit of the PCB concentration has been estimated using the sum of the individual method detection limits for the 29 congeners listed above.

PAH alkyl homologue distributions maximize at C<sub>1</sub> or higher for the three dominant series of two- to four-ring alkyl PAHs (Fig. 4). In both Mackenzie delta suspended particulates and shelf sediments, the series maximum was on average at C<sub>1</sub> for both the phenanthrene/anthracenes and the fluoranthene/pyrenes, and was at C<sub>1</sub> or higher for the naphthalenes. This indicates a petrogenic source (Shaw et al., 1979; Wakeham et al., 1980a; Sporstøl et al., 1983; Yunker et al., 1993). This conclusion is strongly corroborated by isoprenoid, diagenetic 17 $\alpha$ (H),21 $\beta$ (H)-hopane and 17 $\beta$ (H),21 $\alpha$ (H)-moretane data (Yunker et al., 1991, 1993) and by the presence of hydrocarbon sources (oil seeps and source rock bitumens) in the lower Mackenzie watershed that have isoprenoid and hopane patterns similar to those observed in the delta (e.g., Snowdon et al., 1987; Feinstein et al., 1988). In the nearshore Alaskan Beaufort Sea, substantial amounts of alkylated naphthalenes and phenanthrenes are found and have also been attributed to petrogenic sources (Steinhauer and Boehm, 1992).

Hence, a significant component of the lower molecular weight parent PAH (including naphthalene and phenanthrene) is petrogenic. However, there is little precedent for a petroleum source for the higher molecular weight PAHs that comprise the remainder of the parent PAH distribution (Fig. 3).

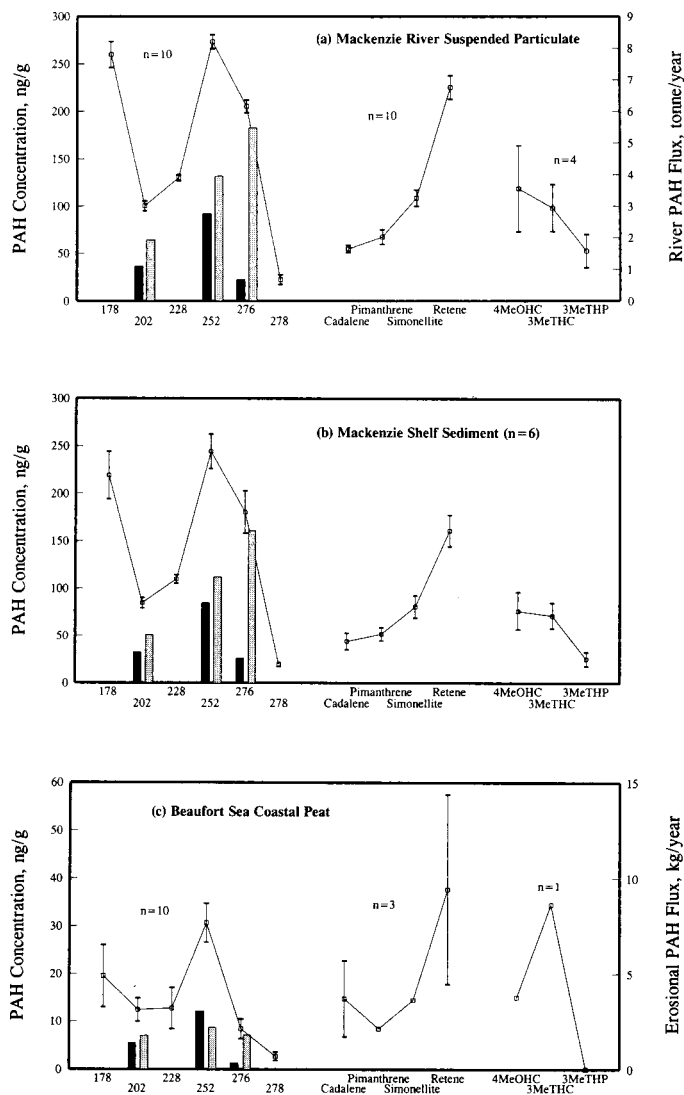


FIG. 3. PAH concentration profiles for (a) suspended particulate from the Mackenzie River at freshet, (b) surficial sediment from the Mackenzie shelf (Stations 1 to 10) and (c) peat from the Beaufort Sea coast. The corresponding annual fluxes of each of the PAHs for the Mackenzie River in 1987 and for eroded coastal peat are also presented in (a) and (c), respectively. Parent PAH molecular mass totals are shown for phenanthrene and anthracene (178), fluoranthene and pyrene (202), benzo(a)anthracene, chrysene and triphenylene (228), benzo(b/j/k)fluoranthene, benzo(a)fluoranthene, benzo(e)pyrene and benzo(a)pyrene (252), indeno(1,2,3-cd)pyrene and benzo(ghi)perylene (276) and dibenz(a,h)anthracene (278). The black (left) bar at 202, 252 and 276 indicates the concentration of fluoranthene, benzo(b/j/k)fluoranthene and indeno(1,2,3-cd)pyrene respectively and the grey (right) bar indicates pyrene, benzo(e)pyrene and benzo(ghi)perylene. Individual concentrations are shown for the alkyl-substituted PAHs cadalene, pimanthrene, simonellite and retene. Alkyl PAH molecular-mass totals are also shown for tetramethyl-octahydrochrysene (4MeOHC), trimethyl-tetrahydrochrysene (3MeTHP) and trimethyl-tetrahydropicene (3MeTHP). Uncertainties are plus or minus one standard error of the normalized concentrations.

#### PAH from Combustion Sources

PAH ratios and molecular-mass profiles may be used effectively to infer the sources of PAHs. When the primary PAH source is combustion, the less stable or kinetic PAH isomer(s) tend to be enhanced relative to the more stable or

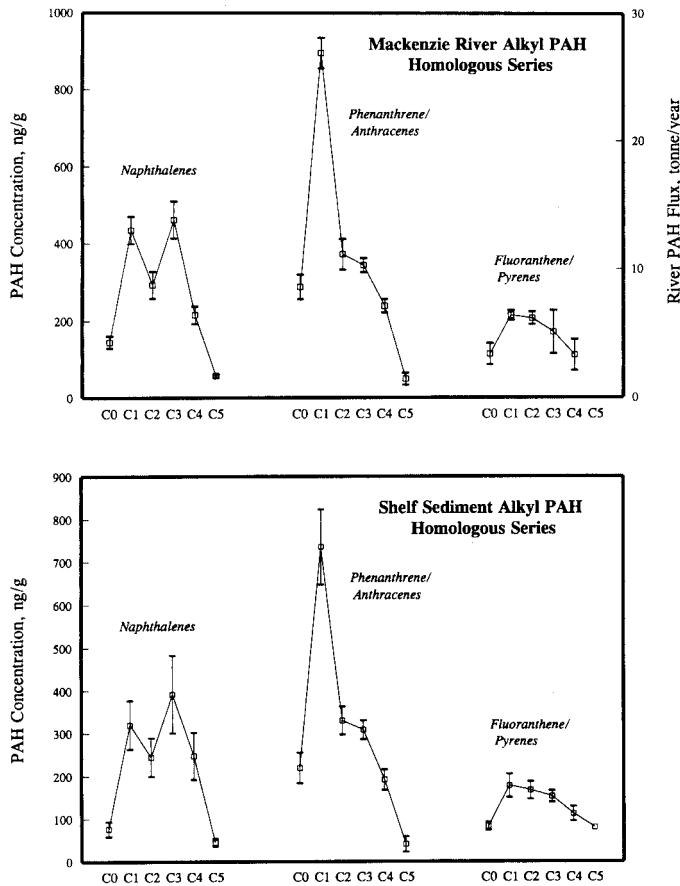


FIG. 4. PAH alkyl homologue concentrations and Mackenzie River annual fluxes for the naphthalenes, phenanthrene/anthracenes and fluoranthene/pyrenes in (a) suspended particulate collected in the Mackenzie River delta ( $n = 7$ ) and (b) sediments from the Mackenzie shelf ( $n = 6$ ). The C0 to C5 homologous series are shown where Cn designates n carbon substituents on the aromatic ring. Uncertainties are plus or minus one standard error of the normalized concentrations.

thermodynamic PAH isomers of the same molecular-mass (Fig. 2a). The less stable isomers are linear or predominantly linear (anthracene, benz(a)anthracene, benzo(a)pyrene, and dibenz(a,h)anthracene) or contain a five-membered ring (fluoranthene, benzo(b/j/k)fluoranthene, and indeno(1,2,3-cd)pyrene). The amount of enhancement that each isomer undergoes varies within each molecular-mass; the relative amounts of the less stable component are also variable. For example, anthracene is almost always a minor component relative to phenanthrene, indeno(1,2,3-cd)pyrene can be either minor or major relative to benzo(ghi)perylene, but fluoranthene is usually comparable in concentration to pyrene. Accordingly, when assessing whether combustion or anthropogenic input has occurred, the best strategy is to consider the ratios of a number of PAHs of different molecular-mass. To assist in this process, concentrations of fluoranthene, benzo(b/j/k)fluoranthene and indeno(1,2,3-cd)pyrene relative to respectively pyrene, benzo(e)pyrene and benzo(ghi)perylene are shown by bars in Fig. 3a to 3c.

We emphasize that one needs to measure both the kinetic and the thermodynamic isomers to make a source assessment (Fig. 2a). Analyses that focus only on the most toxic PAHs often omit key constituents such as benzo(e)pyrene and

benzo(ghi)perylene and limit the source comparisons that could be made. The tragedy is that these compounds can usually be determined at little or no additional cost at the time of analysis, but are quite expensive to determine retroactively.

Concentrations and distributions for a number of PAHs indicate that anthropogenic combustion makes only a minor contribution to the elevated PAH concentrations observed in the Mackenzie estuary. First, individual combustion-specific PAHs are undetectable or only marginally detectable in river particulates and shelf sediments. The m/z 192 and 190 ion profiles for the phenanthrene/anthracenes with one alkyl substituent (the C<sub>1</sub> series) show only a simple four-peak pattern due to the monomethyl phenanthrenes, with no 4,5-methylene phenanthrene evident (Fig. 2b; Wakeham et al., 1980b; Grimmer et al., 1983; Garrigues et al., 1988). Other combustion PAHs such as acenaphthene and acenaphthylene (Laflamme and Hites, 1978) are only marginally detectable in some Mackenzie River or shelf samples.

Second, samples of Mackenzie River particulates and shelf sediments contain only low proportions of the linear or five-membered ring containing PAH isomers. For example, ratios of anthracene/(anthracene + phenanthrene), indeno(1,2,3-cd)pyrene/(indeno(1,2,3-cd)pyrene + benzo(ghi)perylene) and fluoranthene/(fluoranthene + pyrene) are typically very low relative to areas closer to anthropogenic sources (Yunker et al., 1993). In the Mackenzie River these ratios are  $0.03 \pm 0.03$ ,  $0.13 \pm 0.04$  and  $0.38 \pm 0.05$  respectively (mean  $\pm$  one standard deviation;  $n = 10$ ), while values for shelf sediments generally fall within the stated uncertainties. Benzo(b/j/k)fluoranthene is also found in minor amounts relative to its principal molecular-mass 252 isomer, benzo(e)pyrene (Fig. 3). Both the indeno(1,2,3-cd)pyrene and fluoranthene ratios are low relative to the published ratios for arctic aerosol (respectively  $0.50 \pm 0.08$  and  $0.70 \pm 0.09$ ,  $n = 10$ ; Patton et al., 1991).

Finally, multivariate analysis using PCA indicates that PAHs in Mackenzie River particulates, shelf sediments and peat samples from eroding coastal areas of the Beaufort Sea have a composition pattern that is distinctly different from long-range-transported atmospheric aerosol collected at Alert, N.W.T. (Fig. 5; Patton et al., 1991). The atmospheric samples from Alert contain high proportions of fluoranthene, while samples of suspended particulate, sediment and peat from the Beaufort Sea have high proportions of benzo(ghi)perylene, benzo(e)pyrene and benzo(a)pyrene. Because proportions of phenanthrene make only a minor contribution to the difference between aerosol and river/sediment samples, the PCA separation does not reflect a loss of volatile or water-soluble PAHs due to passage through the water column (cf. McVeety and Hites, 1988; Baker et al., 1991).

Thus the low concentration of the molecular-mass 202 PAHs fluoranthene and pyrene in our study area (Fig. 3), together with the low proportions of individual combustion PAHs described above, rules out a significant contribution from pyrolytic PAHs in the river and on the shelf (cf. Laflamme and Hites, 1978; Grimmer et al., 1983).

It could be argued that atmospheric PAHs have been

delivered to the region but are masked by the high natural background. However, organochlorines transported on aerosol particulates (PCBs, DDTs, etc.), which have been measured at Alert along with the PAHs (Patton et al., 1991), are also not detected in river particulates or shelf sediments (Table 1). Furthermore the normally most abundant PCB congener, IUPAC number 138, was undetectable in shelf sediments at a detection limit of 0.02 ng/g. By comparison the PCB 138 concentration in Lake Superior surficial sediment was ca. 50 times this concentration, while the PAH total was only ca. 40% greater than in the Beaufort Sea (Baker et al., 1991). Since we do not find particle active organochlorine constituents, we have no reason to believe that PAHs from haze aerosol input are making a significant contribution to the PAH budget.

On the Mackenzie shelf we do see indications of pyrogenic inputs in particulates collected in shallow water and in some sediments from the shelf edge (Yunker et al., 1993, 1994). In these samples the proportions of non-alkylated to monomethylated fluoranthene/pyrene and of indeno(1,2,3-cd)pyrene to indeno(1,2,3-cd)pyrene plus benzo(ghi)perylene exceed those in all other samples.

#### PAH Derived from Plant Residues

A comparison of the concentrations and distributions of the high molecular weight parent PAHs to the naturally derived PAHs that are produced by the diagenesis of conifer resins and other higher plant lipids can help to identify the origin of the parent PAHs in the Mackenzie River (Wakeham et al., 1980a; Simoneit and Mazurek, 1982; Bouloubassi and Saliot, 1993). In areas where anthropogenic PAH inputs form a significant component of the PAH budget (e.g., the Rhône estuary; Bouloubassi and Saliot, 1993), distributions, and hence particle associations, are distinctly different for the parent and higher plant PAHs.

The natural two- and three-ring PAHs derive from plant sesqui- and diterpenoid essential oils and should have similar solubility and phase distributions as the three- and four-ring parent PAHs. In the Mackenzie estuary, cadalene, pimanthrene, simonellite and retene (with molecular weights ranging from 198-252) are the major representatives of this class of PAH (Fig. 2b; Yunker et al., 1993). Similarly, for higher molecular weight PAHs, a characteristic series of

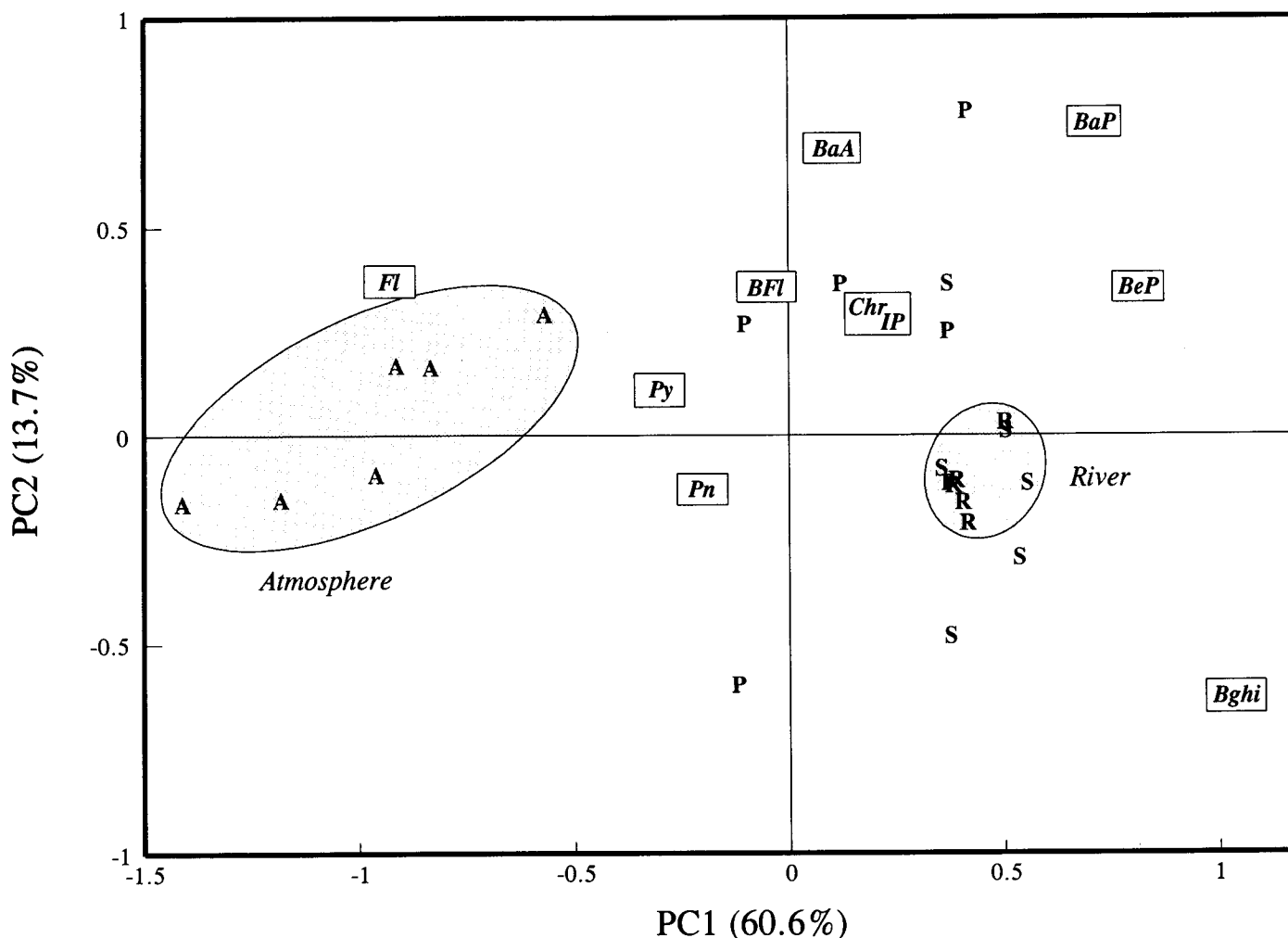


FIG. 5. PCA multivariate comparison of the PAH composition of samples from the Mackenzie estuary and shelf to Arctic atmospheric aerosol (Patton et al., 1991). In this biplot the distance and direction from the axis center has the same meaning for both samples and PAH variables (Kvalheim, 1990). Sample abbreviations indicate atmosphere (A), Mackenzie River suspended particulate (R), Beaufort Sea shoreline peat (P) and shelf sediments (S). Atmospheric samples and river particulate samples are circled. PAH variables are distinguished by a box around the abbreviation (see Table 2).

four- and five-ring PAHs that are produced from the microbially mediated breakdown of plant wax and woody tissue pentacyclic triterpenes can provide a biogenic analogue for the five- and six-ring parent PAHs (Fig. 2b; Wakeham et al., 1980a). Progressive aromatization starting with the A-ring of triterpenes such as  $\alpha$ - and  $\beta$ -amyrin leads to the five-ring picene derivatives, while loss of the A-ring and progressive aromatization starting at the B-ring leads to the four-ring chrysenes (Fig. 2b). In the Mackenzie estuary these PAHs include three isomers of the four-ring tetramethyl-octahydrochrysenes and two isomers each of the four-ring trimethyl-tetrahydrochrysenes and the five-ring trimethyl-tetrahydropicenes (respective molecular weights 292, 274 and 324). On the basis of published mass spectra (Wakeham, 1980a; Simoneit, 1986), the two major isomers for each series had either geminal methyl substitution in the terminal, non-aromatized E-ring (and an apparent link to  $\beta$ -amyrin) or had vicinal methyl substitution in this ring (and a link to  $\alpha$ -amyrin; see Fig. 2b).

The higher plant PAHs cadalene, pimanthrene, simonellite and retene have the same relative proportions in Mackenzie delta suspended particulates and shelf sediments, where concentrations increase in the order given (Fig. 3a and 3b). The presence of higher plant PAHs in concentrations comparable to the parent PAHs indicates a substantial input to the river from higher plant detritus. Concentrations and proportions are more variable at the lower concentrations present in peat (Fig. 3c); retene is still the major constituent, but cadalene is present in a higher proportion than in particulate and sediment.

The relative content of the two- and three-ring higher plant PAHs proves to be remarkably uniform. For example, the ratio of retene/(retene + the 178 to 278 PAH total) is the same in the Mackenzie River at freshet ( $0.20 \pm 0.04$ ;  $n = 10$ ), in all shelf sediments (0.16 in all cases;  $n = 5$ ) and in peat ( $0.19 \pm 0.07$ ;  $n = 8$ ; Yunker et al., 1995). Similar relationships for cadalene, pimanthrene and simonellite are also obtained in all three regimes, which points to plant debris as the common source for these natural PAHs. Sediment concentrations of retene and the PAH total both decrease with distance from the Mackenzie delta, suggesting that airborne retene from combustion (Ramdahl, 1983) is not significant on the shelf.

The sums of the tetramethyl-octahydrochrysenes (4MeOHC), trimethyl-tetrahydrochrysenes (3MeTHC) and the trimethyl-tetrahydropicenes (3MeTHP) are also present in the same concentrations and the same relative proportions in both river particulate and shelf sediment (Fig. 3). Within individual groups of these four- and five-ring PAHs, ratios of the major isomers were also constant in both regimes. In peat (Fig. 3c), the trimethyl tetrahydrochrysenes emerge as the major constituent in the single sample for which data are available.

Ratios of the geminal dimethyl isomer (the  $\beta$ -amyrin analogue; Fig. 2b) to the vicinal dimethyl isomer ( $\alpha$ -amyrin analogue) in individual four- and five-ring PAH groups echoed the general trend observed by Wakeham et al. (1980a) and increased with the degree of aromatization. In the Mackenzie River, the non-aromatized pentacyclic triterpenes

$\beta$ -amyrin and  $\alpha$ -amyrin had a ratio of  $0.64 \pm 0.06$ . The observed geminal/vicinal ratios for the octahydrochrysenes were identical at  $0.59 \pm 0.12$ , but the ratio increased to  $1.57 \pm 0.80$  in the tetrahydrochrysenes and  $1.52 \pm 0.33$  in the tetrahydropicenes ( $n = 4$  in all cases).

Together these data for the two- to five-ring alkyl PAHs suggest that the naturally derived PAHs are preformed in soils and peat and are delivered to the river and transported to shelf sediments with little alteration (cf. Bouloubassi and Saliot, 1993). The agreement in concentrations and ratios between the river and the shelf for both the parent and higher plant PAHs is consistent with the Mackenzie River as the prime source for both components. The majority of the high molecular weight PAHs have been attributed to combustion relicts that have been preserved and concentrated in peat (Yunker et al., 1993).

#### *Potential for Biological Effects*

The possibility of PAH-induced biological effects may be assessed by comparing Beaufort Sea sedimentary concentrations to effects thresholds published in other studies. Furthermore, because bioavailability, and presumably toxicity, are linked to the presence of PAHs in solution in water (e.g., Readman et al., 1984), the potential for biological effects may also be assessed by examining the dissolved phase PAH composition.

A number of studies have linked concentrations of PAHs in sediments to the concentrations of aromatic compound metabolites in bile, the hepatic activities of xenobiotic metabolizing enzymes, and the presence of hepatic neoplasms in bottom fish (Krahn et al., 1986; Varanasi et al., 1987, 1989; Stein et al., 1990, 1992; Collier and Varanasi, 1991; Johnson et al., 1993). Positive correlation from step to step of the progression has also been demonstrated. PAHs alone are apparently sufficient to induce biological effects, because lesions occur in fish at locations where organochlorine contamination is low or undetectable (Krahn et al., 1986; Varanasi et al., 1987, 1989).

While many studies have focused on the biochemistry of PAH toxicity, few studies have defined a threshold for PAH impact. In most studies the number of sample sites and the number of different PAH concentrations are too small to establish such a threshold; this is particularly true when the high variability in the concentrations of both PAHs in sediments and metabolites of aromatic compounds in the bile of bottom fish is considered (Krahn et al., 1986). The role of confounding factors such as the exposure time necessary for effects to be observed and the presence of promoting agents (e.g., PCBs) is unclear (Johnson et al., 1993). The English sole (*Parophrys vetulus*), which has been the subject of many studies, appears to be affected when sedimentary PAH concentrations are as low as 2200 ng/g (Varanasi et al., 1989). By comparison, total PAH concentrations in the Mackenzie estuary are approximately one-half of this level (Table 1).

Payne et al. (1988) have attempted to establish what a safe exposure level of PAHs in oil might be for fish. In their study,



Table 2. Comparison of estimated effects ranges to individual PAH concentrations in Mackenzie River suspended particulate and Mackenzie shelf sediment.

Parameter	PCA Abbrev.	Effects Range	Apparent Effects	River Particulate	Shelf Sediment
		Low <sup>a</sup> ng/g	Threshold <sup>b</sup> ng/g	(n = 10) ng/g (mean ± SD)	(n = 6)
Naphthalene		340	500	138 ± 63	76 ± 39
2-Methyl naphthalene		65	300	222 ± 52	167 ± 69
1-Methyl naphthalene		–	–	218 ± 58	152 ± 73
Acenaphthylene		–	–	1.9 ± 2.5	3.9 ± 1.0
Acenaphthene		150	150	7.2 ± 4.4	8.1 ± 5.2
Fluorene		35	350	41 ± 11	36 ± 23
Phenanthrene	Pn	225	260	251 ± 60	210 ± 86
Anthracene		85	300	8.0 ± 5.7	8.4 ± 5.4
Fluoranthene	Fl	600	1000	36 ± 19	33 ± 9.0
Pyrene	Py	350	1000	64 ± 9.1	51 ± 13
Benz(a)anthracene	BaA	230	550	24 ± 9.0	18 ± 6.8
Chrysene	Chr	400	900	105 ± 10	91 ± 15
Benzo(b/j/k)fluoranthene	BbFl	–	–	92 ± 18	84 ± 23
Benzo(e)pyrene	BeP	–	–	131 ± 24	112 ± 30
Benzo(a)pyrene	BaP	400	700	47 ± 19	42 ± 24
Indeno(1,2,3-cd)pyrene	IP	–	–	22 ± 12	26 ± 8.5
Benzo(ghi)perylene	Bghi	–	–	182 ± 25	161 ± 66
Dibenz(a,h)anthracene		60	100	22 ± 15	19 ± 4.5

<sup>a</sup> Consensus value for the PAH concentration of low effect at the 10th percentile level (Long and Morgan, 1990).

<sup>b</sup> Apparent effects threshold (Long and Morgan, 1990).

low levels of PAH (total of naphthalene, fluorene, phenanthrene/anthracene and fluoranthene/pyrene <1000 ng/g) in oiled sediments were shown to induce small increases in liver mixed-function oxygenase (MFO) enzymes in flounders. Mackenzie estuary concentrations of these PAHs (Table 1) are one-half to two-thirds of the lowest concentration where an increase in the level of MFO enzymes was observed. However, a direct comparison may not be valid, because fluorene was the major PAH in crude oil used in the Payne et al. (1988) study but is only a minor PAH constituent in the Mackenzie estuary.

Long and Morgan (1990) assembled and evaluated biological effects data from a wide variety of methods and produced informal guidelines that can be used to screen sedimentary data. The PAH concentrations observed or predicted by the different methods to produce biological effects were ranked, and the lower 10th percentile (identified as Effects Range-Low), median, and overall Apparent Effects Threshold were identified. The Effects Range-Low and Apparent Effects Threshold for individual PAH are presented in Table 2 along with concentrations for Mackenzie River suspended particulate and Mackenzie shelf sediment.

For our Mackenzie shelf data, concentrations of all PAHs except 2-methyl naphthalene and phenanthrene are below the concentration believed to elicit toxic effects in benthic organisms. Alkyl homologue distributions indicate that these PAHs likely have an origin in petroleum hydrocarbons which are delivered to the shelf by the Mackenzie River (Fig. 4). The question of origin is important, because hydrocarbons from petroleum and combustion sources differ in their resistance to bacterial degradation (Jones et al., 1986), likely have different particle size associations (Yunker et al., 1994) and may differ in their bioavailability (see Payne et al., 1988 for a

recent discussion). Because transport from the river to shelf sediments occurs without substantial change in PAH distributions (Figs. 3 and 4), the majority of the two- to four-ring compounds are most likely encapsulated in eroded bitumen, and hence protected from dissolution in water or bacterial degradation. A lower toxicity would be expected for bitumen-associated PAHs, because their reduced dissolution in water will result in a decreased availability for bioaccumulation by fish.

Hydrocarbons from freshly-seeped crude oil, however, are apparently more available. Lockhart et al. (1992) cite observations of dramatic EROD enzyme induction in burbot (*Lota lota*) in the Mackenzie River by Norman Wells crude oil, indicating that toxic effects are more likely where oil provides a significant component of the PAH budget.

Given that the different solid-phase studies do not reach consensus on the biological effects of PAHs, the presence of PAHs in the dissolved phase may be a more direct link to bioavailability. In the Mackenzie River and on the Mackenzie shelf the total PAH concentration in the dissolved phase was consistently ca. 1 ng/L; this concentration showed little variation either with season or with suspended particle loading in the water column (Yunker et al., 1992, 1994). The lower-molecular weight, more water-soluble PAHs (i.e., those up to molecular-mass 178) usually dominated the dissolved-phase PAH profile. However, these PAHs, while bioavailable, are easily degraded in an aqueous environment.

Perhaps it is more important to ask whether the more persistent, higher-molecular weight PAHs are present in the dissolved phase. These PAHs are strongly particle-associated; as a consequence, the higher molecular weight PAH composition at times was found to be highly variable, particularly on the outer shelf and in the higher-mass range (Yunker

et al., 1994). Nevertheless, all of the PAHs of molecular-mass from 228 to 278 (Fig. 2a), including the mutagenic/carcinogenic benzo(b/j/k)fluoranthene, benzo(a)pyrene, and dibenz(a,h)anthracene (Zedeck, 1980), were detected in the dissolved phase of a number of samples. This presence of the four- to six-ring PAHs indicates that the higher PAHs are transported in the dissolved phase on the Mackenzie shelf, where they are presumably bioavailable.

### CONCLUSIONS

The massive flux of particulate provided by the Mackenzie River dominates the sedimentary geochemistry of the Mackenzie shelf and produces the same PAH composition in shelf sediments as the Mackenzie River at freshet. Anthropogenic hydrocarbons from long-range transport of PAH combustion products make only a minor contribution to the Mackenzie shelf sediments, and are only manifest at the shelf edge for a few compounds. For areas of the Arctic that are further removed from the influence of a large river, atmospheric sources of PAHs are expected to be more important.

PAHs are present at higher concentrations than would be expected for a pristine area, particularly in the Arctic (Yunker et al., 1993). Nevertheless, a full geochemical examination precludes anthropogenic PAH as a significant source of contamination from either combustion or oil exploration and suggests that, despite these high PAH contents, both the Mackenzie River and the sediments of the Beaufort Shelf are still pristine. Most PAH concentrations appear to be below the threshold required for observable effects on bottom fish and other biota. However, there is a strong possibility that the naturally high baseline for PAHs may make biota more susceptible to chronic or accidental spills of PAHs from oil production. Indeed, the prevalent PAH concentrations in the Mackenzie estuary are high enough that this would be a good place to study the effects of induction of metabolizing enzymes by natural PAHs.

The high alkane and hopane background concentrations on the Mackenzie shelf will make delineation of a future oil spill difficult. Specific analytical strategies, including the measurement of particular biomarkers such as the non-hopanes or steranes, will be needed to identify hydrocarbons originating from oil production.

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